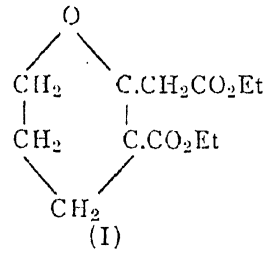
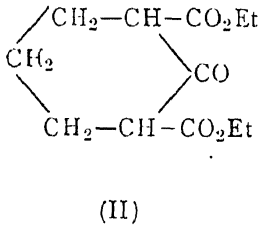
Action of Trimethylene Bromide on Acetonedicarboxylic Ester: A New and More Convenient Method of Synthesis of Ethyl *Cyclo*-hexane-2 : 6-Dicarboxylate.

PERKIN[1] obtained ethyl methyldehydrohexonedicarboxylate (I) by the action of trimethylene bromide upon Na-derivative of ethyl acetonedicarboxylate in alcoholic medium; the corresponding di-acid, m.p. 185°–92°, and the mono-acid mono-ester, m.p. 115°. The reaction was tried in dry benzene suspension by heating for nearly 100 hours at 140°–50° in sealed soda water bottles with the expectation that ethyl *cyclo*hexanone-2 : 6-dicarboxylate, if formed under these conditions, would furnish a convenient starting material for the study of some 1 : 3-bridge formation in the *cyclo*hexane molecule. The reaction mixture was separated into two portions—petrol soluble and petrol insoluble. The former, about half of the whole in quantity, gave a liquid, b.p. 142°/2 mm. along with some unreacted ester and ethyl acetoacetate. The ester, b.p. 142°/2 mm. gave on hydrolysis a dibasic acid, m.p. 172°, and a mono-acid mono-ester, m.p. 83°, agreeing in composition with Perkin's compounds, which are isomeric with ethyl *cyclo*hexanone-2 : 6-dicarboxylate and its derivatives. From the petrol insoluble portion, the phenolic lactone, m.p. 188°[2] was isolated amongst other products not identified.



(I)



(II)

Having found the reaction of sodium or sodium ethoxide, upon acetone dicarboxylic ester is always attended with the formation of phenolic bodies and according to Perkin of compounds containing oxygen in the ring, it was considered desirable to try a milder metallic derivative. Trimethylene bromide reacts with the magnesium derivative of acetone dicarboxylic ester to yield the expected ethyl *cyclo*hexanone-2 : 6-dicarboxylate (II) b.p. 144°/3 mm.; phenyl hydrazone, m.p. 150°, mixed m.p. with a genuine sample remaining undepressed. This new method is more convenient to work with and the yield compares favourably with that obtained by the older method.

This new observation as also the formation of a suberone derivative[3] and of a *cyclo*pentanone derivative[4] from Na-derivative of acetone dicarboxylic ester establish definitely that under suitable conditions it can react in the ketonic form lending itself to the formation of homocyclic compounds and not only in the enolic form as observed by Perkin.

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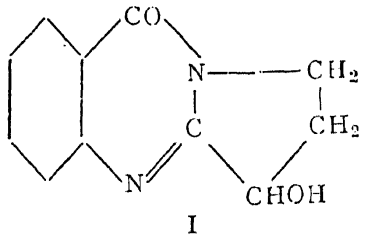
Indian Institute of Science,
Bangalore,
September, 1935.

[1] *J. C. S.*, 1887, **51**, 739.
[2] Jerdan, *J. C. S.*, 1887, **71**, 1106.
[3] Braun, *Ber.*, 1913, **46**, 1792.
[4] Ingold, *J. C. S.*, 1928, p. 365.

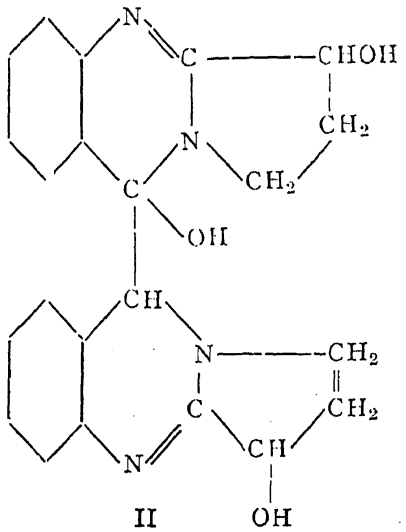
The Oxidation Products of Vasicine with Hydrogen Peroxide.

MORRIS, HANFORD AND ADAMS[1] have found that vasicine does not react with 3% H_2O_2 as stated by Ghose[2] *et al* but does so with 30% H_2O_2 and on interaction at 60°–70° it gives a compound m.p. 214° as stated by Ghose *et al*. To this compound, they have assigned the structure (I).



I

But a second product m.p. 168° obtained by Ghose *et al* was not found and they are of opinion that it was an equi-molecular mixture of I and vasicine.



II