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THE STRUCTURE OF THIELE'S ESTER, A DIMETHYL DICYCLOPENTADIENEDICARBOXYLATE

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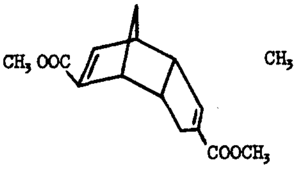
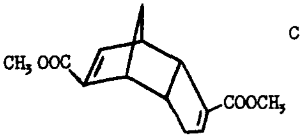
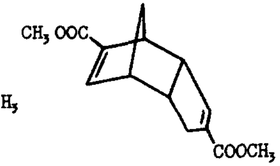
In 1901 Thiele reported (1) that the product obtained from the carbonation of cyclopentadienyl potassium was a dicyclopentadienedicarboxylic acid (Thiele's acid), a dimerization product. He reported also that acid-catalyzed esterification of this acid gave a crystalline dimethyl ester (Thiele's ester). Subsequently, Peters (2) carried out ultraviolet spectroscopic studies on the ester and concluded that both carboxylate groups were conjugated with double bonds, in contrast to the earlier conclusions of Alder et al. (3). Recent nmr spectral data (4) have confirmed Peters' results. However, none of these investigations were able to determine the precise locations of the carboxylate groups. We wish to present evidence here that of the four isomeric alternatives for Thiele's ester (Ia-d) Ia is the correct one, in contrast to a recent report (5) in which it was concluded that Id (as the diacid) best represented the structure of Thiele's acid.



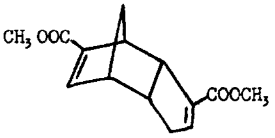
Ia



Ib

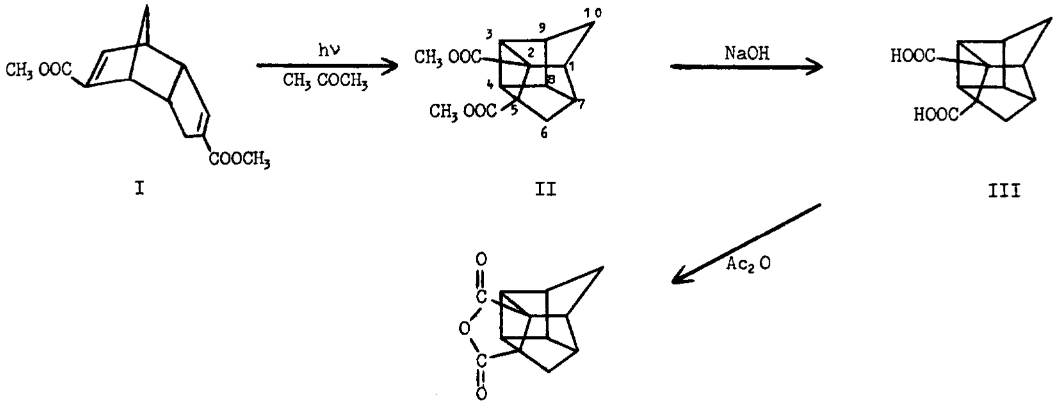


Ic



Id

Thiele's ester (I), mp 83-84°, was prepared by acid-catalyzed esterification of Thiele's acid (6) in the manner described by Peters (2). Its nmr spectrum (7) was identical to that reported by Finnegan and McNees (4). A solution of I in acetone irradiated for 24 hr in a quartz immersion photolysis apparatus equipped with a 450 watt Hanovia medium pressure mercury vapor lamp gave a saturated ester in 66% yield to which we have assigned the structure II (see below), dimethyl pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-2,5-dicarboxylate [bp 124-128° (1.25 mm); infrared absorption (neat) at 1725 cm^{-1} (ester C=O)]. Hydrolysis of II, by heating in 10% aqueous

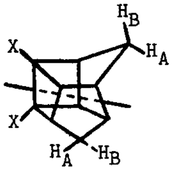


I II III

IV

sodium hydroxide, gave a 52% yield of the pentacyclodecane diacid III [mp 206-207°; infrared absorption at 1710 cm^{-1} (acid C=O)], which then was heated in refluxing acetic anhydride to give a 59% yield of anhydride IV [mp 162-163°; infrared peaks (CCl$_4$) at 1854 and 1787 cm^{-1} (anhydride C=O)].

The fact that I undergoes photochemical cyclization to give II confirms earlier conclusions (2,3,5) that Thiele's ester possesses endo stereochemistry. The positions of the infrared peaks at 1854 and 1787 cm^{-1} in anhydride IV are indicative of a 5-membered cyclic anhydride. By analogy, 1,2-cyclobutanedicarboxylic anhydride (5-membered) absorbs at 1859 and 1786 cm^{-1} (8) while 1,3-cyclobutanedicarboxylic anhydrides (6-membered) (9) generally absorb at about 1815 and 1765 cm^{-1}. On the basis of the infrared characteristics of IV we can eliminate Ib and Ic as structural alternatives for Thiele's ester, since the pentacyclodecane diacids derived from them would lead to 6-membered cyclic anhydrides, if anhydride formation could take place at all. Of the two remaining structural possibilities for the photocyclized diacid (III or V), both of which would lead to a 5-membered cyclic anhydride, we believe structure III to be the correct one based on the following interpretation. The pentacyclodecane diacid V (from Id), like the parent hydrocarbon VI (10) in which the two methylene groups appear as a single AB quartet (J_{AB}= 11Hz), possesses a C_2 axis of symmetry passing through the center of the C_1-C_7 and C_3-C_4 bonds.



V, X=COOH
VI, X=H

Thus, symmetry demands that the nmr patterns of the two methylene groups in V be identical and superimposed. However, examination of the nmr spectrum of the photocyclized diacid we obtained showed that the two methylene groups appeared as separate and distinct absorptions, an AB quartet (J_{AB}=12Hz) with A at $\delta \sim 2.20$ (d, 1H) and B at $\delta \sim 1.75$ (d, 1H) and a broad singlet at δ 1.62 (2H). This result leads to the conclusion that the diacid must have structure III and not V, and therefore that Ia is the correct structure for Thiele's ester.

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6. The Thiele's acid used in this work was obtained from the Augusta Chemical Co., Augusta, Georgia. A comparison of the physical and spectral properties of the dimethyl ester of this acid with a sample of Thiele's ester kindly supplied by Dr. C. J. Bouboulis, Esso Research and Engineering Co., indicated that the two were identical.
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