electron density at the carbon to which they are attached,[7,9] no one previously appears to have related the rate of cycloaddition of such systems to the pmr of a proton at a carbon atom which would be involved in the creation of a new σ bond. This is surprising in that Hobgood and Goldstein[10] nearly a decade ago demonstrated an "approximately linear" relationship between the chemical shift of the proton at the 4-trans position of substituted butadienes and the log of the rate constant for cycloaddition with maleic anhydride.

We feel that this correlation of chemical shift and cycloaddition rates will prove to be particularly important in the study of steric *vs.* electronic effects in polar cycloaddition.

(9) *E.g.*, T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); P. J. Frank and H. S. Gutowsky, *Arch. Sci.*, **11**, 215 (1958); A. Veillard, *J. Chim. Phys.*, **59**, 1056 (1962); A. Veillard and B. Pullman, *C. R. Acad. Sci.*, **253**, 2418 (1961); K. T. Potts and J. Bhattacharyya, *J. Org. Chem.*, **37**, 4410 (1972).

(10) R. T. Hobgood, Jr., and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964).

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RECEIVED MAY 30, 1973

Two-Step Synthesis of a Triketone of the *endo*-Tetracyclo[5.5.1.$0^{2,6}$.$0^{10,13}$]tridecane[1] Series. X-Ray Crystallographic Proof of Its Structure and Stereochemistry

Summary: A compound (**6**), obtained by reaction of glyoxal with dimethyl 3-ketoglutarate in aqueous solution at room temperature and subsequent treatment of an intermediate β-keto ester (**5**) with acid, is shown by X-ray crystallography to be *endo*-tetracyclo[5.5.1.$0^{2,6}$.$0^{10,13}$]tridecane-4,8,12-trione.

Sir: Reaction of glyoxal (**1**) with dimethyl 3-ketoglutarate (**2**) in aqueous solution at room temperature and pH 5.0 has been found[2] to give the ester **3**,[3] which yields *cis*-bicyclo[3.3.0]octane-3,7-dione (**4**)[3,4] on treatment with acid. Compound **4** was accompanied[2] by another ketone $C_{13}H_{14}O_3$ (mp 148–151°)[5] having spectroscopic properties very similar to those of **4**; it is undoubtedly derived from a β-keto ester analogous to **3** which, however, was not isolated. We now wish to report the isolation of this intermediate, and the elucidation of structure and stereochemistry of the C_{13} compound by X-ray crystallography.

Formation of a compound $C_{13}H_{14}O_3$ through reaction of **1** with **2**, followed by treatment with acid, could be rationalized by assuming that **3** forms initially and subsequently reacts with one molecule each of **1** and **2** in an aldol reaction analogous to the one taking place in its own formation; for the resulting β-keto ester, structure **5** appears logical.[6] Assuming the usual cis stereochemistry at the junction of two cyclopentane rings,[7] formula **5** represents two stereoisomers with ring D in syn or anti relationship to rings A and B. Treatment of **5** with acid would then give **6**, $C_{13}H_{14}O_3$, which could again be the syn or anti isomer.

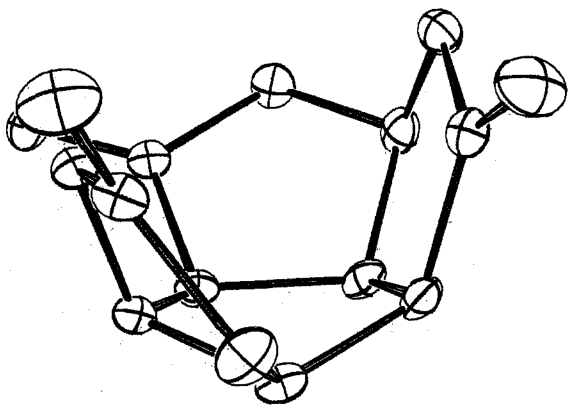


Figure 1.

An ester **5**, mp 173–176°, having the expected composition[8] and spectroscopic properties, was obtained in 10% yield when **1** and **2** were allowed to react in the required molecular ratio 2:3 for 1 week in aqueous solution at room temperature and pH 3 instead of the pH 5 used in the earlier work;[2] trituration of the resulting precipitate with methanol and recrystallization from the same solvent gave pure **5**. Treatment of **5** with hot 25% HCl[2] yielded **6**.

An X-ray crystallographic investigation has now shown that structure **6** is indeed correct and that the compound has the all-cis stereochemistry (**6a**). The crystals were monoclinic, $P2_1/n$, $a = 6.299$ (1) Å, $b = 15.511$ (1) Å, $c = 10.943$ (1) Å, $\beta = 105.78$ (1)°, $Z = 4$. A total of 1933 independent X-ray intensities (328, unobserved) were measured by means of an Enraf-Nonius CAD-4 diffractometer. The structure was solved by direct methods using our own semiautomatic program. With anisotropic thermal parameters for the C and O atoms and isotropic parameters for the hydrogen atoms, the structure has been refined by full-matrix least-squares to an R factor of 0.036. Estimated standard deviations of C–C and C–O bond lengths are typically 0.003 Å. An ORTEP drawing[9] of **6** (Figure 1) shows its conformation and demonstrates that the molecule is chiral, lacking the mirror plane which the conventional structural formula would indicate. The observed conformation is very reasonable if intramolecular interactions are taken into consideration. Since the crystals are centrosymmetrical,

(1) Dr. K. L. Loening, Director of Nomenclature, Chemical Abstracts Service, has advised us that compound **6** can be correctly designated either as octahydro-1*H*-dicyclopenta[*a*,*cd*]pentalene-1,4,6(2*H*,4a*H*)-trione or as tetracyclo[5.5.1.$0^{2,6}$.$0^{10,13}$]tridecane-4,8,12-trione. We wish to thank Dr. Loening for his helpful interest.

(2) J. M. Edwards and U. Weiss, *Tetrahedron Lett.*, 4885 (1968).

(3) G. Vossen, Dissertation, Bonn, 1910; P. Yates, E. S. Hand, and G. R. French, *J. Amer. Chem. Soc.*, **82**, 6347 (1960).

(4) H. W. Wanzlick, *Chem. Ber.*, **86**, 269 (1953).

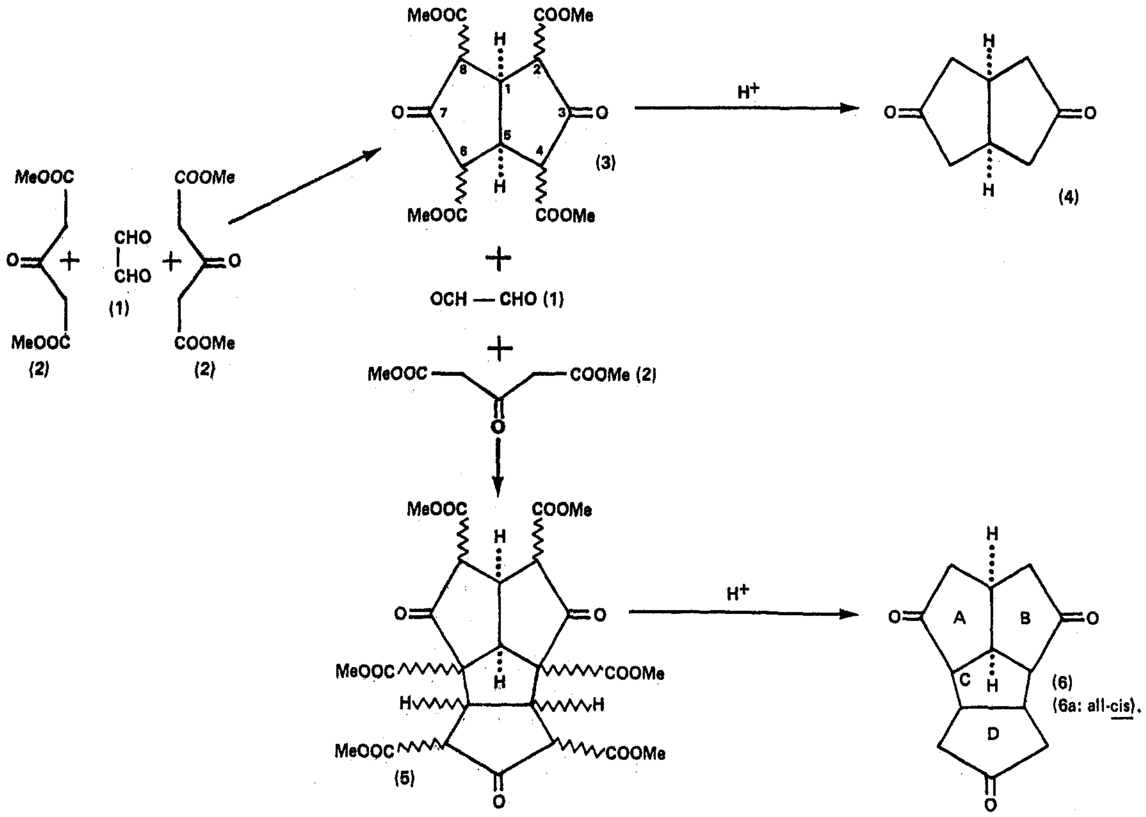
(5) It has been observed recently that recrystallization from methanol raises the melting point to 160°. The sample used for X-ray crystallography has this melting point.

(6) Reaction of **3** with **1** and **2** could also take place at positions 2 and 4, or 2 and 6. However, the resulting β-keto esters isomeric with **5** could undergo decarboxylation to a C_{13} compound only with violation of Bredt's rule and are thus quite unlikely. This point was brought to our attention by a referee on our earlier paper.[2]

(7) *Cf.* E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 273–274.

(8) Satisfactory analytical and mass spectrometric data were obtained for **5**.

(9) C. K. Johnson, ORTEP Report ORNL-3794 (2nd revision), 1970, Oak Ridge National Laboratory, Oak Ridge, Tenn.



both enantiomers are present. The X-ray crystallographic results will be published in detail in *Acta Crystallographica*.

The reaction which yields **5** and **6** provides a surprisingly simple entry into the *endo*-tetracyclo-$[5.5.1.0^{2,6}.0^{11,13}]$tridecane series; the low yields (probably capable of being much improved) are hardly surprising in view of the numerous possibilities for interaction of such reactive bifunctional compounds as **1** and **2** and are offset by ready availability of the starting materials and ease of manipulation. After completion of our work, the first representative of this ring system, a trienic hydrocarbon, was described by Srinivasan,[10] who prepared it from cycloheptatriene by a three-step sequence of photochemical and pyrolytic reactions.

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RECEIVED MAY 18, 1973

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(10) R. Srinivasan, *J. Amer. Chem. Soc.* **94**, 8117 (1972).