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The Internal Addition of an a-Keto-carbene to an Enone Double Bond

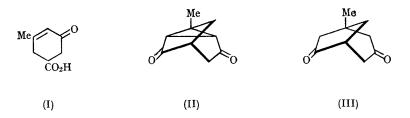
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Much work has been reported recently on the internal addition of $\alpha\text{-}keto\text{-}carbenes, generated from diazo-ketones, to an isolated double bond, thereby giving bridged systems containing a cyclopropane ring. We have been interested in extending this type of reaction to the particular case where the double bond is conjugated to a carbonyl group, since the resulting diacylcyclopropane should$

hydrogenolyse easily and unambiguously, thus affording a convenient route to polyfunctional bridged-ring systems.

Treatment of the unsaturated keto-acid (I)² in benzene with oxalyl chloride in the presence of pyridine and then with diazomethane gave the derived diazo-ketone. Decomposition of the latter in boiling cyclohexane in presence of anhydrous



G. Stork and J. Ficini, J. Amer. Chem. Soc., 1961, 83, 4678; W. V. E. Doering, E. T. Fossel, and R. L. Kaye, Tetrahedron, 1965, 21, 25; S. Masamune, J. Amer. Chem. Soc., 1964, 86, 735; F. Medina and A. Manjerrez, Tetrahedron, 1964, 20, 1807; S. Julia, M. Julia, and G. Linstrumelle, Bull. Soc. chim. France, 1964, 2693.
D. S. Nolby and L. J. Nolby, J. Org. Chem., 1961, 26, 1732.

cupric sulphate gave in 38% yield the tricyclic diketone (II), m.p. $46.5-47^{\circ}$, $\lambda_{\rm max}$ 206 (ϵ 3800) and 290 m μ (ϵ 54) (in MeOH), $\nu_{\rm max}$ 1710 and 1740 cm.⁻¹ (in CCl₄). Catalytic reduction of the latter (Pd/C in MeOH) proceeded rapidly and gave in

71% yield 1-methylbicyclo[3,2,1]octane-3,6-dione (III), m.p. $64^{\circ}, \nu_{max}$ 1710 and 1745 cm. $^{-1}$ Analytical figures and n.m.r. spectra support these assignments.

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