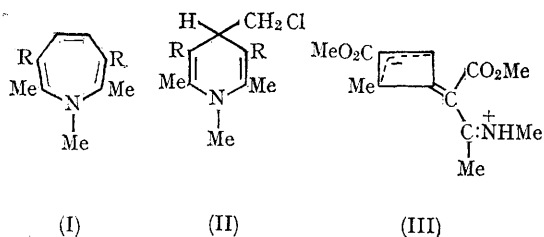


## Rearrangement of an *N*-Methylazepine to an $\alpha$ -Methylaminofulvene

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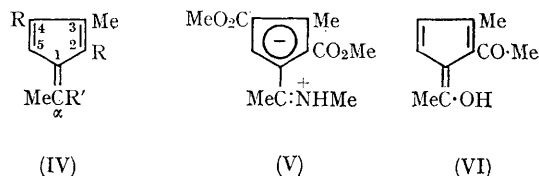
WHEN dimethyl 1,2,7-trimethylazepine-3,6-dicarboxylate (I; R = CO<sub>2</sub>Me), obtained by the action of potassium *t*-butoxide on the dihydropyridine ester (II; R = CO<sub>2</sub>Me), was heated under reflux in benzene solution, it gave an isomeric product which, on spectral evidence, was considered to be a zwitterion (III) containing a four-membered ring.<sup>1</sup> The same rearrangement product has been obtained by heating the dihydropyridine ester (II; R = CO<sub>2</sub>Me) in mesitylene in presence of barium carbonate. However, as a result of further work, particularly the interpretation of the mass-spectral fragmentation pattern, we now regard the rearrangement product as the fulvene (IV; R = CO<sub>2</sub>Me, R' = NHMe), the relationship to (III) being emphasised in the resonance hybrid (V). Fulvenes related to (IV; R = CO<sub>2</sub>Me) and containing  $\alpha$ -amino- or  $\alpha$ -hydroxyl substituents are



known,<sup>2</sup> but these contain nuclear acyl rather than ester substituents. As with these compounds, however, potassium hydroxide brings about a ready nucleophilic substitution of the  $\alpha$ -methylamino-group of (IV; R = CO<sub>2</sub>Me, R' = NHMe) to give (IV; R = CO<sub>2</sub>Me, R' = OH), which shows acidic properties and exhibits strong intramolecular hydrogen bonding between the  $\alpha$ -hydroxyl and the C-2 ester carbonyl group.

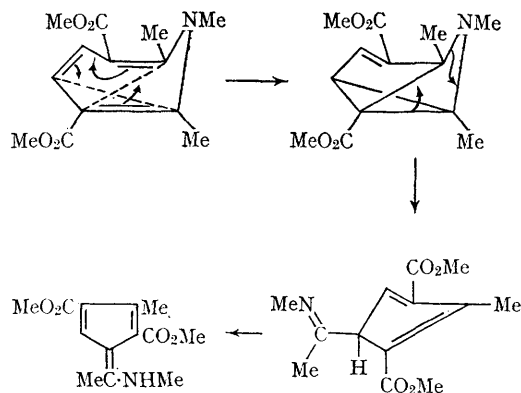
Confirmation of these structures has been derived from the parallel series of compounds based on the dihydropyridine ester (II; R = CO<sub>2</sub>Me) (*cf.* ref 3). When this was heated in mesitylene in presence of barium carbonate it yielded the fulvene (IV; R = CO<sub>2</sub>Me, R' = NHMe) which was converted into (IV; R = CO<sub>2</sub>Me, R' = OH) with

potassium hydroxide. This compound was synthesised by another route in which sodium methylcyclopentadienide was treated with acetyl chloride to give a product from which the fulvene (VI) was isolated. Hafner has shown<sup>2</sup> that such compounds



are subject to formylation at C-4. When (VI) was acetylated under Friedel-Crafts conditions a 2,4-diacetyl derivative was obtained which was identical with the product obtained from (II; R = CO<sub>2</sub>Me) by rearrangement and hydrolysis.

The rearrangement of *N*-methylazepines to  $\alpha$ -methylaminofulvenes may be depicted as shown, the driving force presumably being the increased stability consequent on the formation of the aromatic ring system. Spectral properties of all the compounds described in this Communication are consistent with the assigned structures.



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<sup>1</sup> R. F. Childs and A. W. Johnson, *Chem. Comm.*, 1965, 95.

<sup>2</sup> K. Hafner, K. H. Vöpl, G. Ploss, and C. König, *Annalen*, 1963, **661**, 52; K. Hafner, G. Schulz, and K. Wagner, *ibid.*, 1964, **678**, 39; K. Hafner, H. E. A. Kramer, H. Musso, G. Ploss, and G. Schulz, *Chem. Ber.*, 1964, **97**, 2066; W. J. Linn and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1957, **79**, 4970.

<sup>3</sup> E. Benary, *Ber.*, 1918, **51**, 577.