Tetrahedron Letters,Vol.23,No.7,pp 747-750,1982 0040-4039/82/070747-04$03.00/0
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STRUCTURE PROOF FOR THE TRIMER FROM 3-METHYLCYCLOHEX-2-ENONE

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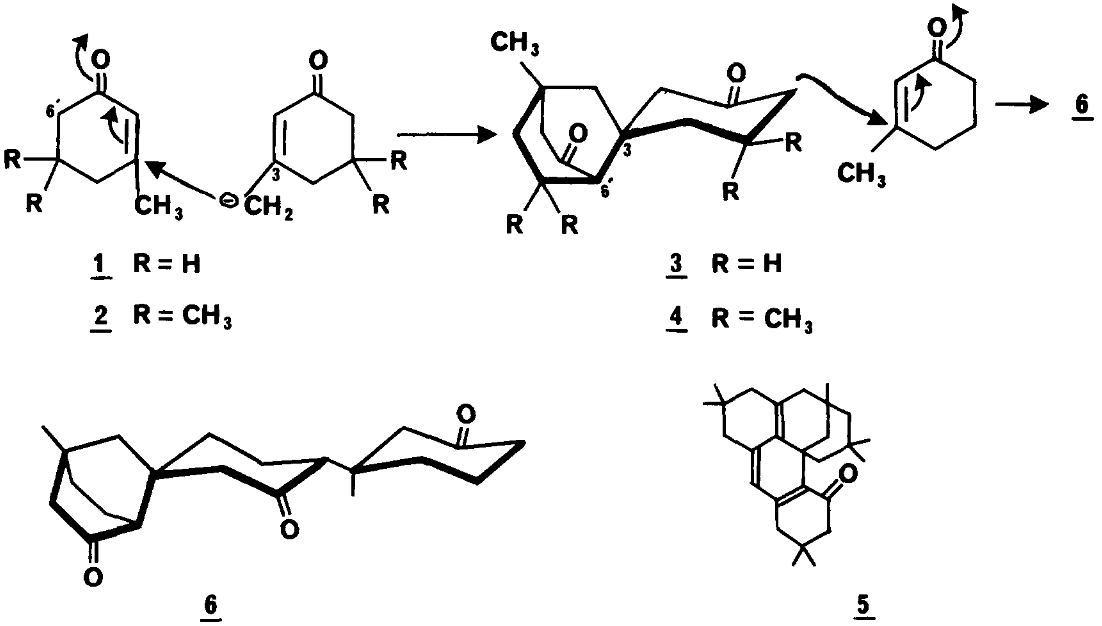
Summary: Previously it has been shown that under base-catalyzed conditions isophorone forms a "trimer", actually a condensation product involving the loss of two moles of water. In contrast we show by X-ray crystallography that 3-methylcyclohex-2-enone forms a true trimeric saturated triketone under the same conditions.

In 1958, Buchi and his co-workers[1] proposed a set of structures for the dimeric materials obtained from the base-catalyzed condensations of 3-methylcyclohex-2-enone (1) and from isophorone (2). These compounds had been described earlier by Ruzicka[2], and subsequently by French[3] and by Swiss[4] workers. Recently, X-ray crystallography has been utilized to confirm Buchi's structural assignments and to unequivocally determine the stereochemistry of these products.[5,6] These enones yield *syn*-dimers (1->3 and 2->4) in 50-55% yield presumably by sequential inter- and intra-molecular Michael addition reactions. Other stereoisomers have not been isolated.

Buchi[1] described an additional compound obtained from the reaction of 3-methylcyclohex-2-enone in ether or benzene with powdered KOH or sodium amide. The compound was not thoroughly studied but it was thought to be a tetramer from freezing point depression studies. Later, House and his co-workers[7] utilized X-ray crystallography to determine the structure (5) of a trimer (C_{27}) obtained from isophorone under various reaction conditions. It therefore seemed of considerable interest to fully characterize the higher molecular weight material (6) which is obtained along with the dimer from (1). Regrettably, a direct comparison between Büchi's compound (m pt 186) and ours (m pt 194-196) was not possible.

Of immediate interest was the result that the molecular weight of our material (from mass spectroscopy) was 330 amu. Obviously the compound is a trimer. C-13 NMR spectroscopy yields 21 peaks attributable to the compound which corroborates the evidence from mass spectrometry. House's isophorone "trimer" is a colored material which has strong UV absorption. Our material is a white, crystalline compound with no intense UV absorption. Furthermore, the C-13 NMR spectrum best fits a structure with no unsaturation and with three carbonyl groups in only slightly differing environments. Although the lack of ultraviolet absorption and data from mass spectrometry, infrared spectroscopy, proton/carbon NMR were consistent with a structure based on a reasonable mechanistic proposal (see Scheme), it seemed appropriate to determine by X-ray crystallography the full structure of this interesting material.



SCHEME

Crystals of (6), grown from petroleum ether-benzene solution, are monoclinic, space group $P2_1/c$, a=12.945(5), b=10.733(2), c=29.062(7) Å, β=115.11(3), U=3651 Å^3 , Z=8, d_{calc}=1.202 g cm^{-3}, d_{meas}= 1.20 g cm^{-3}. One quadrant of intensity data up to $2\theta \leq 115^0$ was measured on a Syntex $P2_1$ automated diffractometer using Cu-K_α radiation and a $\theta/2\theta$, variable speed scanning mode. The structure was solved using MULTAN 77[8] and refined to R 0.057 over observed reflections.[9]

A view of the two crystallographically independent molecules is shown in Figure 1. The two independent molecules are very similar to one another except for the rotation of *ca.* 60^0 about the C(4')-C(1") bond (see Figure 2). Also, for analogous portions of the molecules, the conformation of (6) and of the dimers from 3-methylcyclohex-2-enone (3) and from isophorone (4) appear similar.

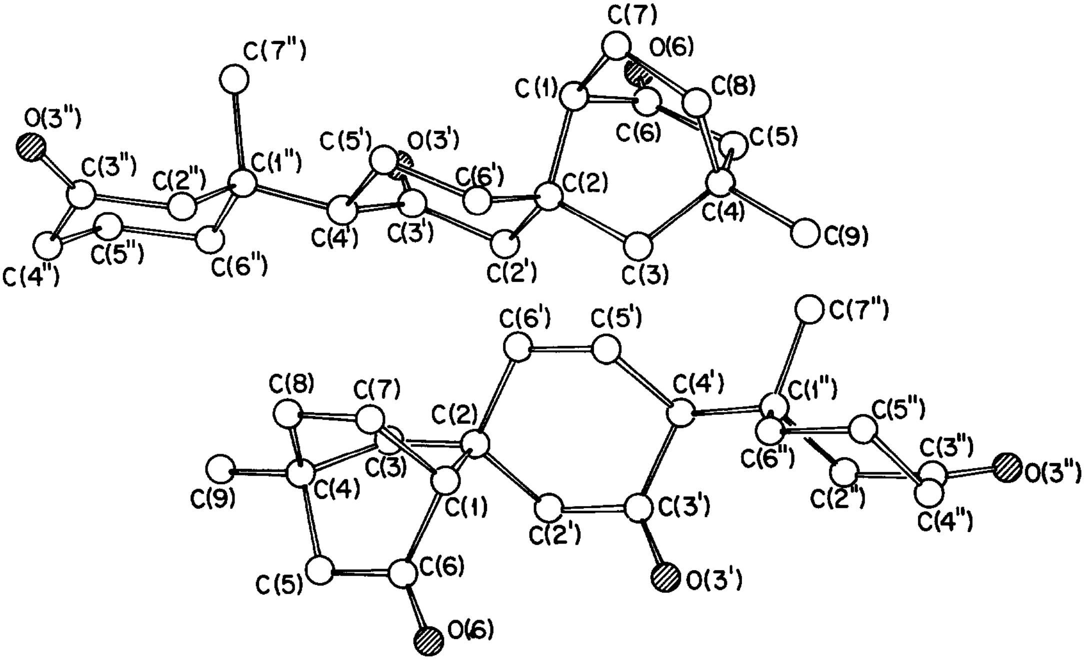


Figure 1. An ORTEP[10] drawing showing a general view of the molecular structure of compound 6 in the crystal (hydrogen atoms omitted for clarity).

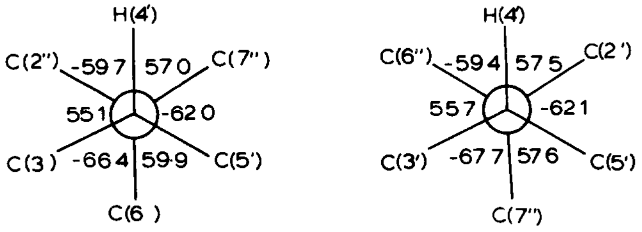


Figure 2. Newman projections about the C(4')-C(1") bond for the two crystallographically independent molecules of 6.

Thus, it would appear that while there are now three examples[11] of compounds which yield dimeric materials of comparable structures, and that these three dimers are formed by mechanisms with similar stereochemical demands, it seems that the two most closely related examples ((1) and (2)) yield very different trimeric compounds. At this time, we offer no explanation.

ACKNOWLEDGEMENT.- We (KDO) are grateful to the National Science Foundation which provided support towards the Syntex $P2_1$ diffractometer. The assistance of Prof. D. A. Lightner, Dr. B. V. Crist, and Mr. Donald Wijekoon of the University of Nevada at Reno in obtaining the C-13 NMR spectra is greatly appreciated. Mr. J. Moore of the Environmental Protection Agency (Gulf Breeze, Florida) determined the mass spectrum.

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(Received in USA 11 November 1981)