Tetrahedron Letters No.54, pp. 5635-5638, 1968. Pergamon Press. Printed in Great Britain.

THE CARBOXYLATION OF CYCLOOCTATETRAENE DIANION

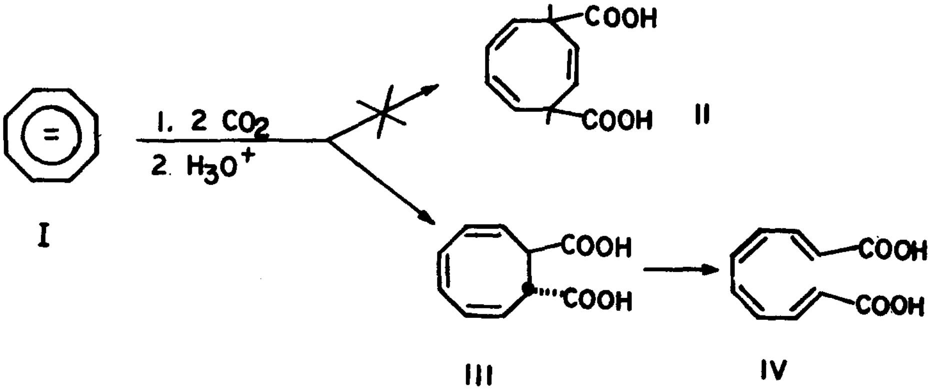
Thomas S. Cantrell

Department of Chemistry, Rice University

Houston, Texas, USA 77001

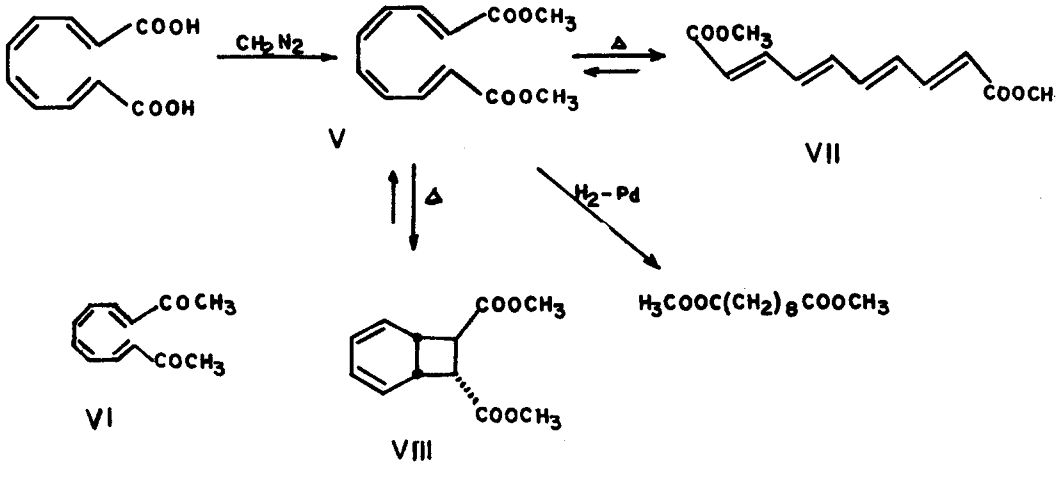
(Received in USA 5 July 1968; received in UK for publication 4 October 1968)

The chemistry of cyclooctatetraene dianion (I) has been the subject of much recent interest and has been found to be more varied and interesting than originally suspected.[1-5] Acylations, alkylations, and condensation reactions with carbonyl compounds lead to novel intramolecular reactions and ring closures. The carboxylation of I was described by Reppe and his coworkers in their original paper on cyclooctatetraene chemistry.[6] The product was assumed to be 1,3,6-cyclooctatriene-5,8-dicarboxylic acid (II) by analogy with the protonation of I, which gave 1,3,6-cyclooctatriene.[6,7] Since many of the structures reported by early workers in cyclooctatetraene chemistry were erroneous,[5,8] it seemed worthwhile to establish the structure of the carboxylation product with certainty.



Treatment of ethereal dilithium cyclooctatetraenide with powdered solid carbon dioxide, followed by quenching with water and acidification of the clear tan aqueous layer gave a dull yellow solid (76% as $C_{10}H_{10}O_4$), evidently the "chamois-colored powder" described by Reppe. This material could be recrystallized, with considerable losses, from n-propanol to give IV as dull yellow microcrystals, m. p. 270-284°(dec),[9] IR (KBr) 1705 (C=O), cm^{-1}. The major component of this mixture of acids is <u>trans</u>, <u>cis</u>, <u>cis</u>, <u>trans</u>-2,4,6,8-decatetraene-1,10-dioic acid on the basis of the evidence presented herewith.

Treatment of an ethereal suspension of crude IV with diazomethane under nitrogen gave 63% of the dimethyl ester V as tiny pale yellow needles, m.p. 114-115°;[9] IR (KBr), 1702 (C=O) 1615 (C=C), and 694 (<u>cis</u>-CH=CH-)cm^{-1}; UV (EtOH)338 nm(ϵ = 36,000); nmr(CCl_4), τ 2.24 (area 2,2 doublets, J = 16.0, J' = 11.8, H's β to C = O), 3.12 (area 2,2 doublets, J = 9.4, J' = 2.1, H's δ to C=O), 3.60 (area 2, multiplet, H's γ to C=O), 4.02 (area 2, doublet, J = 16.0, H's α to C=O), and 6.22, singlet, $COOCH_3$) The gross structure of V was established by its hydrogenation over palladium to dimethyl sebacate. The assignment of double bond geometry in V is suggested by its nmr spectrum; the coupling constants and chemical shifts of the vinyl hydrogens are very similar to those of ketone VI, one of the products of acetylation of I.[1,4] Further evidence for the stereochemistry of V is its isomerization on heating above the melting point to all-<u>trans</u> dimethyl 2,4,6,8-decatetraene-1,10-dioate (VII), m.p. 212-213°, identical with an authentic sample.[10,11,12] Diacid IV is apparently formed by electrocyclic ring opening of an intermediate diacid III, produced by carboxylation of I at C-1 and C-2. The Woodward-Hoffman orbital symmetry correlations[13] suggest that in the monocyclic intermediate III, the carboxyl groups are <u>trans</u>.



From silica gel chromatography of the mother liquors of V there could be isolated, besides considerable gummy, highly polar material and additional V, a second methyl ester, VIII. Compound VIII is the major product of thermal isomerization of V at ≥ 50° and is apparently an artifact. Heating solutions of V to ≥ 50° for two hours caused isomerization to a mixture of VII and VIII in a ratio of ~ 10:90. Diester VIII[9] is assigned the structure shown, trans-7,8-dicarbomethoxybicyclo[4.2.0]octa-2,4-diene, on the basis of (1) spectral data: IR(CCl$_4$)1726 (C=O) and 1170-1200 (C-O)cm^{-1}; UV(CH$_3$OH)270 nm(ϵ = 3000); nmr τ 4.0 - 4.7(4H, multiplets, -CH=CH-), 6.05-6.24 (2H, multiplets, H-7 and H-8), 6.28 and 6.31 (3H each, singlets, OCH$_3$), and 6.5-7.0 (2H, multiplets, H-1 and H-6) and (2) its reaction at room temperature with N-phenylmaleimide to give a Diels-Alder adduct (IX)[9], m.p. 185-186°

The formation of VIII from V represents a further example of the now well-known valence isomerization in the octatetraene-cyclooctatriene-bicyclooctadiene series.[4,5,12-14] This case is unusual in that the major isomer at equilibrium is the bicyclic form, in which the carbomethoxy groups are not in conjugation with the olefinic system. In previous cases involving unsaturated substituents the acyclic tetraenes were the favored isomers, presumably because of the stability gained by having the substituents in conjugation.

Esterification of IV in refluxing methanol containing a trace of sulfuric acid led to a somewhat different result. In addition to considerable VIII, there was isolated after chromatography on silica gel, a methyl ester believed to be dimethyl bicyclo [4.2.0] octa-2,4-diene-2,5-dicarboxylate (X), m.p. 69-70°; IR (KBr), 1708 (C=O), 1572 (C=C), and 1245(C-O)cm^{-1}; UV (EtOH)max, 327 nm (ϵ = 9200); nmr, τ 2.28 (area 2, singlet, vinyl H's), 6.20 (area 6, COOCH$_3$), 6.3 (area 2, unresolved multiplet, methine H's), and 7.1-7.4 (area 4,unresolved multiplets, methylene H's). The chemical shifts of the saturated hydrogens are similar to those of the corresponding hydrogens in other bicyclo [4.2.0] octadienes.[14] The wavelength of the ultraviolet absorption maximum is exactly that predicted for X by adding an increment of 18 nm for the fused four-membered ring (the difference in λ_{max} of the parent hydrocarbons 1.3-cyclohexadiene [256 nm] and bicyclo [4.2.0] octadiene [274 nm] to the value for the model system dimethyl 1,3-cyclohexadiene-1,4-dicarboxylate [309 nm][15]. The isomer of X with carboxyls at the 3,4 positions would be expected to absorb at ca.292 nm. The conversion of IV to X can be rationalized by a series of extensive thermal and acid-catalyzed reorganizations; although some of the linear isomer VII could be isolated, it does not appear to be converted to X.

REFERENCES

1. T. S. Cantrell and H. Shechter, *J. Am. Chem. Soc.*, **85**, 3300(1963).
2. T. J. Katz and P. J. Garrat, *ibid.*, **86**, 53 (1964).
3. D. A. Bak and K. H. Conrow, *J. Org. Chem.*, **31**, 3958 (1966).
4. T. S. Cantrell and H. Shechter, *J. Am. Chem. Soc.*, **89**, 5868 (1967).
5. T. S. Cantrell and H. Shechter, *ibid.*, **89**, 5877 (1967).
6. W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).
7. A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2512 (1950).
8. Compare ref. 4 and V. Azatyan, *Izvest. Akad, Nauk SSR*, Otdel Khim. Nauk, **14**, 451 (1961).
9. All compounds so designated gave acceptable elemental analyses.
10. R. Kuhn and C. Grundmann, *Ber.*, **69**, 1757 (1936).
11. J. R. Schenck, M. P. Hargie, D. S. Tarbell and P. Hoffman, *J. Am. Chem. Soc.*, **75**, 2274 (1953). We are grateful to Dr. Tarbell for furnishing a sample of the all-*trans* acid.
12. H. Hover, *Tetrahedron Letters*, 256 (1962).
13. R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 395 (1965).
14. R. Huisgen, G. Boche, W. Hechtl, and G. Huber, *Ang. Chem.* Int'l Ed., **5**, 535 (1966).
15. G. Smith, C. L. Warren and W. R. Vaughn, *J. Org. Chem.*, **28**, 3323 (1963).