Structure and Aromatic Character
of Non-benzenoid Cyclically Conjugated Systems

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Dedicated to Professor Dr. Karl Ziegler on the occasion of his 65th birthday

The chemistry of aromatic compounds was originally confined to benzenoid hydrocarbons and their derivatives but has been enriched in the last decade by the discovery of numerous non-benzenoid, cyclically conjugated systems that are more or less like benzene in their properties. This has necessitated a new conception of "aromatic character". Theoretical and experimental studies have been applied to this problem. In this connection, several selected representatives of this class of compound are described, mostly from studies by the author's own group, and relationships between structure and "aromatic character" are indicated.

Introduction

At an early stage in organic chemistry the characteristic differences in physical properties and chemical reactivity between benzenoid hydrocarbons and their acyclic analogues induced *Kekulé* [1] to make his fundamental studies on the structure of benzene. Since that time, the theory of "aromatic character" has attracted the interest of organic chemists to an ever-increasing degree. Alongside the benzenoid compounds numerous non-benzenoid heterocyclic and carbocyclic systems with very similar properties have appeared, which have robbed the classical aromatic substance, benzene, of its special position and have necessitated a wider and deeper definition of the concept of "aromatic character". In this thorough studies of the chemical and physical properties of new kinds of non-benzenoid, cyclically conjugated compounds and numerous theoretical investigations have made very significant contributions [2].

The theory of "aromatic character" has thereby undergone manifold changes. The empirical generalization of the "aromatic sextet" [3] was followed by Hückel's rule [4], which was based upon quantum-mechanical considerations. According to this rule, benzenoid properties should be displayed not only by compounds with a π-electron sextet but also by any fully conjugated, planar, monocyclic polyolefin with $4n+2$ π-electrons ($n = 0, 1, 2, 3, 4, \ldots$).

[1] *A. Kekulé*, Bull Soc. chim. France (2) *3*, 98 (1865); Liebigs Ann. Chem. *137*, 129 (1866); *162*, 77 (1872).

[2] a) *D. Ginsburg:* Non-Benzenoid Aromatic Compounds. Interscience, New York 1959; b) *M. E. Vol'pin*, Russian chem. Reviews *29*, 129 (1960); c) *W. Baker* and *J. F. W. McOmie*, in *J. W. Cook:* Progress in Organic Chemistry. Butterworths, London 1955, Vol. 3, p. 44; d) *W. v. E. Doering:* Theoretical Organic Chemistry. Butterworths, London 1959; e) *A. Streitwieser:* Molecular Orbital Theory for Organic Chemists. J. Wiley, New York 1961.

[3] *J. W. Armit* and *R. Robinson*, J. chem. Soc. (London) *121*, 827 (1922); *127*, 1604 (1925); *R. Robinson*, Tetrahedron *3*, 323 (1958).

[4] *E. Hückel*, Z. Physik *70*, 204 (1931); Grundzüge der Theorie ungesättigter und aromatischer Verbindungen. Verlag Chemie, Berlin 1938.

Chemical reactivity was often the preferred criterion of "aromatic character", *i.e.* "aromaticity" was associated with thermal stability and reluctance to undergo addition reactions; as a result, it was the energy content of the excited state which was chiefly considered. However, more recently, greater importance has been assigned to those physical quantities which depend upon the extent of delocalization of the π-electrons of a cyclically conjugated system and which permit statements concerning its ground state. Thus "aromatic" compounds are characterized not only by the shift of their light absorption to longer wavelengths compared with olefinic systems, but also by a ready polarizability, by anisotropy of their diamagnetic susceptibility, by changes in bond lengths and charge distribution related to delocalization of the π-bonds, and by their resonance energy. This latter criterion of "aromatic character" in particular allows a limited statement only, despite its widespread use, because the value for the resonance energy is empirical, derived as it is from thermochemical data. The total stabilization represented by the thermochemical data is certainly not only related to the dynamic behavior of the electrons, which largely determines the properties of a molecule [5].

Recent investigations of cyclically conjugated, non-benzenoid compounds have revealed the difficulties associated with the definition of "aromatic character" and the often very different behavior of non-benzenoid, cyclically conjugated molecules in the ground and excited states. A high degree of electron delocalization, *i.e.* a strong ring current of the π-electrons, does not always guarantee benzene-like reactivity and stability. It therefore appears justified to distinguish between "aromatic character" of the ground state and "aromatic" reactivity and stability. This is impressively borne out *inter alia* by the investigations of annulenes [6] and the

[5] *R. B. Turner:* Theoretical Organic Chemistry. Butterworths, London 1959; *C. A. Coulson*, J. physic. Chem. *56*, 311 (1952).

[6] *L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky*, and *A. A. Bothner-By*, J. Amer. chem. Soc. *84*, 4307 (1962), where further references are given.

manifold studies of cyclically conjugated systems with either 4n+2 or 4n π-electrons; among these, special interest was attached to the charged ring systems, the cyclopropenium cation *(1)* [7], the cyclopentadienyl anion *(2)* [8], the tropylium cation *(3)* [9], and the most recently discovered cyclooctatetraenyl dianion *(4)* [10].

(1)   *(2)*   *(3)*   *(4)*
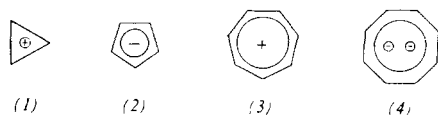
Investigations of various compounds derived from these monocyclic systems have broadened our knowledge of the relationships existing between structure and "aromatic character". In this connection the relationships between derivatives of the cross-conjugated fulvene system and their isomeric benzenoid counterparts were summarized from this point of view in a recent article [11]. Investigations of several mono- and polycyclic conjugated 5- and 7-membered ring systems are described in the following discussion.

Cross-conjugated 7-Membered Ring Systems

The cross-conjugated fulvene system *(5)* [11] should be compared with that of heptafulvene *(6)* [12]. Like fulvene itself, the 7-membered ring system synthetized by

(5)

(6)
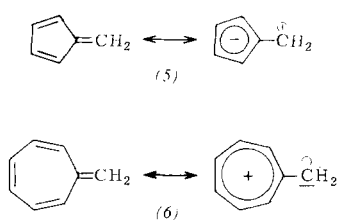
Doering and *Wiley* [13] is distinguished by its very low thermal stability, which for a long time prevented its isolation.

Nevertheless, introduction of electron acceptors on the exocyclic carbon atom of heptafulvene *(6)* effects an

increase in the cyclic conjugation of the 7-membered ring together with a considerably greater chemical stability just as the electron sextet in fulvene is stabilized by electron donors on the exocyclic carbon atom. This is shown particularly clearly by 8,8-dicyanoheptafulvene *(8)* [14,15], which is stable up to 300 °C and reacts neither with dienophiles nor with electrophilic reagents. Com-

(7)   *(9)*   *(8)*
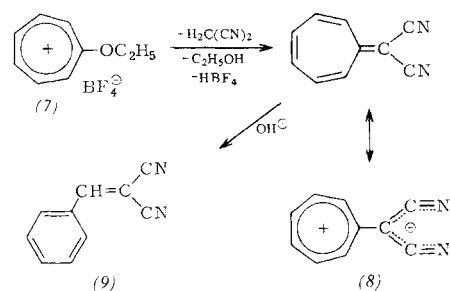
pound *(8)* is obtained by condensation of the alkoxytropylium fluoroborate *(7)* [14] with malononitrile. In contrast to its inertness toward the reagents already mentioned, it undergoes ring contraction to give the dicyanostyrene *(9)* under the influence of bases. Similar but smaller sextet stabilization in the 7-membered ring occurs in several other heptafulvenes [15] with one or two electron-attracting substituents on the exocyclic carbon atom. The 8-acetyl derivative *(11)* [16] obtained from tropylacetone *(10)* is the simplest stable representative

(10)

(11)
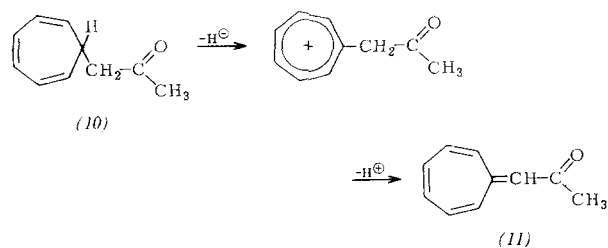
of this class of compounds; another example is 8,8-diphenylheptafulvene, which was prepared by *Dauben* [16a] in a similar way.

Surprisingly, it has not yet been possible to isolate sesquifulvalene *(12)*, for which theory predicts [12,17] a

(12a)   *(12b)*
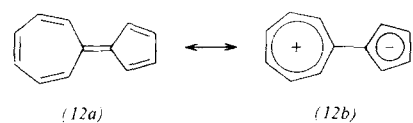
high delocalization energy and which should be stabilized by the two sextet systems in the dipolar structure *(12b)*. Only some benzo- and polyphenyl-substituted

[7] *J. D. Roberts, A. Streitwieser,* and *C. M. Regan,* J. Amer. chem. Soc. *74,* 4579 (1952); *R. Breslow, H. Hover,* and *H. W. Change,* ibid. *84,* 3168 (1962), and earlier publications.

[8] *J. Thiele,* Ber. dtsch. chem. Ges. *34,* 69 (1901).

[9] *M. J. S. Dewar,* Nature (London) *155,* 50 (1945); *W. v. E. Doering* and *L. H. Knox,* J. Amer. chem. Soc. *76,* 3203 (1954); *W. v. E. Doering* and *H. Krauch,* Angew. Chem. *68,* 661 (1956).

[10] *T. J. Katz,* J. Amer. chem. Soc. *82,* 3784, 3785 (1960); *T. J. Katz* and *H. L. Strauss,* J. chem. Physics *32,* 1873 (1960); *T. J. Katz, W. H. Reinmuth,* and *D. E. Smith,* J. Amer. chem. Soc. *84,* 802 (1962); *H. L. Strauss, T. J. Katz,* and *G. K. Fraenkel,* ibid. *85,* 2360 (1963).

[11] *K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploß, G. Schulz, E. Sturm,* and *K. H. Vöpel,* Angew. Chem. *75,* 35 (1963); Angew. Chem. internat. Edit. *2,* 123 (1963).

[12] *G. Berthier* and *B. Pullman,* Trans. Faraday Soc. *45,* 484 (1949); *E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman,* and *B. Pullman,* Bull. Soc. chim. France *18,* 684 (1951); *G. E. Wheland* and *D. E. Mann,* J. chem. Physics *17,* 264 (1949); *A. Julg,* J. Chim. physique *52,* 50 (1955); *A. Julg* and *B. Pullman,* ibid. *52,* 481 (1955).

[13] *W. v. E. Doering* and *D. W. Wiley,* Tetrahedron *11,* 183 (1960).

[14] *K. Hafner, H. W. Riedel,* and *M. Danielisz,* Angew. Chem. *75,* 344 (1963); Angew. Chem. internat. Edit. *2,* 215 (1963).

[15] *T. Nozoe,* in *J. W. Cook* and *W. Carruthers:* Progress in Organic Chemistry. Butterworths, London 1961, Vol. 5, p. 159; *T. Mukai, T. Nozoe, K. Osaka,* and *N. Shishido,* Bull. chem. Soc. Japan *34,* 1384 (1961).

[16] *K. Hafner* and *W. aus der Fünten,* unpublished results.

[16a] *H. J. Dauben, Jr.,* personal communication.

[17] *J. F. Tinker,* J. chem. Physics *19,* 981 (1951).

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derivatives of this hydrocarbon possess the expected thermal stability [18]. 8-Benzylsesquifulvalene *(13)*

(13)   *(14)*
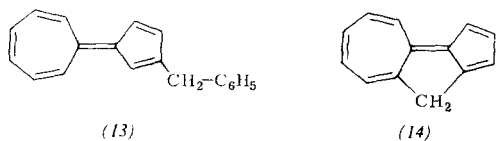
neatly prepared by *Prinzbach* and *Rosswog* [19] has poor stability and polyene character; this suggests that the parent substance *(12)* itself may lack the supposed resonance stabilization, possibly owing to a non-planar arrangement of the 5- and 7-membered rings relative to one another. Such twisting of the central C-C bond should be inhibited in the tricyclic derivative *(14)*, a non-benzenoid isomer of fluorene, in which resonance in the sesquifulvalene moiety might perhaps confer some stability.

In contrast to *(12)*, the heptafulvene system with a resonance-stabilized sextet typified by the deeply colored

(15)
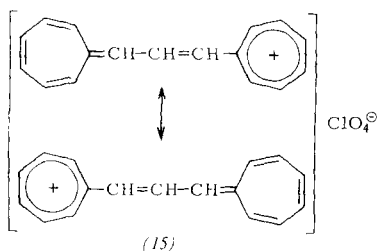
polymethine salt *(15)* [14] is distinguished by remarkable stability. Compound *(15)* reacts only with nucleophilic reagents with loss of conjugation [20].

Azulene

A formal combination of two charged monocyclic sextet systems, *viz.* the cyclopentadienyl anion and the tropylium cation, is encountered in the 10 π-electron system of azulene *(16)* [2a–c,2e,21], whose properties

are largely determined by structures with charge separation. The ultraviolet spectrum [22] of azulene and its electron delocalization energy [22] of *ca.* 35 kcal/mole indicate a state of bonding very similar to that

(16)

in benzenoid systems and show the relationship of this non-alternant hydrocarbon to its isomer naphthalene. The similarity between azulene and the cyclopentadienyl anion is made particularly clear by two characteristic reactions of the bicyclic hydrocarbon. With organometallic compounds of the alkali metals it reacts readily to form isolable cyclopentadienylmetal compounds of type

(16)   *(17)*   *(18)*
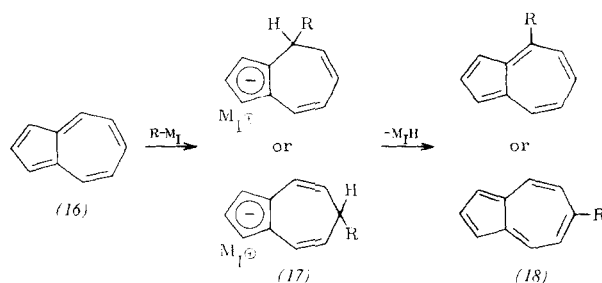
(17) [23] which are intermediates in the nucleophilic substitution at the 4-, 6-, or 8-position of the 7-membered ring, since they reafford the bicyclic decet system *(18)* with loss of a molecule of alkali metal hydride. The second reaction depends upon the acidity of primary or secondary alkyl groups in the 4-, 6-, and 8-positions, the positions of least electron density in azulene. The alkyl groups are activated by the positively polarized 7-membered ring of the azulene. Strong bases are able to extract a proton from these positions to form resonance-

(19)   *(20)*

stabilized alkylideneazulenate salts *(19)* [24], in which the heptafulvene system is fused to the cyclically conjugated 5-membered ring. These salts react with electro-
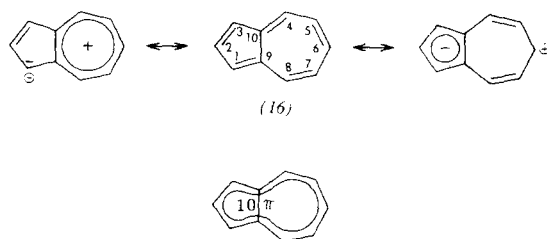
[18] *B. Pullman, A. Pullman, E. D. Bergmann, H. Berthod, E. Fischer, Y. Hirshberg, D. Lavie,* and *M. Mayot,* Bull. Soc. chim. France *19*, 73 (1952); *H. Prinzbach* and *D. Seip,* Angew. Chem. *73*, 169 (1961).

[19] *H. Prinzbach* and *W. Rosswog,* Angew. Chem. *73*, 543 (1961).

[20] See also *Ch. Jutz,* Angew. Chem. *74*, 502 (1962).

[21] *W. Treibs, W. Kirchhof,* and *W. Ziegenbein,* Fortschr. chem. Forsch. *3*, 334 (1955); *K. Hafner,* Angew. Chem. *70*, 419 (1958); *T. Nozoe* and *S. Itô,* in *L. Zechmeister,* Fortschr. chem. org. Naturstoffe *19*, 32 (1961).

[22] *E. Heilbronner* in [2a].

[23] *K. Hafner* and *H. Weldes,* Liebigs Ann. Chem. *606*, 90 (1957); *K. Hafner, C. Bernhard,* and *R. Müller,* ibid. *650*, 35 (1961).

[24] *K. Hafner, H. Pelster,* and *H. Patzelt,* Liebigs Ann. Chem. *650*, 80 (1961).

philic reagents reforming the azulenoid system *(20)*; with ferrous chloride, on the other hand, the heptafulvene structure is fixed in the blue-green ferrocene derivative *(21)* [25] which is formed.
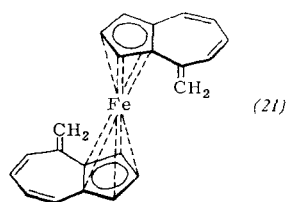
Conversely, it is also possible for azulene to form the tropylium cation. Addition of protons or onium ions at the 1- or 3-positions of the 5-membered ring — the positions of highest electron density — yields isolable azulenium salts of type *(22)* [26], which as intermediates in the electrophilic substitution readily give up a proton to reform the bicyclically conjugated system *(23)*. Condensation with carbonyl compounds in presence of acids
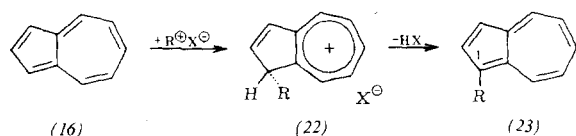
can also convert the decet system into the sextet system of the tropylium cation via a hydroxyalkylation. The alkylideneazulenium salts *(24)* [27] thereby obtained contain the cross-conjugated fulvene system fused to the cyclically conjugated 7-membered ring. With nucleophilic reagents these compounds can reform the bicyclic azulene system *(25)*.
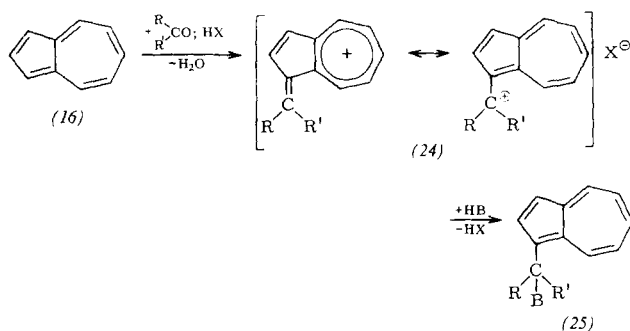
These conversions of the 5- and 7-membered fulvenoid systems of conjugation into the azulenoid system are evidently energetically favored, and furthermore the bicyclic system of 10 π-electrons is less favored energetically than the benzenoid sextet. These factors determine the reactivity of the fulvenoid system which will be illustrated by three further examples.

The dihydro derivative *(26)* is readily accessible by Birch reduction [28] of azulene with sodium in liquid

[25] *K. Hafner, H. Pelster*, and *W. aus der Fünten*, unpublished experiments.

[26] *K. Hafner, A. Stephan*, and *C. Bernhard*, Liebigs Ann. Chem. *650*, 42 (1961).

[27] *K. Hafner, H. Pelster*, and *J. Schneider*, Liebigs Ann. Chem. *650*, 62 (1961).

[28] *A. J. Birch*, Quart. Reviews (chem. Soc., London) *4*, 69 (1950).

ammonia [29]. This derivative reacts with carbonyl compounds in the presence of base to yield stable fulvenes of structure *(27)*, which are readily rearranged into the
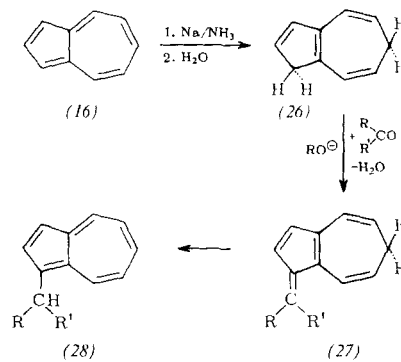
azulenoid system *(28)* (formally by migration of a hydride ion) in the presence of suitable hydride-ion acceptors and donors [29]. This simple conversion of the cross-conjugated fulvene system into the cyclically conjugated decet system is also encountered in the alkylation
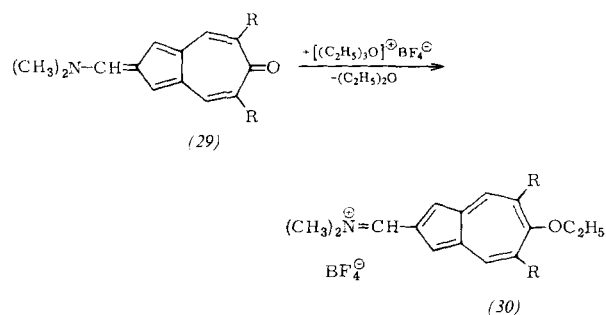
of fulvenotropones of structure *(29)*, which are thereby rapidly transformed into the azulene system of conjugation *(30)* [30].

As expected, the reverse transformation of the azulene derivative *(31)* into the fulvenotropone system *(32)* by proton migration [31] is not possible.
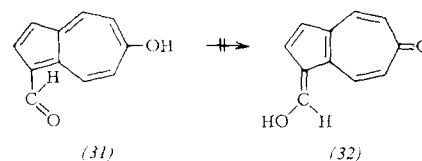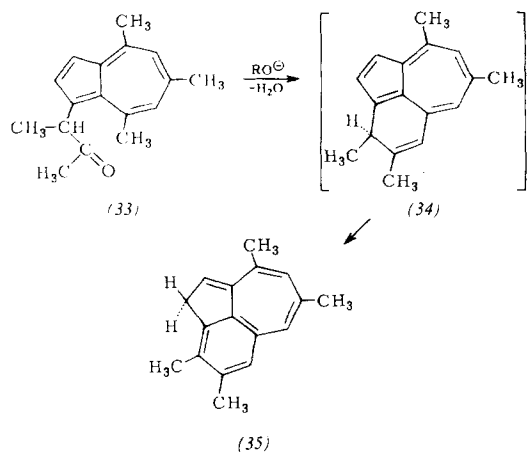
However, the cyclic conjugation of the azulenoid system of 10 π-electrons is readily disrupted if a possibility exists of forming the benzenoid sextet. This is borne out not only by the thermal isomerization [32] of azulene to naphthalene, but also by the synthesis of the tricyclic hydrocarbon *(35)*. The product expected from intramolecular ring-closure of the ketone *(33)* is *(34)*, in which the azulene is fused to a cyclohexadiene system.

[29] *K. Hafner* and *W. Klinner*, unpublished experiments.

[30] *K. Hafner, K. H. Vöpel, G. Ploß*, and *C. König*, Liebigs Ann. Chem. *661*, 52 (1963).

[31] *H. Kaiser*, Ph. D. Thesis, Universität Marburg/Lahn, 1959.

[32] *E. Heilbronner, P. A. Plattner*, and *K. Wieland*, Experientia *3*, 70 (1947); *E. Heilbronner* and *K. Wieland* Helv. chim. Acta *30*, 947 (1947).

(33) → *(34)*

(35)

Isolation of this compound is prevented by its isomerization to the benzoheptafulvene derivative *(35)* [33] with loss of the bicyclic conjugation of azulene. Compound *(35)* is a non-benzenoid isomer of phenalene [34], and like the latter, can be transformed by proton-abstraction with strong bases into the anionic system *(36)*


(35) +HClO₄ → *(38)*

·LiCH₃ | –CH₄

–(C₆H₅)₃CH⁺ ⟋ (C₆H₅)₃C⊕ ClO₄⊖

(36) Li⊕ ‖‖

(37) ClO₄⊖ ‖‖
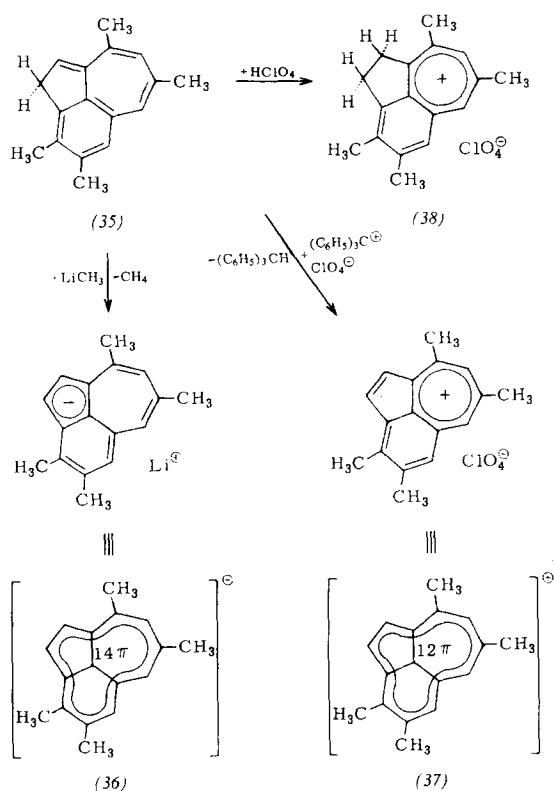
containing 14 π-electrons, and can form the cation *(37)* [35] containing 12 π-electrons under the influence of hydride-ion acceptors. The heptafulvene system in *(35)* is stabilized in a characteristic manner by addition of a proton to give the benzotropylium ion *(38)* [33].

The two non-alternant hydrocarbons, pentalene *(39)* and heptalene *(40)*, are cyclically conjugated systems of 8 and 12 π-electrons, respectively, and therefore belong

(39)   *(40)*

(41)

(42)
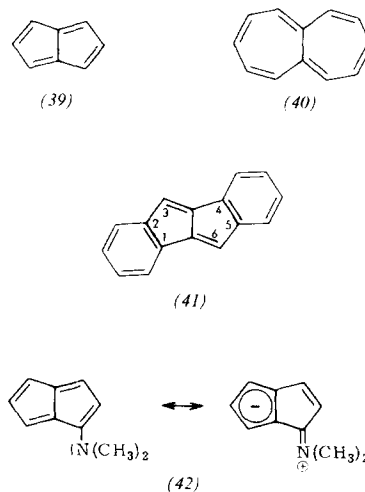
to the systems of 4n π-electrons which, according to Hückel's rule, should possess no "aromatic character", *i.e.* only low delocalization energy and no benzene-like reactivity. Although this hypothesis was confirmed by the experimental results of several groups of workers, theoretical calculations led to different conclusions [36]. The marked olefinic properties of dibenzo[*a,e*]pentalene *(41)* [37] (ring-closed *trans*-1,4-diphenyl-1,3-butadiene) suggest that the resonance stabilization lacking in pentalene (in contrast to azulene) may be compensated by electron-releasing substituents, as, for example, in *(42)*. Pentalene derivatives of type *(42)* are not yet known, however. Nevertheless, the tricyclic pentalene derivative *(43)* was synthetized by attachment of a 5-membered ring across the 1,8-positions of azulene [38]. The 7-membered ring in this derivative can formally accept a partial positive charge, whereas the two 5-membered rings are

(43)

(43a)   *(44)*

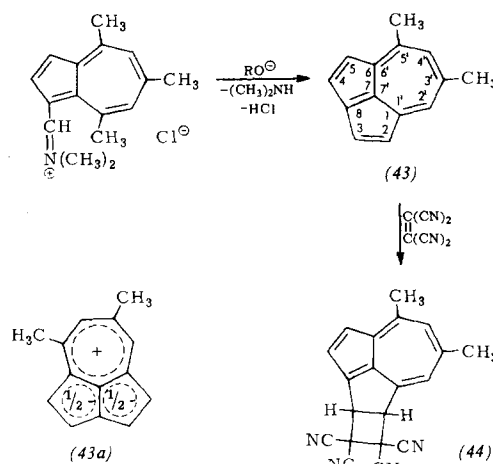[33] K. Hafner and H. Schaum, Angew. Chem. 75, 90 (1963); Angew. Chem. internat. Edit. 2, 95 (1963).

[34] R. Pettit, Chem. and Ind. 1956, 1306; J. Amer. chem. Soc. 82, 1972 (1960); V. Boekelheide and C. E. Larrabee, J. Amer. chem. Soc. 72, 1245 (1950).

[35] K. Hafner and H. Schaum, unpublished experiments. MO-LCAO calculations for the cation, anion, and free radical of *(35)* have recently been carried out by R. Zahradnik, C. Parkanyi, and J. Michl, Prague (personal communication from Dipl.-Ing. R. Zahradnik).

[36] E. D. Bergmann in [2a].

[37] C. T. Blood and R. P. Linstead, J. chem. Soc. (London) 1952, 2255, 2263; C. C. Chuen and S. W. Fenton, J. org. Chemistry 23, 1538 (1958).

[38] K. Hafner and J. Schneider, Liebigs Ann. Chem. 624, 37 (1959).

negatively polarized according to formula *(43a)*. Probably as a result of the angle strain at carbon atom 6 or 7 caused by the ethylene bridges in the 2,3- or 4,5-positions, the hydrocarbon does not show the properties of its underlying azulene system, but behaves like a polyolefin, which is prone to spontaneous addition of dienes or dienophiles onto one of the double bonds in the two 5-membered rings, with reformation of the cyclic conjugation of azulene *(44)* [38]. This behavior of the "stabilized" pentalene derivative *(43)* as well as that of the hydrocarbon *(41)* confirms the theoretical predictions, according to which no "aromatic character" is to be expected of the parent substance *(39)*, whose synthesis has not yet been accomplished despite numerous attempts. Neither hexaphenylpentalene *(45)*, which was recently prepared by *Le Goff* [39], nor the pentalene dianion *(46)*, which contains 10 π-electrons and was prepared by *Katz* [40], permit assertions concerning the unsubstituted, uncharged bicyclic system *(39)*.

(45)   *(46)*
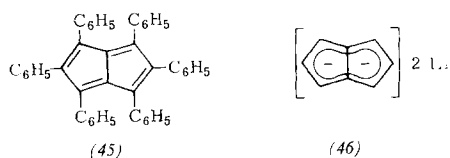
It was also possible in the case of heptalene *(40)* [36] to confirm predictions based on the relations between constitution and "aromatic character". In the tricyclic heptalene derivative *(47)* [38,41,42], the 5-membered ring bears a partial negative charge which should stabilize the bicyclic heptalene to a certain extent by affording an additional opportunity for resonance in the sense of the collective structure *(47a)*; compound *(47)*

(47)

(47a)
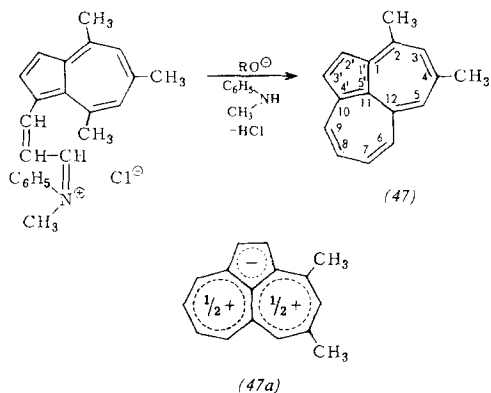
allowed valuable statements to be made about the parent substance, which have recently been confirmed by an elegant synthesis of the latter [43].

The thermally stable hydrocarbon *(47)* is readily accessible by fusion of a further 7-membered ring onto azulene across the 1,8-positions and shows chemical and

spectroscopic properties unlike those expected of the analogue of acenaphthylene, "aceheptylene" [44], since the ethylene bridge forming the 5-membered ring has no olefinic character. In accord with MO-LCAO calculations [45], *(47)* is much more like an azulene with a diene bridge across the 1,8-positions, in which the π-electrons of the conjugated diene participate more or less

(47b)

(48)   *(49)*
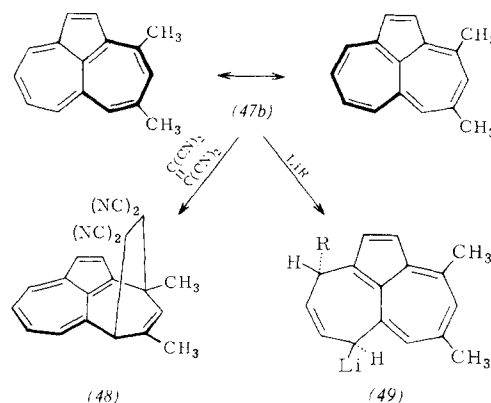
in the resonance of the bicyclic decet system of the azulene *(47b)*.

This is indicated by the electrophilic substitution which takes place at the 3'-carbon atom of the 5-membered ring, the Diels-Alder reaction of the diene system of the dimethylated 7-membered ring with tetracyanoethylene (or similarly with maleic anhydride) to give the adduct *(48)*, the formation of blue azulene derivatives of type *(49)* by 1,4-addition of lithium alkyls onto the more electrophilic unsubstituted 7-membered ring, and the bathochromically shifted absorption spectrum of the hydrocarbon, which is nevertheless characteristic of the azulene system [38,41].

This picture is further confirmed by the course of the protonation of the dimethylamino derivative *(50)*. Formation of the ammonium salt *(51)* with tricyclic conjugation does not occur; instead, compound *(50)* reacts as an enamine adding a proton at the β-position relative to the amino group, whereby the system of 14 π-electrons is transformed into the preferred decet system of the azulene *(52)* [42].

(51)   *(50)*

(52)

[39] *E. LeGoff*, J. Amer. chem. Soc. *84*, 3975 (1962); see also ibid. *84*, 1505 (1962).
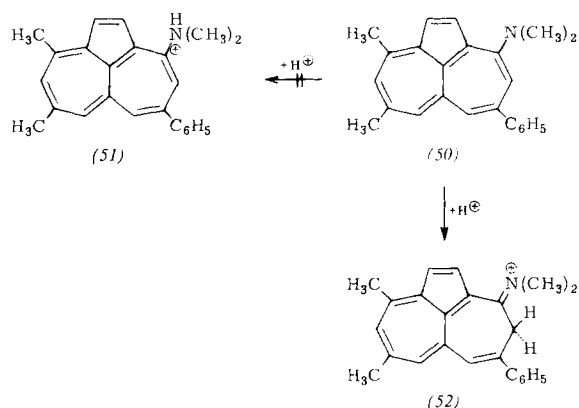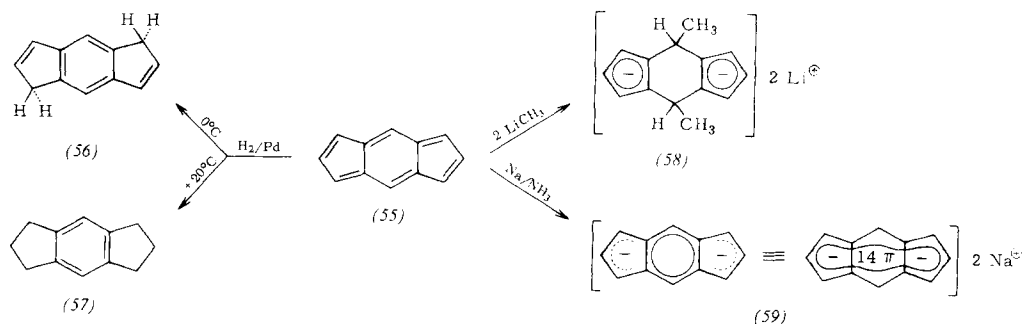
[40] *T. J. Katz* and *M. Rosenberger*, J. Amer. chem. Soc. *84*, 865 (1962).

[41] *K. Hafner* and *G. Schneider*, Liebigs Ann. Chem. *672* (1964), in the press.

[42] *K. Hafner* and *K. F. Bangert*, Liebigs Ann.Chem.*650*,98 (1961).

[43] *H. J. Dauben, Jr.* and *D. J. Bertelli*, J. Amer. chem. Soc. *83*, 4659 (1961).

[44] Nomenclature proposed by Prof. *H. J. Dauben*.

[45] *M. Asgar Ali* and *C. A. Coulson*, Molecular Physics *4*, 65 (1961); *A. Rosowsky, H. Fleischer, S. T. Young, R. Partch, W. H. Saunders, Jr.*, and *V. Boekelheide*, Tetrahedron *11*, 121 (1960); *A. Streitwieser* [2e].

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The energetic advantage of the π-electron decet of azulene over the 12 π-electron system of heptalene is confirmed by the typically olefinic character of the very thermolabile parent substance *(40)*, and by its NMR spectrum, in which the location of the ring-proton signals in the frequency range that is characteristic of olefinic protons (between 4 and 5 τ) [43] indicates very little π-electron delocalization.

protons. Catalytic hydrogenation below 0 °C rapidly transforms the hydrocarbon into the benzenoid derivative, 1,5-dihydro-*s*-indacene *(56)*, and hydrogenation at 20 °C gives *s*-hydrindacene *(57)* [49], with gains in resonance energy.

In agreement with *Brown*'s predictions [47], nucleophilic attack takes place at the 4- and 8-positions of the tricyclic system. The reaction profits from the energy gain

s-Indacene

s-Indacene *(55)* [46] was often the subject of theoretical and experimental studies, because it is a further example of a system of 4n π-electrons related to the still unknown pentalene and one which allows the relations between structure and "aromatic character" to be clearly recognized. According to LCAO calculations carried out by *R. D. Brown* [47], this hydrocarbon should possess an electron delocalization energy similar to that of the tropylium cation, yet the system can be expected to show high reactivity on account of the low energy difference between its ground and excited states. A simple synthesis of *s*-indacene was effected recently [11] which has allowed the theoretical predictions to be tested.

The surprisingly great tendency of the fulvene *(53)* to form the tricyclic compound *(55)* by way of the non-isolable intermediate *(54)* even below −30 °C (a fine
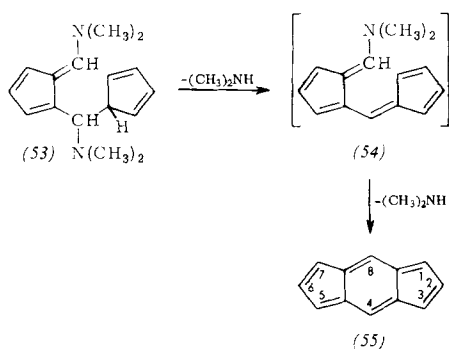
example of the effectiveness of the "principle of rigid groups" [48]) stands in contrast to the remarkably small thermal stability of this system. Limited π-electron delocalization is indicated by the NMR spectrum of *s*-indacene, which displays signals between 2.4 and 3.7 τ in the intensity ratio 1:2:1 corresponding to the 8 ring

associated with the formation of the two isolated sextet systems of cyclopentadienyl anions. Compound *(55)* reacts with methyl-lithium even at −30 °C to give the stable, isolable lithium salt *(58)* [50]. Birch reduction [28] of *s*-indacene *(55)* with sodium in liquid ammonia leads to the disodium salt *(59)* of the tricyclic system. As befits a system of 14 π-electrons obeying Hückel's rule, like the dianion *(4)* with 10 π-electrons prepared in the same way by *Katz* et al. [10] from cyclooctatetraene, the salt *(59)* can be isolated as a thermally stable, but air-sensitive, colorless compound [50]. On hydrolysis, it yields 1,5-dihydro-*s*-indacene *(56)* of established structure. As a cyclopolyene, *(55)* reacts with silver nitrate to form a red, crystalline metal π-complex of only low thermal stability [50].

The properties of *s*-indacene *(55)* give reason to suppose that its still unknown asymmetrical isomer *(60)* [47,51] is subject to even less resonance stabilization. In contrast to the two equivalent Kekulé structures of *s*-indacene, the asymmetrical isomer can be described only as a resonance hybrid of the two canonical forms *(60a)* and *(60b)*, which are *p*- and *o*-quinonoid, respectively.
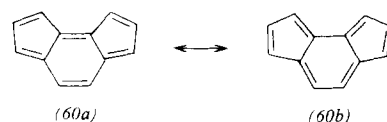
Heterotropilidenes

Whereas bi- and polycyclic non-benzenoid systems of 4n π-electrons (such as pentalene derivatives, heptalene, and *s*-indacene) have been synthetized and recognized (by their ultraviolet and NMR spectra, thermochemical

[46] *A. Streitwieser* [2e]; *D. P. Craig* in [2a].

[47] *R. D. Brown*, J. chem. Soc. (London) *1951*, 2391.

[48] *W. Baker*, Ind. chim. Belge *17*, 633 (1952).

[49] *R. T. Arnold* and *E. Rondestvedt*, J. Amer. chem. Soc. *67*, 1265 (1945).

[50] *E. Sturm*, unpublished experiments.

[51] *A. Etienne* and *A. LeBerre*, C. R. hebd. Séances Acad. Sci. *242*, 1453 (1956); *O. Chalvet* and *J. Peltier*, Bull. Soc. chim. France *1956*, 1667.

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properties, and reactivities) as representatives of a class of compounds that differ considerably from the systems with 4n+2 π-electrons, only a few observations are available concerning monocyclic conjugated systems with 4n π-electrons. These include studies by different groups of workers on compounds which are isoelectronic with the cycloheptatrienyl anion (64) and which differ from it in replacement of one of the methine groups by a hetero-atom. These are oxepine (61), thiepine (62),

(61)   (62)

(63)   (64)
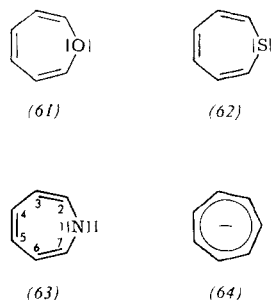
and azepine (63). None of these three heterotropilidenes has been prepared as yet. On the other hand, the cycloheptatrienyl anion (64) was recently detected by Dauben [52], and its heptaphenyl derivative by Breslow and Chang [53]. Both systems of 8 π-electrons prove to be thermally very unstable. Further investigations of the fine structure and reactivity in these octet systems are necessary in order to recognize similarities to and differences from the corresponding tropylium cations.

So far only several mono-, di-, and tribenzo derivatives of the three heterotropilidenes (61) to (63) have been prepared as well as some polysubstituted derivatives stabilized by additional opportunities for resonance, and various dihydro derivatives [54,55]. Only limited conclusions are permissible from the chemical and physical

COOR

IX   (65), X = O, S, N–CH₃

COOR
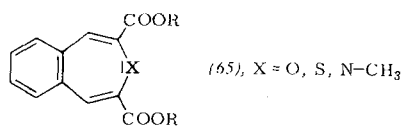
behavior of the benzoheterotropilidenes (65) studied by Dimroth and Freyschlag [54] concerning the properties of the hypothetical monocyclic compounds (61) to (63), because in the bicyclic derivatives (65) stabilization of the benzene moiety by its electron sextet presumably far outweighs any stabilization of the heterocyclic 7-membered ring.

[52] H. J. Dauben, Jr., J. Amer. chem. Soc. 85, 3041 (1963).

[53] R. Breslow and H. W. Chang, J. Amer. chem. Soc. 84, 1484 (1962).

[54] K. Dimroth and H. Freyschlag, Chem. Ber. 89, 2602 (1956); 90, 1623, 1628 (1957); K. Dimroth and G. Lenke, ibid. 89, 2608 (1956); K. Dimroth and G. Pohl, Angew. Chem. 73, 436 (1961); R. H. F. Manske and A. E. Ledingham, J. Amer. chem. Soc. 72, 4797 (1950); F. A. L. Anet and P. M. G. Bavin, Canad. J. Chem. 35, 1084 (1957); R. Huisgen, E. Laschtuvka, and F. Bayerlein, Chem. Ber. 93, 392 (1960); R. Huisgen, E. Laschtuvka, J. Ugi, and A. Kammermeier, Liebigs Ann. Chem. 630, 128 (1960); E. D. Bergmann and M. Rabinovitz, J. org. Chemistry 25, 827 (1960); G. Westöö, Acta chem. scand. 13, 604 (1959).

[55] R. Huisgen, D. Vossius, and M. Appl, Chem. Ber. 91, 1 (1958); R. Huisgen and M. Appl, ibid. 91, 12 (1958); M. Appl and R. Huisgen, ibid. 92, 2961 (1959).

On the other hand, the investigations of Huisgen et al. [55] are of greater significance in this connection. Thermolysis of phenyl azide in aniline yielded a monocyclic isomer of azepine, the cyclic amidine or azatropilidene derivative (69) [*]. According to these workers' findings, the aryl nitrene (66), i.e. the reactive intermediate arising from the aryl azide by elimination of nitrogen, is supposedly converted in an equilibrium reaction into the similarly highly reactive bicyclic azirine (67), which then undergoes a first (but still incomplete) stabilization to 2-anilino-1H-azepine (68) by addition of one mole of aniline and subsequent isomerization to the 7-membered ring. The 1H-azepine (68) rapidly rearranges into the tautomeric form (69) which is energetically favored by amidine resonance.

(66)   (67)

(69)   (68)
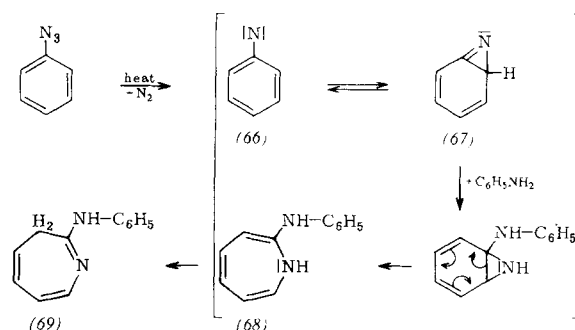
A synthesis recently discovered in our laboratory [56] of a simple azepine derivative and a study of its properties give an answer to the question of the "aromatic character" of this octet system. N-Ethoxycarbonylazepine (71) can be prepared readily by either photochemical or thermal ring-expansion of benzene with ethyl azidoformate in a reaction analogous to that of Buchner [57]. The azepine derivative (71) is presumably formed by way of the intermediate aziridine (70), its valence-isomer.

(70)

(71)
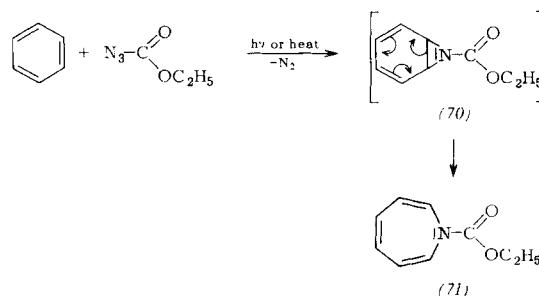
The NMR spectrum of this heterocycle displays a multiplet at 4.0–4.7 τ due to the six ring protons. Compared with the spectrum of the homologous N-ethoxycarbonylpyrrole (ring-proton signals at 3.0 and 4.0 τ), this indicates some π-electron delocalization (ring current), the extent of which has still not been determined exactly,

[*] According to more recent investigations and contrary to earlier statements, (69) possesses the constitution of 2-anilino-3 H-azepine (personal communication from Prof. R. Huisgen).

[56] K. Hafner and C. König, Angew. Chem. 75, 89 (1963); Angew. Chem. internat. Edit. 2, 96 (1963).

[57] E. Buchner and Th. Curtius, Ber. dtsch. chem. Ges. 18, 2377 (1885); see also G. O. Schenck and H. Ziegler, Liebigs Ann. Chem. 584, 221 (1953).

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and thus a difference in degree only, but not in kind, between systems with 4n+2 and 4n π-electrons. At the same time, however, the urethane resonance also contributes to the stabilization of *(71)*. This is borne out by the extreme thermal instability of *N*-methylazepine *(72)*,
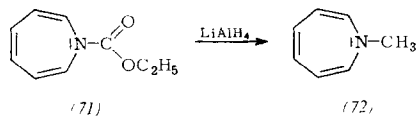

which is accessible by reduction of the azepine derivative *(71)* with lithium aluminum hydride, and whose cyclic system of 8 π-electrons is not stabilized by functional groups. The structureless ultraviolet spectrum of this vinylogue of *N*-methylpyrrole is like that of the 5-membered parent heterocycle with a π-electron sextet but shifted bathochromically by about 30mμ, in accordance with the extension of the conjugated system [58].

In contrast to the 7-membered carbocyclic sextet systems, the ethoxycarbonylazepine *(71)* reacts rapidly with dienophiles to form adducts. According to present findings, the product obtained with tetracyanoethylene [58] is the 1,6-adduct *(73)*, and not the equally conceivable tricyclic Diels-Alder adduct *(74)* which could arise from a mobile equilibrium of the two valence-isomeric
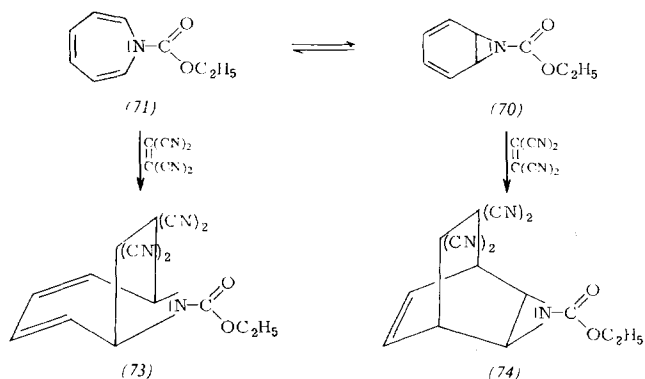

forms *(70)* and *(71)* analogous to the comparable reaction of tropilidene [59]. The lower stability of the π-electron octet than that of the benzenoid π-electron sextet is confirmed by the reaction of *N*-ethoxycarbonyl-azepine *(71)* with acids. This rapidly leads to ethyl *N*-phenylurethane *(76)*, which is presumably formed after initial protonation of the oxygen by way of the aziridine intermediate *(75)*, from which the benzenoid system is

then formed irreversibly with a considerable gain in resonance energy [60].
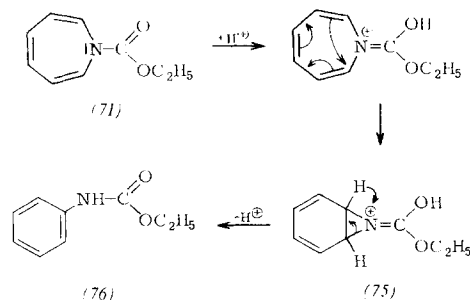
Alkaline hydrolysis of the azepine derivative *(71)* offers a route to 1*H*-azepine *(78)* itself. The alkali metal salt of the carbamic acid *(77)* which is initially formed decarboxylates readily under the influence of dilute acids.
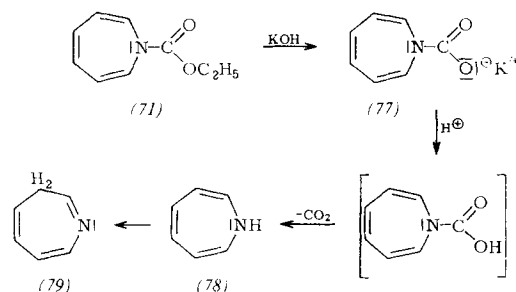
1*H*-Azepine *(78)* thereby obtained in solution is thermally very unstable; spectroscopically, like its *N*-methyl derivative, it resembles pyrrole. Its formation is followed rapidly by a rearrangement, presumably into the tautomeric 3*H*-azepine *(79)* [61], effecting stabilization as in the preparation of *Wolff* and *Huisgen*'s azepine derivative *(69)* [55], although the latter compound also profits from the gain in resonance energy associated with the formation of the amidine system. On the other hand, the driving force for the transformation of the double enamine *(78)* with its 8 π-electrons into the azatriene system *(79)* should possibly be sought in the accompanying rehybridization of the nitrogen atom and its involvement in the conjugation.

[58] *K. Hafner* and *G. Schneider*, unpublished experiments.
[59] *K. Alder* and *G. Jacobs*, Chem. Ber. *86*, 1528 (1953); *K. Alder*, *K. Kaiser*, and *M. Schumacher*, Liebigs Ann. Chem. *602*, 80 (1957); vgl. auch *E. Vogel*, Angew. Chem. *74*, 829 (1962); Angew. Chem. internat. Edit. *2*, 1 (1963).

[60] *K. Hafner* and *D. Zinser*, unpublished experiments.
[61] *K. Hafner* and *W. aus der Fünten*, unpublished experiments.