Bis-adamantylidenemethane

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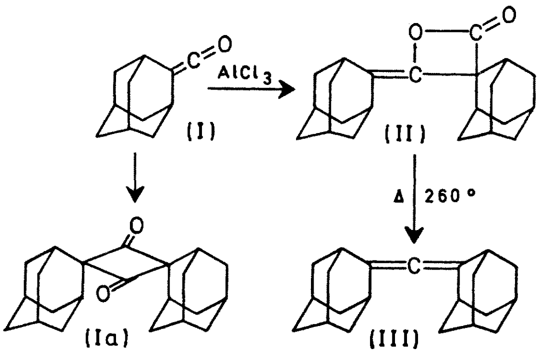
Summary The β-lactone dimer (II), derived from the keten 2-carbonyladamantane (I), gave the allene (III) on pyrolysis.

KETENS embodying the adamantane skeleton were recently prepared in our laboratory.[1] One of the ketens, (I), dimerized readily to the cyclobutane-1,3-dione derivative (Ia). We now report the direct dimerization of the keten (I) to the β-lactone (II) and the transformation of the latter into the allene (III).[2,3]



The dimerization was effected by adding a catalytic amount of aluminium chloride to a refluxing dilute ethereal solution of 2-carbonyladamantane (I) and concentrating it by distilling the solvent slowly until a concentration of about 1 g of substance in 3 ml of ether was reached. Treating the mixture with water, and extraction with chloroform, furnished yellow solid material. Crystallizations from ethanol and octane yielded the β-lactone dimer [50%; m.p. 195—196°; i.r. (KBr): 1861 and 1720 cm^{-1}; M.W. (mass spectr.) 324; analysis correct for $C_{22}H_{28}O_2$].

On pyrolysis, this compound easily lost CO_2 and a solid, the bisadamantylidenemethane (III), was produced in yields up to 95% as colourless needles, m.p. 224—226°, from acetone. The structure of (III) has been assigned on the following evidence (in addition to a correct elemental analysis): the i.r. spectrum shows a weak band at 1970 cm^{-1} due to the allenic linkage, and the absence of olefinic absorption. The n.m.r. spectrum consists of two peaks τ 7·5—7·7, a singlet of 4 protons adjacent to the allene system, and τ 7·9—8·2, a multiplet of 24 adamantyl protons. The mass spectrum exhibits a parent peak at m/e 280.

In view of the unique properties of a double bond between the adamantane skeletons[4] a study of the reactivity of this allene is of considerable interest.

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[1] J. Strating, J. Scharp, and H. Wynberg, *Rec. Trav. chim.*, 1970, **89**, 23.

[2] Houben-Weyl, Methoden der Organische Chemie, Band VII/4, p. 276.

[3] R. N. Lacey, *Adv. Org. Chem.*, 1960, **2**, 213; D. G. Farnum, I. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Amer. Chem. Soc.*, 1965, **87**, 5191. The suggestion by Farnum and his co-workers concerning the mechanism of the β-lactone formation appears eminently sound in view of the large steric requirements of the adamantane group.

[4] J. Strating, J. H. Wieringa, and H. Wynberg, *Chem. Comm.*, 1969, 907.