Tetrahedron Letters Vol. 21, pp 3223 - 3226
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0040-4039/80/0815-3223$02.00/0

THE STEREOCHEMISTRY OF THE PRODUCT DERIVED FROM THE BASE-CATALYZED DIMERIZATION OF 3-METHYLCYCLOHEX-2-EN-1-ONE

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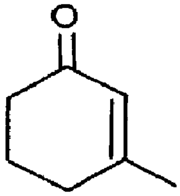
Summary Single-crystal *X*-ray analysis of the product derived from the base-catalyzed dimerization of 3-methylcyclohex-2-en-1-one has established that it possesses a saturated diketone structure with a *syn*-stereochemistry rather than an *anti*-arrangement as previously proposed.

In 1958, Büchi *et al.*[1] proposed a structure for the saturated diketone which arises from the base-catalyzed dimerization of 3-methylcyclohex-2-en-1-one (1), a compound first described in 1920.[2] Determination of this structure was carried out in a clever and thorough manner which relied mainly on classical techniques with little assistance from modern spectroscopic instrumentation. From their work, these authors were able to assign structure (2) or (3)[3] to the compound formed in 53% yield, with the former being favored on the basis of the proposed reaction intermediate, although there was no evidence to support this choice. The reaction has been further studied by other investigators,[4-6] none of whom has questioned or amplified upon the assignment made by Büchi *et al.*

We have now prepared the above saturated diketone using KOH in ether[6a] and recorded its ^{1}H and ^{13}C n.m.r. spectra as well as its mass spectrum;[7] ^{13}C n.m.r. ($CDCl_3$) δ 18.95, 21.93, 26.79, 30.77, 33.40 (low intensity), 34.91, 39.94 (low intensity), 40.93, 44.75, 49.91, 53.35, 54.91, 209.91, 214.54. Although the spectral data are completely compatible with the structure(s) proposed by Buchi *et al.*, we elected to perform a single-crystal *X*-ray analysis on this compound in order to establish its structure and stereochemistry unequivocally. Crystals of the diketone ($C_{14}H_{20}O_2$), grown from petroleum ether, belong to the monoclinic system, space group $P2_1/c$, with $a = 9.513(4)$, $b = 9.848(4)$, $c = 13.176(6)$ Å, $\beta = 92.91(2)°$, $U = 1233$ Å^3, $d_{meas} = 1.195$ g cm^{-3}, $Z = 4$, $d_{calc} = 1.187$ g cm^{-3}. The structure



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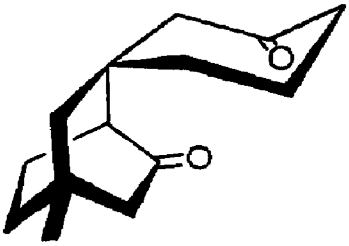

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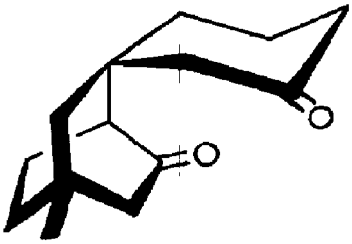

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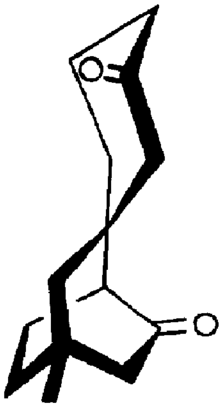

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was solved by direct methods by use of MULTAN.[8] Full-matrix least-squares refinement of atomic positional and thermal (anisotropic C, O; isotropic H) parameters converged to R = 0.066[9] over 1681 statistically significant $[I > 2.0\sigma(I)]$ reflections measured on an Enraf-Nonius CAD-3 automated diffractometer (Ni-filtered Cu-K_α radiation; θ-2θ scans). A view of the structure and solid-state conformation is shown in the Figure.[10] The results of the *X*-ray analysis reveal that the compound is really the *syn*-isomer (3) and not the *anti*-isomer (2) as previously proposed. Furthermore, the conformation adopted in the solid-state is correctly represented by (4) rather than (3) which empirical force-field calculations[11] indicate to be less stable by *ca*. 3 kcal mole^{-1}.

At this point there seems to be no obvious reason for the selectivity of this reaction.

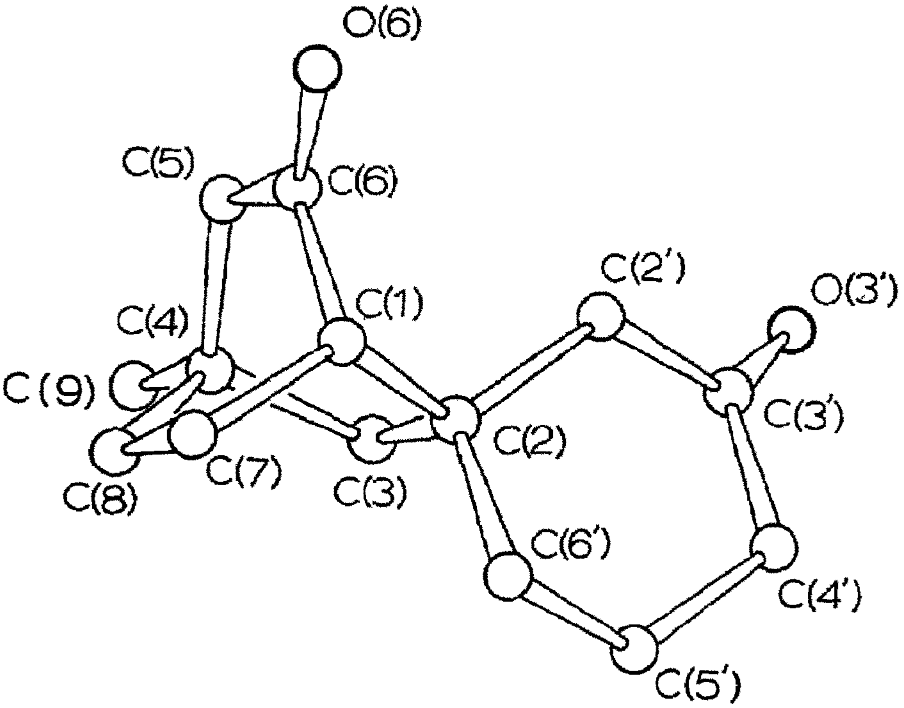

FIGURE. Solid-state conformation of diketone (4); hydrogen atoms have been omitted for clarity

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3. Compound (2), the *anti*-isomer is (1*R**, 2*S**, 4*S**)-4-methylspiro{bicyclo[2.2.2]octane-2,1'-cyclohexane}-3',6-dione. The *syn*-isomer (3) is (1*R**, 2*R**, 4*S**)-4-methylspiro-{bicyclo[2.2.2]octane-2,1'-cyclohexane}-3',6-dione. Only one enantiomer of the racemic pair is shown. We thank Dr. K. L. Loening of *Chemical Abstracts* for assistance with this nomenclature.
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7. We thank Professor D. A. Lightner and Mr. B. V. Crist of the University of Nevada, Reno, for their assistance in obtaining these spectra.
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9. $R = \sum||F_o| - |F_c||/\sum|F_o|$.
10. Atomic co-ordinates for this work have been deposited with the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.
11. D. N. J. White and M. J. Bovill, *J. C. S. Perkin 2*, 1610 (1977); see also, R. W. Miller and A. T. McPhail, *J. C. S. Perkin 2*, 1527 (1979).

(Received in USA 7 April 1980)