The Formation of Perhydropyranene Derivative

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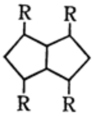
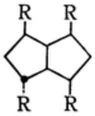
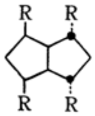
Although acepentylene¹⁾ and pyranene²⁾ are of special interest in respect to their aromatic characters the synthesis of them or their derivatives has not been reported except triquinacene.³⁾ In an attempt to synthesize these interesting hydrocarbons, the intramolecular acyloin condensation of tetramethyl bicyclo[3.3.0]octane-2, 4, 6, 8-tetracarboxylate (I) was carried out; this paper describes the result of our investigation.



Ia

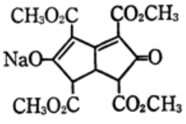


Ib



Ic

$R=CO_2CH_3$



II

From the inspection of molecular models, it is clear that the acyloin condensation of I is only possible between the carbomethoxy groups at C-2 and C-8 position when the pair are endo-cis configuration.*1 Therefore, Ia should be the most reasonable starting material for our purpose.

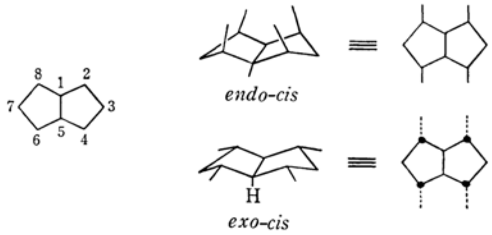


Fig. 1. Configuration of carbomethoxy groups.

Yates and his co-workers⁵⁾ obtained two isomeric tetramethyl bicyclo[3.3.0]octanetetracarboxylates from Schroeter and Vossen's red salt (II)⁵⁾ through the multi-step reaction sequence and assigned the structures Ib and Ia for them on the basis of the anhydride formation of the corresponding acids. We have obtained Ia in three-steps starting from isodrin.

Isodrin was dechlorinated with lithium and *t*-butyl alcohol to afford the diene (III).⁶⁾ III was

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1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y. (1961), pp. 90, 290.

2) J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954).

3) R. B. Woodward, T. Fukunaga and R. C. Kelly *J. Am. Chem. Soc.*, **86**, 3162 (1964).

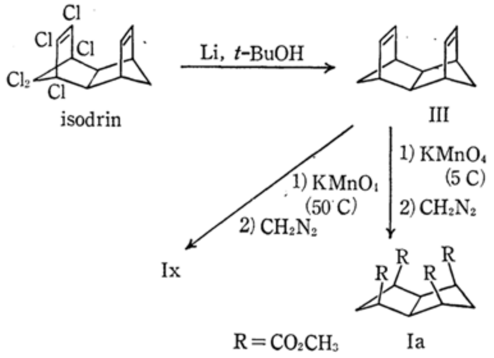
*1 This consideration is supported by the fact that Ic failed to give the corresponding cyclic acyloin.⁴⁾

4) E. R. Hanna, K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **82**, 6342 (1960).

5) P. Yates, E. S. Hand and G. B. French, *ibid.*, **82**, 6347 (1960).

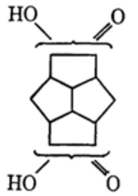
6) P. Bruck, D. Thompson and S. Winstein, *Chem. & Ind. (London)*, **1960**, 405.

oxidized with potassium permanganate at low temperature and the resulting acid was esterified with diazomethane. The structure of the product must be Ia, since no change in the configuration of the four carbomethoxy groups would be expected to occur during these mild treatments. Ia was proved to be identical (melting point and IR) with one of Yates' tetraesters, thus confirming the Yates' assignment.



When the oxidation was carried out at higher temperature and the resulting acid was esterified, another product (Ix) was obtained. Its structure was proved to be identical (melting point and IR) with the other tetraester obtained by Yates.

When Ia was subjected to acyloin condensation according to Sheehan's procedure,⁷⁾ the tetracyclic acyloin (IV) was produced. IV gave possitive Fehling test and its infrared spectrum showed absorptions at 3450 cm^{-1} (νOH) and 1750 cm^{-1} ($\nu_{C=O}$), similar to the corresponding values for 2-hydroxycyclopentanone (3450 cm^{-1} and 1749 cm^{-1}).⁸⁾ Its ultaviolet spectrum showed a maximum at 265 mμ, which shifted to 302 mμ in alkaline medium. This shift is characteristic of acyloins.⁹ᵃ,⁹ᵇ⁾ On the other hand, Ix did not give the corresponding cyclic acyloin under the same condition. This fact suggests that two pairs of carbomethoxy groups at C-2, C-4 and at C-6, C-8 are not endo-cis. From this standpoint, Yates' presumption that Ix may be assigned to Ib seems to be doubtful.



IV

Experimental

Tetramethyl Bicyclo[3.3.0]octane-2, 4, 6, 8-tetracarboxylate (Ia). To a suspension of 4 g of III in 150 m*l* of water was added 21 g of potassium permanganate with stirring for five hours. The reaction temperature was maintained below 5°C. After stirring was continued for further two hours, the precipitated manganese dioxide was separated by filtration and washed with 100 m*l* of water. The combined filtrates were acidified with 12 m*l* of concentrated hydrochloric acid. The solution was allowed to stand overnight in an ice box and the precipitate was filtered and air-dried to give 900 mg of crude acid. The acid was esterified with diazomethane, without further purification, and the resulting ester was recrystallized from chloroform-ether to give 800 mg of Ia as colorless plates, mp 154—154.5°C, IR: 1726 cm^{-1}. No depression was observed in mixed melting point determination with a sample of Yates' tetra ester (mp 154—155°C)

Tetramethyl Bicyclo[3.3.0]octane-2, 4, 6, 8-tetracarboxylate (Ix). To a suspension of 3 g of III in 250 m*l* of water was added 16 g of potassium permanganate within thirty minutes with stirring. The reaction temperature rose to 50°C. After one hour the manganese dioxide was filtered and washed with 100 m*l* of hot water. The combined filtrates were concentrated to 20 m*l* under reduced pressure and acidified with 14 m*l* of concentrated hydrochloric acid. The solution was allowed to stand overnight, and the precipitate was collected by filtration and dried to give 150 mg of solid, which was then esterified with diazomethane. The product was purified by chromatography (alumina-ether) and recrystallized from ether-petroleum ether to give 70 mg of colorless needles, mp 94—95°C, IR: 1730 cm^{-1}. Mixed melting point determination with a sample of Yates' tetraester (mp 94.5—95°C) showed no depression.

Acyloin Condensation of Ia. To a three-necked flask fitted with stirrer, addition funnel and nitrogen system was added 70 m*l* of dry ether, 200 m*l* of liquid ammonia and 800 mg of sodium. A solution of 800 mg of Ia in 600 m*l* of dry ether was added dropwise in a period of two hours with stirring under nitrogen and stirring was continued for one hour. After evaporation of ammonia the excess sodium was decomposed by addition of 5 m*l* of methanol in 10 m*l* of ether. The resulting yellow mixture was acidified with 20 m*l* of 6 N hydrochloric acid. The ethereal layer was separated and the aqueous layer was extracted with three 50 m*l* portions of chloroform. The combined organic layers were dried and freed from solvent under reduced nitrogen atomosphere to give 100 mg of the crude product, which was purified by chromatography (silicagel-acetone), bp 100—110°C/10^{-3}—10^{-4} mmHg (molecular still).

Found: C, 63.80; H, 6.73%. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%.

IR: 3450, 1750 cm^{-1}, UV: λ_{mxa}^{EtOH} 265 mμ, $\lambda_{max}^{alkali\ EtOH}$ EtOH 302 mμ.

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7) J. C. Sheehan and R. C. Coderre, *J. Am. Chem. Soc.*, **75**, 3997 (1953).

8) J. C. Sheehan, R. C. O'Neill and M. A. White, *ibid.*, **72**, 3376 (1950).

9) a) C. Kashima, K. Kuo, Y. Omote and N. Sugiyama, This Bulletin, **38**, 255 (1965); b) K. Yamada, M. Eda and N. Sugiyama, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 868 (1965).

Attempted Acyloin Condensation of Ix. An attempt of acyloin condensation of Ix (600 mg) was carried out and worked up in the same manner as described in the preceding experiment, giving 50 mg of gum. This gave a negative Fehling test.

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