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CONFIRMATION OF THE TRICYCLO[6,2,0,0^{3,6}]-DECANE STRUCTURE FOR THE PHOTODIMER OF DIMETHYL 3-OXO-1,4-PENTADIENE-1,5-DICARBOXYLATE

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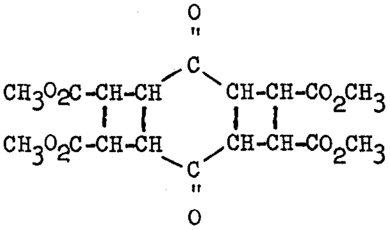
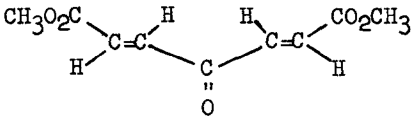
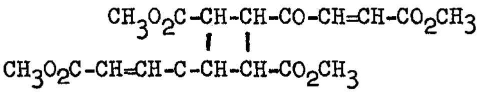
APPARENTLY the only suggested tricyclo[6,2,0,0^{3,6}]-decane derivative in the literature is tetramethyl tricyclo[6,2,0,0^{3,6}]-2,7-dioxodecane-4,5,9,10-tetracarboxylate (I). Stobbe and Färber[1] proposed the tricyclic-structure for the photodimer of dimethyl 3-oxo-1,4-pentadiene-1,5-dicarboxylate[2] (II) rather than the monocyclic dimer (III) on the basis of substitution by bromine rather than addition and the lower absorption maxima (not quantitatively measured).



(I)



(II)



$$\begin{array}{l} \phantom{CH_3O_2C\text{-}CH{=}CH\text{-}}CH_3O_2C\text{-}CH\text{-}CH\text{-}CO\text{-}CH{=}CH\text{-}CO_2CH_3 \\ \phantom{CH_3O_2C\text{-}CH{=}CH\text{-}CH_3O_2C\text{-}C}|\phantom{H\text{-}C}| \\ CH_3O_2C\text{-}CH{=}CH\text{-}C\text{-}CH\text{-}CH\text{-}CO_2CH_3 \end{array}$$

(III)

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[1] H. Stobbe and E. Färber, Ber. 58, 1548 (1925).

[2] F. Straus, Ber. 37, 3297 (1904).

The tricyclic structure has not been accepted by standard reference works[3].

The proton magnetic resonance spectra of dilute solutions of the monomer and dimer[1,2] in trifluoroacetic acid containing approximately 1% tetramethylsilane (TMSi) as an internal reference were obtained at 60 Mc. using a Varian magnet and spectrometer. This solvent reference system has recently been used in a study of the spectra of amino acids and peptides[4]. In the conjugated olefinic region of the spectrum of (II) a single "nonequivalence" quartet occurs, the unsymmetrical doublets having shielding values of 2.50 and 2.95[5], and a 15.0 cycle splitting. Confirmation of the all-trans configuration of II[6] is provided by the presence of only one quartet and a typical trans value for the spin-spin coupling constant. The methoxyl resonance of II occurs at 5.99.

The NMR spectrum of the dimer shows a complete absence of protons attached to conjugated doubly-bonded carbon and thus excludes structure III, and corroborates structure I of Stobbe and Färber. A symmetrical

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[3] (a) Elsevier's Encyclopedia of Organic Chemistry, Edited by E. Josephy and F. Radt, Elsevier Publishing Co., Inc., Vol. 13, p. 6, New York, 1946. (b) A. M. Patterson and L. T. Capell, The Ring Index, Reinhold Publishing Co., New York, 1940. (c) R. A. Raphael, Chemistry of Carbon Compounds, Edited by E. H. Rodd, Vol. IIA, Chap. IX, Elsevier Publishing Co., New York, 1953.

[4] F. A. Bovey and G. Tiers, J. Amer. Chem. Soc. 81, 2870 (1959).

[5] All shielding values are given in ppm. in respect to the TMSi resonance taken as 10 ppm.

pair of incompletely resolved multiplets centered at 5.30 and 5.80 must arise from all the spin-coupled ring protons. This shape is fully consistent with two identical four-spin systems of the A_2B_2 type as required by I. A single methoxyl resonance, now located slightly up field at 6.09, shows the complete equivalence of all these groups as required by I, but not by III.

Because functional group shielding values have not been thoroughly established in trifluoroacetic acid, succinic anhydride was run in this solvent to obtain an approximate value for a proton on a carbon α and β to carboxyl groups. Its methylene resonance was found at 6.81. A further small reduction of a few tenths of a ppm. would be expected in going from a methylene to a methine proton and from the addition of a β-carbonyl group.

The reduction in the shielding of the ring protons of the dimer by more than one ppm. from the value for a proton on a carbon α and β to carbonyls must be due to the strong deshielding experienced by protons constrained to the plane of specially adjacent carbonyl groups. Jackman[7] has demonstrated this marked unshielding in the case of some diene dicarboxylic esters. A proton that is both cis to and β and γ to two carboxylate groups is 1.7 ppm. less shielded than when in the totally trans configuration. The magnitude of the reduction in shielding of the ring protons of the dimer may be explained if the four-membered rings are joined by trans fusions to the cyclohexanedione ring, since only in this case is each proton cis and β to two carbonyl

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[6] Midorikawa, H., Bull. Chem. Soc. Japan 26, 302 (1953).

groups. It should be mentioned that for this interpretation to be correct, the protons α to the carbomethoxy groups on the same four-membered ring must be trans to each other and trans to the adjacent protons on the junction carbon atoms.

The ultraviolet absorption spectrum of I is typical of saturated cyclohexanones and shows no conjugation to be present. The infrared spectra are confirmatory of structure I for the dimer. Strong carbonyl stretching absorption occurs in KBr disk samples of the dimer at 1723 and 1758 cm^{-1} and of the monomer at 1685 and 1732 cm^{-1}. These values are about those expected[8] for structures I and II, the lower frequency arising from the keto and the higher from the ester group. Structure III, on the other hand, would show α,β-unsaturated keto and ester frequencies close to those of the monomer.

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[7] L. M. Jackman, Nuclear Magnetic Resonance Spectroscopy, Pergamon Press, London, 1959, p. 124.

[8] L. J. Bellamy, The Infra-red Spectra of Complex Molecules, Metheun and Co., Ltd., London, 2nd Ed., 1958, pp. 132,179.