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2, 4-DIMETHYLTRICYCLO[1. 1. 1. $0^{2,4}$]PENTAN-5-ONE[1]

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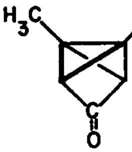
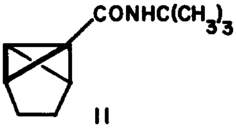
TRICYCLO[1. 1. 1. $0^{2,4}$]PENTANE is the parent representative of one of the more extreme members of the set of strained ring systems. Formally, it is a more highly condensed, more highly strained derivative of bicyclo[1. 1. 0]butane,[3] in which there is a bridge between carbon atoms 2 and 4. The example presented in this communication has as its bridge a single carbon atom in the form of a carbonyl group (I) and may be compared with Meinwald's compound (II)[4] in which the bridge consists of two carbon atoms or with Moore's compound (III)[5] in which the bridge is three-membered.



I

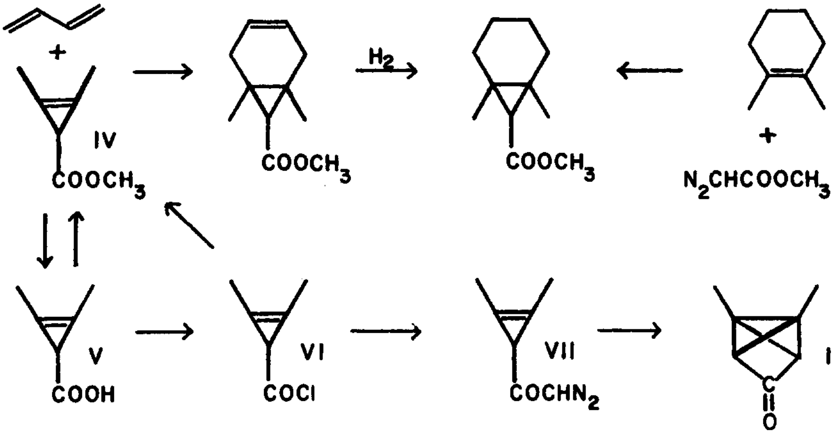


II

III

The starting material for the synthesis of I is methyl 1, 2-dimethylcyclopropene-3-carboxylate (IV)[6] which is prepared according to the method of Doering and Mole by irradiating a solution of methyl diazoacetate and 2-butyne. The free acid, 1, 2-dimethylcyclopropene-3-carboxylic acid (V), m.p. 77-78° after three recrystallizations from pentane, was obtained by saponification with potassium hydroxide in boiling methanol and could be reesterified with diazomethane to pure IV. Treatment of V with oxalyl chloride, following the related conversion of

1, 2-diphenylcyclopropene-3-carboxylic acid,[7] afforded the corresponding acid chloride VI which reacted with methanol to regenerate quantitatively



the methyl ester IV and with ammonia to form 1, 2-dimethylcyclopropene-3-carboxamide, m.p. 152-153° [C_6H_9NO requires C, 64.8; H, 8.2. Found: C, 64.8; H, 8.0].

Strengthening of the structural assignment within this interrelated group is given by the results of a Diels-Alder reaction. Like cyclopropene itself[3] but at a slower rate, IV reacts with butadiene (93% after 43 hr at 78°) to give methyl cis-1, 6-dimethylbicyclo[4. 1. 0]hept-3-en-7(endo)-carboxylate (carboxylic acid, m.p. 168.5-169°), the dihydro derivative of which is identical with one of the two products of photolyzing a solution of methyl diazoacetate in 1, 2-dimethylcyclohexene.

The diazoketone VII was obtained by the reaction of VI with two equivalents of diazomethane and was purified by crystallization from ether at -85°. Treatment of VII with copper powder suspended in hexane at the boiling point,[9] followed by molecular distillation, g.l.p.c. and recrystallization from pentane gave 2, 4-dimethyltricyclo[1. 1. 1. $0^{2,4}$]pentan-5-one, m.p. 57-58° (C_7H_8O requires C, 77.8; H, 7.5. Found: C, 77.7;

H, 7.8), in ca. 1% of theoretical yield. The remainder of the product was much less volatile.

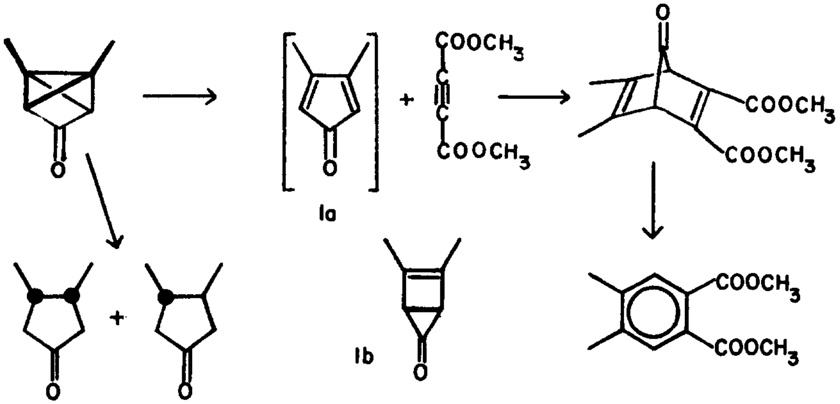
A molecular weight of 141 was determined by vapor pressure osmometry, but this method was found to give high values for other similarly volatile ketones. From the allowed space groups, unit cell dimensions[10] and density (determined by flotation in aqueous salt solution), molecular weights of 214, 107 or 54 were indicated. Major peaks in the mass spectrum were located at m/e 108, 80 (loss of carbon monoxide) and 28. A molecular weight of 108 is thus established.

Catalytic hydrogenation of I proceeds slowly over platinum in methyl acetate with the absorption of two equivalents of hydrogen over a 12-hr period and affords cis- and trans-3, 4-dimethylcyclopentanone (45% and 27%, respectively) in addition to recovered starting material (28%). These two substances were synthesized by the Dieckmann condensation (followed by saponification and decarboxylation) of dimethyl 3, 4-dimethyladipate.[11] Configurational assignment rests on their recent synthesis from meso- and dl-3, 4-dimethyladipic acid.[12]

From the infrared spectrum, the presence of a carbonyl group (1786 and 1766 cm^{-1}; doubled by Fermi resonance) is confirmed while the presence of a cyclopropane ring is suggested (3080 cm^{-1} and 1029 cm^{-1}). The position of the carbonyl band is close to that of the carbonyl group in cyclobutanone (1788 cm^{-1}).[13]

From the N.M.R. spectrum which consists of two sharp bands at δ = 2.05 and 1.73 p.p.m. of relative area 3 : 1, the general symmetry of the molecule is indicated and the presence of vinyl hydrogen (and therefore of structure Ia) is precluded. The unexceptional ultraviolet spectrum [λ_{max} 280 mμ (ϵ = 32) and two shoulders at 252 mμ (ϵ = 43) and 225 mμ (ϵ = 130)] is likewise inconsistent with structure Ia.

The exclusion of structure Ib depends on the absence in the Raman and infrared spectra[14] of strong absorption in the region 1675-1685 cm^{-1} where the double bond in 1,2-disubstituted cyclobutene derivatives absorbs.[15] The major Raman bands are at 1749 cm^{-1} (strong); 1615 cm^{-1} (weak) and 1442 cm^{-1} and 1091 cm^{-1} (both medium). However, before structure Ib can be finally rejected, independent confirmatory evidence is desirable.



Within the past few days, Masamune[16] has reported the synthesis of the 2,4-diphenyl analogue [m.p. 140°] of I by the identical method used here, but for replacing copper catalysis by photolysis. In the structural assignment which was based on carbonyl absorption [1785 cm^{-1}], catalytic reduction exclusively to cis-3,4-diphenylcyclopentanone and N.M.R. spectrum [two singlets, $\delta = 7.35$ and 2.88 p.p.m. of relative areas 10 : 2], alternatives of type Ia and Ib were not considered explicitly. Although the former exists only as the dimer[17] and is thus excluded, the latter, 2,3-diphenylbicyclo[2.1.0]pent-2-en-5-one, requires further evidence for its conclusive rejection. Indeed, it could be held to accommodate better the ultraviolet spectrum [λ_{max} 242 mμ, log ϵ 4.16] and the coupling constant of the two hydrogen atoms [$\delta = 2.88$ p.p.m.; J = 14 c.p.s.].

I is soluble in water and fails to react with semicarbazide hydrochloride. It reacts with iodine rapidly to give an insoluble precipitate.

Heating at 156° for 20 hr in the presence of hydroquinone produces only polymeric material.

However, when I is heated with dimethyl acetylenedicarboxylate at 198° for 24 hr in the presence of a small amount of hydroquinone, two products can be separated by gas chromatography. The minor product is identified as dimethyl 4, 5-dimethylphthalate by comparison of its infrared spectrum with that of an authentic sample, prepared by the dehydrogenation of the Diels-Alder adduct of 2, 3-dimethylbutadiene and dimethyl acetylenedicarboxylate. This reaction is simply rationalized by assuming thermal rearrangement of I to Ia, 2, 3-dimethylcyclopentadienone, which undergoes a Diels-Alder addition with dimethyl acetylenedicarboxylate followed by decarbonmonoxylation to 4, 5-dimethylphthalate.

REFERENCES AND FOOTNOTES

(1) This work is taken from the dissertation of M. Pomerantz presented August 1963 to Yale University in partial fulfillment of the requirements of the Ph.D. degree. It was supported in part by the National Science Foundation through research grant 11378 and grants 22689 and 19110 for the purchase of a Varian A-60 Analytical N.M.R. Spectrometer and a Bendix Time-of-Flight Mass Spectrometer.

(2) Our deep gratitude for the award of fellowships to the Woodrow Wilson Fellowship Foundation (1959-60), the Leeds and Northrup Company (1960-62) and the National Science Foundation (1962-63).

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(10) Our thanks to Dr. A. Tulinsky and Mr. R.E. Davis for determination of the space group and unit cell dimensions of crystalline I.

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(14) Our deepest gratitude to Dr. R. Amster and Mr. N.B. Colthrup of the American Cyanamid Co., Stamford, Conn., for measuring and interpreting the Raman and infrared spectra.

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