azulenoid system resonance into the energetically more favorable benzenoid system *(6)*. Compound *(6)* crystallizes in golden-yellow needles of m.p. 116 to 117 °C; its ultraviolet spectrum has a strong fine structure: λ_{max} = 231 mμ (log ε = 4.55); 235 (4.55); 280 (3.91); 291 (3.80); 312 (3.71); 325 (3.69); 340 (3.59); and 406 (3.20).

Compound *(6)* absorbs 3 moles of H_2 to form the indane derivative *(7)*. With trityl perchlorate, *(6)* gives the stable orange carbonium salt *(8)*, m.p. 236 to 238 °C with decomposition. With methyl-lithium, *(6)* forms a green compound *(9)*, which is sensitive to hydrolysis. Compound *(9)* is an example of a cyclic conjugated 14 π-electron system with the general structure *(10)*.

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

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N-Ethoxycarbonylazepine

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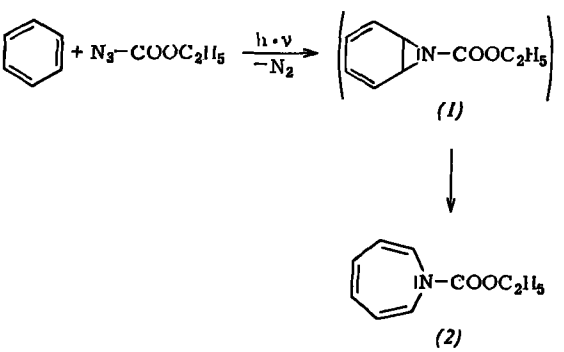
By irradiating a solution of ethyl azidocarbonate in benzene with ultraviolet light, we obtained *N*-ethoxycarbonylazepine *(2)* in *ca.* 70 % yield as a stable yellow oil, b.p. 130 °C/20 mm (λ_{max} = 208 mμ (log ε = 4.44) and λ_{max} = 330 mμ (log ε = 2.72) in n-hexane).



This new ring expansion reaction resembles the photolytic reaction of benzene with diazomethane to yield cycloheptatriene. Here, however, instead of the methylene group, the ethoxycarbonylazene group [1] reacts with the benzene, probably to give first the azanorcaradiene derivative *(1)*, which rearranges at once to its isomeric azepine *(2)*.

Compound *(2)* is the first monocyclic azepine derivative to have been prepared [2]. Catalytic hydrogenation of *(2)* with Pd/H_2 at 20 °C affords *N*-ethoxycarbonyl hexamethylene imine (b.p. 118–120 °C/20 mm; n_{21}^{D} = 1.4635), which we also prepared from hexamethylene imine [3] and ethyl chloroformate. The two products proved to be identical, judging from their infrared and nuclear magnetic resonance spectra. The NMR-spectrum of *(2)* shows a multiplet for the 6 ring protons at 4–4.7 τ, in addition to the characteristic signals for the protons of the ethyl group (quartet at 5.8 τ, triplet at 8.7 τ).

The stability of the 8 π-electron system in *(2)* appears to be due at least in part to the claim on the free electron pair on the nitrogen made by mesomerism of the urethane system. In the presence of protic acids, *(2)* resinifies rapidly at 20 °C. Attempts to extend this ring expansion reaction with azides to other aromatic systems are in progress.

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Synthesis of Dehydroquinolizinium Systems

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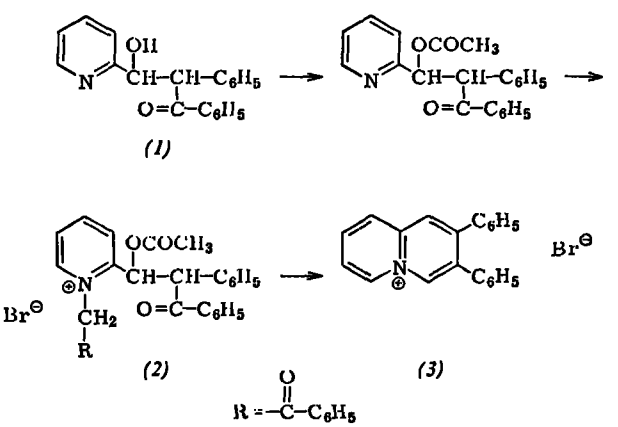
It has been shown [1] that 1,2-diketones can be condensed readily with *N*-methylene-α-picolinium salts to give dehydroquinolizinium derivatives. Here the first component supplies the two ketonic groups necessary for cyclization, and the second supplies the two activated methylene groups. We have now gone over to using two reactants, each of which contains both a ketonic group and an activated methylene group, so that monoketonic compounds derived from *N*-methylene-pyridinium-2-aldehyde can be used for the synthesis of dehydroquinolizinium systems.

The 1,3-ketol *(1)* formed from pyridine-2-aldehyde and deoxybenzoin was esterified and converted into the quaternary ammonium salt *(2)* using bromoacetophenone; the salt *(2)* was then cyclized using dibutylamine in boiling acetone to give 2,3-diphenyl-dehydroquinolizinium bromide *(3)*. In this way, as also in the synthesis mentioned above [1], the activating residue R is split off as benzoic acid. The yields of the individual reaction stages are between 65 and 80 %.



Judging from its melting point (284–285 °C), mixed melting-point, and infrared spectrum, compound *(3)* is identical with the compound obtained from benzil and *N*-carbethoxy-α-picolinium bromide [2].

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[1] *O. Westphal, K. Jann*, and *W. Heffe*, Arch. Pharmac. *294*, 37 (1961).

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Bis-Silylated Carboxamides

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Silylation of 1 mole of acetamide with 1 mole of trimethylchlorosilane in the presence of triethylamine gives *N*-trimethylsilylacetamide [2]. On the other hand, reaction of a