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Studies in catalytic dehydrogenation : Part X†—Syntheses of alkylsubstituted spirol[4,6]undecanes and dehydrogenation of 1-ethyl-8,9- benzospiro[4,6]undecane

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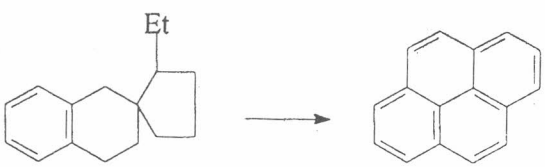
Acylation of benzene with 2-alkylsubstituted cyclopentan-1,1-diacetic anhydrides gives the keto acids (**2**, R = Me, Et, Pr^n, Pr^i) which are converted into the desired alkylsubstituted spiro[4,6]undecanes **5** by Paar hydrogenation followed by cyclisation and Wolff-Kishner reduction. Catalytic dehydrogenation of 1-ethyl-8,9-benzospiro[4,6]undecane **5b** with Pd-C gives a complex mixture of products from which a few major products like naphthalene, 2-methylnaphthalene, 1-ethylnaphthalene, 1,2-dimethylnaphthalene, 1,4,6-trimethylnaphthalene, anthracene and 1-methylanthracene are identified by comparative GC-mass spectra. A plausible explanation of the formation of these products is suggested.

Sengupta and Chatterjee[1,2] have extensively studied catalytic dehydrogenation of tetralin derivatives containing different alkyl substituents on the spirocyclopentane ring. Presence of a methyl group in the spirocyclopentane ring undergoes ring transformation during dehydrogenation to afford methylphenanthrene or its derivatives. However, spiran with ethyl or *n*-propyl substituent leads to the formation of pyrene and 1-methylpyrene respectively in identical condition.

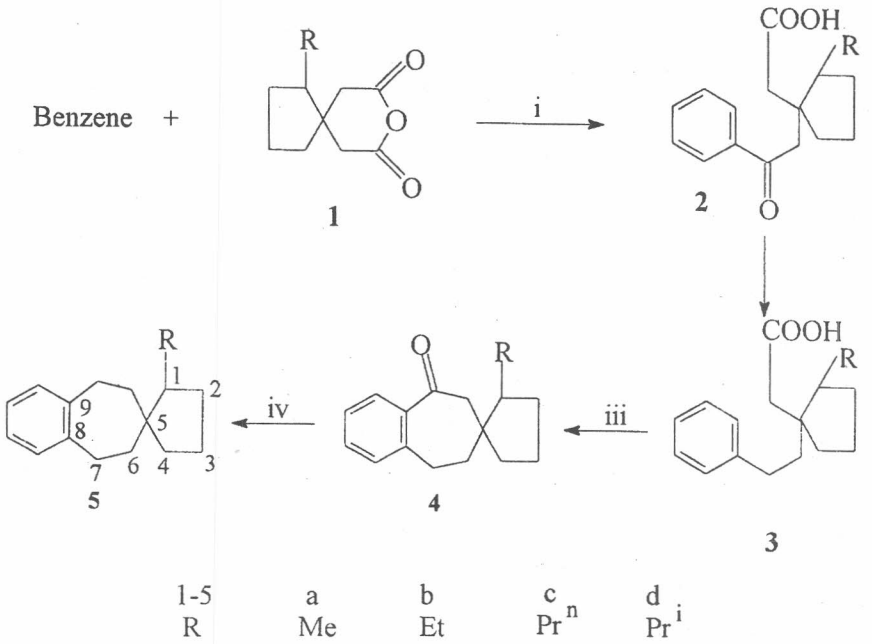


We have synthesised several 6-alkylbenzocycloheptanes[3] and contrary to an early report[4], dehydrogenation yielded a mixture of naphthalene and its alkyl derivatives. In order to gain insight into the mechanism of the dehydrogenation suggested by us[3], we became interested in 1-substituted-8,9-benzospiro[4,6]undecane ring system. The present note deals with the synthesis of several 1-alkyl-8,9-benzospiro[4,6]undecanes (**5**, R=Me, Et, Pr^n, Pr^i) and dehydrogenation studies of 1-ethyl derivative as a representative of the above system.

The anhydrides **1** with benzene in the presence of anhydrous aluminium chloride furnished the keto acids **2** which on Paar hydrogenation in the presence of Pd-C gave the reduced acids **3**. **3** on cyclisation with polyphosphoric acid afforded the spiroketones **4** which finally yielded the desired benzospiro[4,6]undecanes **5** on Wolff-Kishner reduction (Scheme I). The structures of the compounds, **2-5**, were confirmed by spectral analyses.

Earlier[3] it was reported that 6-alkylbenzocycloheptanes on dehydrogenation with Pd-C at 400° in a sealed tube yielded a mixture of compounds of which among others, 1-methylnaphthalene was identified as the major product. The suggested mechanism entails that one of the two benzylic carbons of benzocycloheptane is lost during the aromatisation process. In order to test the generality or otherwise of the above mechanism, 1-ethyl-8,9-benzospiro[4,6]undecane **5b** was subjected to dehydrogenation. Accordingly,

†Part IX, Reference no. 8.



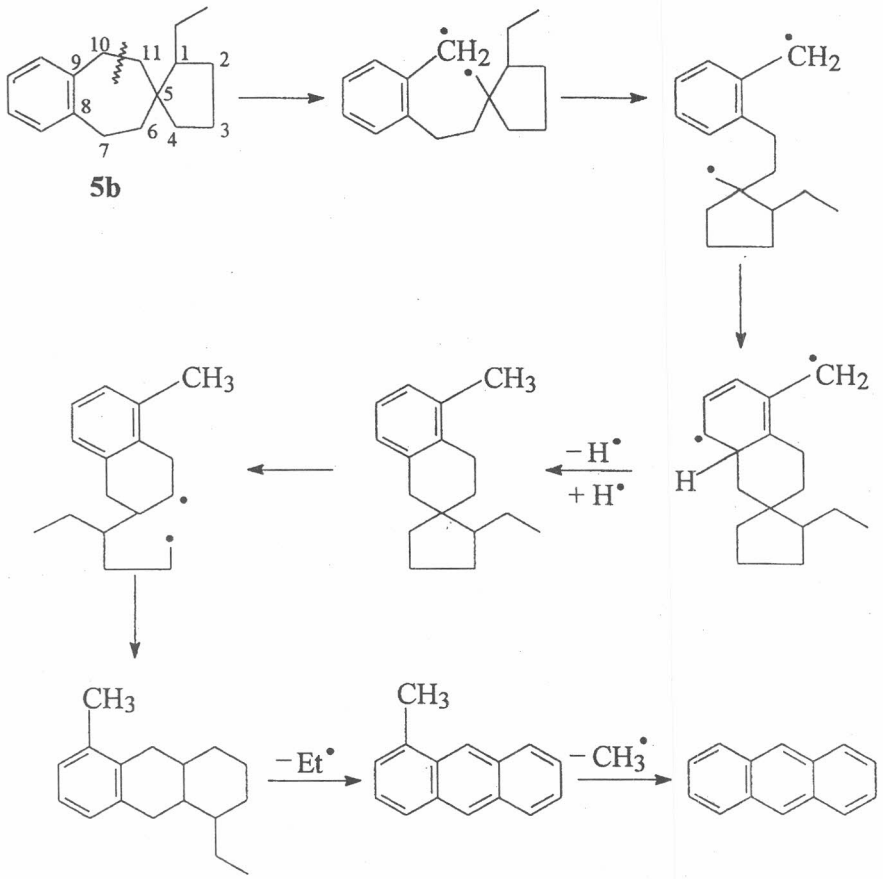
Reagents : i) Anhydrous $AlCl_3$
ii) 10% Pd-C/H_2 , 60 lbs/psi, ethanol
iii) PPA
iv) NH_2NH_2-KOH-ethylene glycol[a]

a) 4a was reduced by Clemmensen reduction

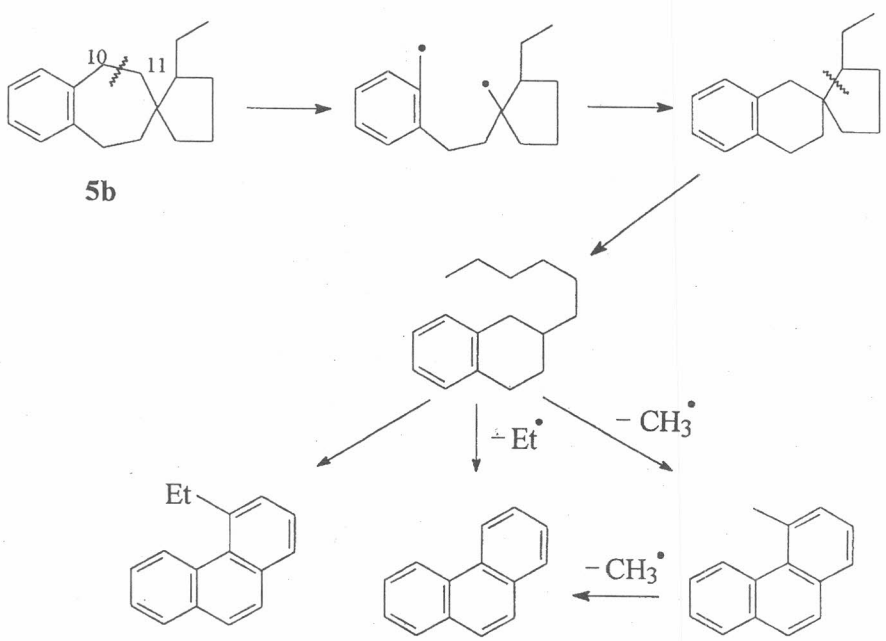
Scheme I

5b was heated in a sealed tube at 380-400° with 10% Pd-C for 12 hr and the product was subjected to fractional chromatography on Brockmann alumina using light petroleum as eluent. GC mass spectra of the first fraction showed the presence of a complex mixture of at least thirty hydrocarbons of which six hydrocarbons namely, (i) naphthalene, (ii) 2-methyl-, (iii) 1-ethyl-, (iv) 1,2-dimethyl- and (v) 1,4,6-trimethylnaphthalenes and (vi) 1-methylanthracene were present in major amounts. The second fraction also consisted of five major products of which four (i-iv) were common to the first fraction established by the comparative GC mass spectra and Vth product was anthracene. In the third fraction there was present one major product, 2-methylnaphthalene which was also common to early fractions. Besides the major components mentioned above three more compounds namely, phenanthrene, 9-methyl-9*H*-fluorene and 1-methyl-9*H*-fluorene (vii-ix) with appreciable concentration were detected in the first fraction by comparative GC mass spectra.

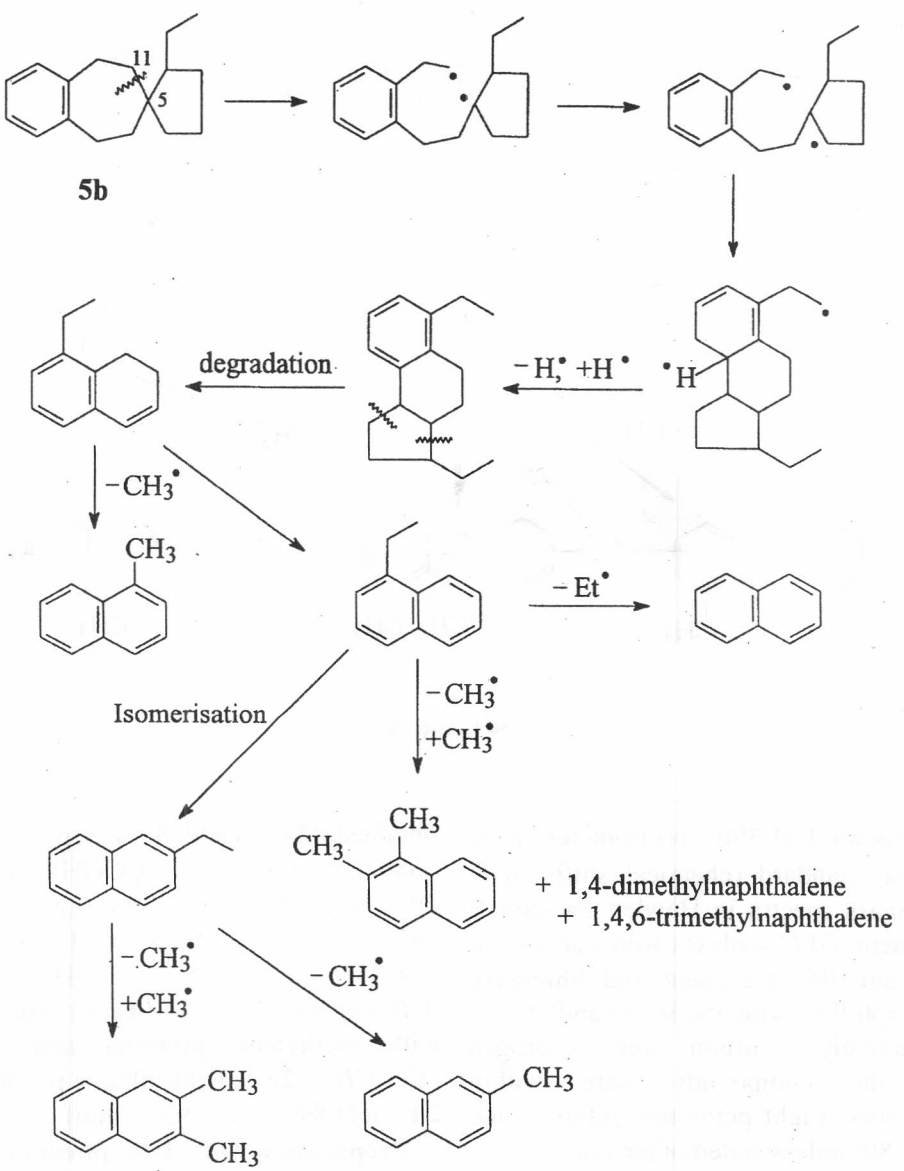
It is extremely difficult to interpret the formation of all the major products from GC-mass fragmentation-pattern analysis. However, attempt was made to offer plausible explanation (Schemes II-V) for the formation of a few products present in the complex mixture obtained after dehydrogenation of 1-ethyl-8,9-benzospiro[4,6]undecane **5b.** Non-equivalent nature of the benzylic C-10 and allylic C-11 carbons in **5b** reveals that the dehydrogenation process is initiated by the homolytic cleavage at more than one particular bond in the cycloheptane ring, and subsequent



Scheme II



Scheme III



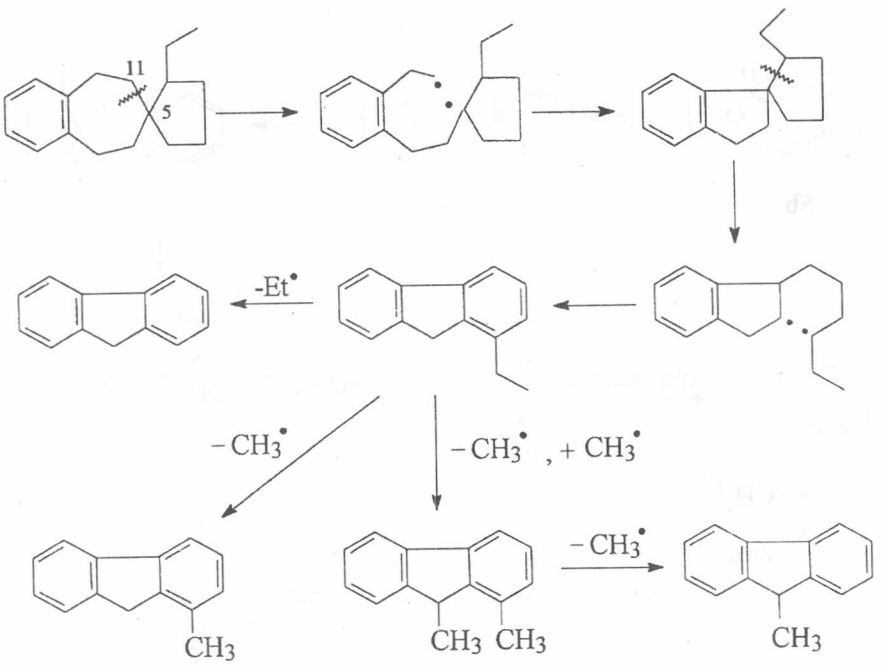
Scheme IV

cyclisation, degradation, aromatisation and isomerisation may give rise to several products. Thus, homolytic cleavage of C-10, C-11 bond (benzylic) is ultimately expected to lead mainly to tricyclic hydrocarbons, anthracene (Scheme II) and phenanthrene (Scheme III) derivatives. The possibility of the cleavage of the bonds other than benzylic ones cannot be ruled out. Accordingly, the major products arising from the initial cleavage of C-11, C-5 bond are expected to be naphthalene (Scheme IV) and fluorene (Scheme V) derivatives.

Attempts to dehydrogenate other spirohydrocarbons (**5a, 5c, 5d**) were abandoned due to complex nature of dehydrogenation reaction of **5b**

Experimental Procedure

Boiling points and melting points are uncorrected. IR spectra in KBr were recorded on a Pye-Unicam SP 200 G spectrophotometer (ν_{max} in cm^{-1}), ^1H NMR spectra in $CDCl_3$ (unless otherwise



Scheme V

stated) on a Varian EM-390 spectrometer using TMS as internal standard (chemical shifts in δ, ppm) and GC-mass spectra in Hewlett Packard II GC-MS instrument. GLC analyses were carried out on a Pye-Unicam-104 instrument and Shimadzu gas chromatograph-9A using 5% SE-30 and OV-17 column respectively. Carbon and hydrogen analyses of the compounds were within experimental errors. Light petroleum refers to the fraction b.p. 60-80° unless stated otherwise.

2-Alkylcyclopentane-1,1-diacetic acid anhydrides 1. These were prepared by refluxing the corresponding 2-alkylcyclopentane 1,1-diacetic acids[5] with acetic anhydride. The anhydrides **1a**, **1b, 1c, 1d** had b.p. 158°/10 mm, 170°/2 mm, 160°/1 mm and 135°/0.2 mm respectively.

Preparation of 1-benzoylmethyl-1-carboxymethyl-2-alkylcyclopentane 2 : General procedure. To a well-stirred suspension of anhydrous $AlCl_3$ (0.26 mole) in dry and purified benzene (150 mL) was added slowly a solution of the anhydride, **1** (0.13 mole) in the same hydrocarbon (150 mL) at 5°. After stirring for 5 hr, the mixture was left overnight, cooled and decomposed. Following usual work-up[6] the corresponding 1-benzoylmethyl-1-carboxymethyl-2-alkylcyclopentane **2** is obtained [**2a** : yield 83%, b.p. 175°/1 mm; IR : 1680 (>C=O), 1710 (-COOH). It gave positive DNP test; **2b** : yield 79%, b.p. 195°/1 mm; IR : 1670 (>C=O), 1710 (-COOH);. ^{1}H NMR : 8.10-7.30 (5H, m, Ar-H), 3.2-2.5 (4H, m, PhCOCH_2 and -CH_2COOH), 2.2-1.4 (9H, m, ring cyclopentane with methylene protons) and 0.9 (3H, m, –CH_2CH_3); **2c** : yield 90%, b.p. 185-90°/0.5 mm; **2d** :yield 89%, b.p. 195°/1 mm].

Preparation of 1-(ω-phenethyl)-1-carboxymethyl-2-alkylcyclopentane 3: General procedure. The keto acid **2** (0.046 mole) was reduced with hydrogen in a Paar apparatus in ethanol (25 mL) in the presence of 10% Pd-C as catalyst under 60 lbs/p.s.i. The theoretical amount of hydrogen as judged from the pressure drop was taken up in 2 hr. Removal of catalyst by filtration and evaporation of solvent left the acid **3** which was distilled under reduced pressure. In case of **3c** and **3d**, the reduction was carried out at room temperature after addition of a few drops of perchloric acid [**3a** : yield 78%, b.p. 190-95°/1 mm; IR : 1710 (-COOH); **3b**: yield 80%, b.p. 185°/0.7 mm; IR : 1710 (-COOH); **3c**: yield 56%, b.p. 192°/0.9 mm; **3d** : yield 83%, b.p. 190°/0.7 mm].

PPA cyclisation of 3: Formation of 4: General procedure. The acid **3** (0.09 mole) was heated with PPA (prepared from 265g P_2O_5 and 156 mL of phosphoric acid) on a steam-bath while stirring for nearly 1 hr where the colour of the mixture turned deep brown. Decomposition of the mixture with ice followed by solvent extraction and removal of the uncyclised acid by Na_2CO_3 left the cyclic ketone 4, which was purified by distillation under reduced pressure.

4a: Yield 79%, b.p. 160-70°/1.5 mm; IR : 1685 (>C=O).

4b: Yield 80%, b.p. 160°/2 mm; IR : 1675 (>C=O); ^{1}H NMR : 7.70 (1H, dd, Ar-H *peri* to CO), 7.35-6.9 (3H, m, Ar-H), 3.05-2.8 (2H, m, ArCH_2), 2.75-2.30 (2H, m, ArCOCH_2), 2.2-1.1 (11H, m, PhCH_2CH_2 and cyclopentane ring with methylene protons), 0.85 (3H, t, CH_2CH_3). It gave positive DNP test.

4c: Yield 83%, b.p. 198°/3 mm; IR : 1685 (>C=O); ^{1}H NMR : 7.80 (1H, dd, Ar-H *peri* to CO), 7.4-7.3 (3H, m, Ar-H), 3.1-2.9 (2H, m, ArCH_2), 2.8-2.4 (2H, m, ArCOCH_2), 2.1-1.1 (13H, m, PhCH_2CH_2 and cyclopentane ring with methylene protons), 0.9 (3H, t, $CH_2CH_2CH_3$). Its DNP derivative had m.p. 207°.

4d: Yield 85%, b.p. 160°/0.5 mm; IR : 1680 (>C=O); ^{1}H NMR : 7.85 (1H, dd, Ar-H *peri* to CO), 7.5-7.2 (3H, m, Ar-H), 3.2-3.1 (2H, m, ArCH_2), 2.8-2.4 (2H, m, ArCOCH_2), 2.0-1.4 (10H, m, PhCH_2CH_2 and cyclopentane ring with C*H*< substitution), 1.1-0.9 (6H, dd, $CH\langle \frac{CH_3}{CH_3}$. Its DNP derivative had m.p. 247°.

Preparation of 1-alkyl-8,9-benzospiro[4,6]undecane 5: General procedure. The spiran **5b-d** prepared in 75-80% yields by Huang-Minlon reduction of the preceding cyclic ketones **4** had boiling points 130-32°/4 mm, 135-37°/0.4 mm and 160°/1 mm, respectively. The ketone **4a** on Huang-Minlon reduction gave **5a** in poor yield. However, Clemmensen reduction of **4a** afforded **5a** in good yield (60%), b.p. 140°/1.5 mm. The compound **5** was checked for the absence of carbonyl peak in its IR spectrum.

Dehydrogenation of 5b. The hydrocarbon **5b** (2 g) was heated with 10% Pd-C (0.2 g) in a sealed tube at 380-400° for 12-14 hr. On opening the sealed tube the issuing gas burnt with a blue flame. The product was extracted with ether and benzene, the solvent removed, and the residual oil subjected to chromatographic fractionation on a Brockmann alumina column using light petroleum as eluent. The elutes, each 25 ml, were collected and all the compounds got eluted in the first three fractions. Each fraction was subjected to GC mass analysis.

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References

1 Sengupta S C & Chatterjee D N, *J Indian chem Soc*, 29, **1952**, 438; 30, **1953**, 27; 31, **1954**, 11.
2 Chatterjee D N, *J Am chem Soc*, 77, **1955**, 5131 and references cited therein.
3 Sen P K, Lahiri S & Das T K, *Indian J Chem*, 23B, **1984**, 821.
4 Chakraborty P S, *Indian J Chem*, 10, **1972**, 385.
5 McElvain S M & Clemens David H, *J Am chem Soc*, 20, **1958**, 3915.
6 Sen P K & Lahiri S, *Indian J Chem*, 29B, **1990**, 741.