

Table I. Optical Data for Cyclic Dicarboxylic Acids in TFE^a

Compd	UV		ORD		CD		Assignment
	λ , $m\mu$	ϵ/res	λ , $m\mu$	$[\phi]$, deg	λ , $m\mu$	$[\theta]/res$, deg	
2,3-BCO	208	74	227	-2900	210	-4620	$\pi \rightarrow \pi^*$
			215	0			
1,2-CP	207	55	(190)	(+6000)	203	-561	$\pi \rightarrow \pi^*$
			226	(+2300)			
1,2-CH	208	83	216	0	210	-3366	$\pi \rightarrow \pi^*$
			(190)	(+4800)			
1,3-CH	210	59	(190)	(+780)	219	-362	$n \rightarrow \pi^*$
					204	0	$\pi \rightarrow \pi^*$
					200	+132	

^a Measured with a Jasco ORD/CD/UV-5 spectropolarimeter, 0.1–10-mm cells, concentration range 10^{-2} – 10^{-4} residue/l., in TFE. Values in parentheses do not represent maxima.

mation was preponderant in solution,³ but these conclusions were questioned later and the diequatorial conformation was proposed.⁴ Crystal structure studies⁵ have recently shown that, in the solid state, 1,2-CH exists in the diequatorial conformation. Since repulsion of polar groups and solvent interaction could, in principle, convert the conformation from diequatorial to diaxial in going from the solid state to solution, we have investigated the nmr spectra of 1,2-CH and some related compounds seeking independent evidence. The results are collected in Table II.

Table II. Chemical Shifts of Axial and Equatorial Tertiary Hydrogen Nuclei of Cyclohexanecarboxylic Acids

	δ^a	Conformation
<i>trans</i> -1,2-CH	140	e,e
<i>cis</i> -1,2-CH	161	a,e
<i>trans</i> -1,3-CH	150	a,e
<i>cis</i> -1,3-CH	140 ^b	e,e
<i>trans</i> -1,4-CH	130 ^b	e,e
CHCA	137 ^b	e

^a Measured in cycles per second from TMS as internal reference, in DMSO-*d*₆, with a Varian A-60 spectrometer. ^b Approximate center of broad band.

The tertiary hydrogen peak in *trans*-1,2-CH is shifted upfield (21 cps) with respect to the corresponding peak for the *cis*-1,2-CH. This is what would be expected if *trans*-1,2-CH exists in the diequatorial conformation.^{6,7}

In fact, *cis*-1,2-CH is undergoing inversion ($a,e \rightleftharpoons e,a$) and its tertiary protons experience an averaged shielding. If *trans*-1,2-CH existed preferentially in the a,a conformation, its tertiary protons should experience a deshielding effect and would, therefore, appear downfield with respect to the *cis*-1,2-CH.

Furthermore, as shown in Table II, this peak in *trans*-1,2-CH is very close to that of cyclohexanecarboxylic acid (CHCA), *trans*-1,4-CH, and *cis*-1,3-CH, all of which should exist, preferentially, with the carboxyl groups in the equatorial position.

(3) J. C. Speakman, *J. Chem. Soc.*, 490 (1941); D. H. R. Barton and G. A. Scheidler, *ibid.*, 1197 (1948); G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, New York, N. Y., 1956, p 434; ref 1.

(4) J. Sicher, F. Sipos, and J. Jonas, *Collection Czech. Chem. Commun.*, 26, 262 (1961).

(5) P. Corradini, private communication.

(6) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

(7) E. L. Eliel and M. H. Gianni, *Tetrahedron Lett.*, 97 (1962).

From the difference between the tertiary hydrogen peak of *trans*- and *cis*-1,2-CH (about 20 cps), it can be calculated⁷ that the chemical shift value for the *trans*-1,2-CH in the diaxial conformation would be approximately 180 cps. Unfortunately, no compound of this kind is available, at the moment, to us, but it is interesting to note here that for *trans*-2,3-BCO (which structurally approximates a diaxial *trans*-1,2-CH arrangement) the tertiary hydrogen peak is found at 172 cps.

In the 1,2-CP case, our evidence that the molecule is flexible agrees with what is known from the conformational behavior of *trans*-1,2-dihalocyclopentanes. These molecules were, in fact, found to be in dynamic equilibrium between two conformers (diaxial and diequatorial).⁸

It can be concluded that if an optically active molecule possesses two identical neighboring chromophores, optical rotatory techniques provide a way to test for conformational rigidity through application of the exciton theory.²

The four acids investigated have been prepared and resolved according to previously reported procedures.⁹

Acknowledgment. The authors wish to thank Mr. R. Veneski for his help in the preparation of the acids.

(8) C. Altona, H. R. Buys, and E. Havinga, *Rec. Trav. Chem.*, 85, 973 (1966).

(9) Y. Nishimura, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1966; J. Boeseken and E. J. Peck, *Rev. Trav. Chim.*, 44, 841 (1925); A. Werner and H. E. Conrad, *Ber.*, 32, 3046 (1899); D. E. Applequist and N. D. Werner, *J. Org. Chem.*, 28, 48 (1963); F. W. Kay and W. H. Perkin, *J. Chem. Soc.*, 87, 1073 (1905).

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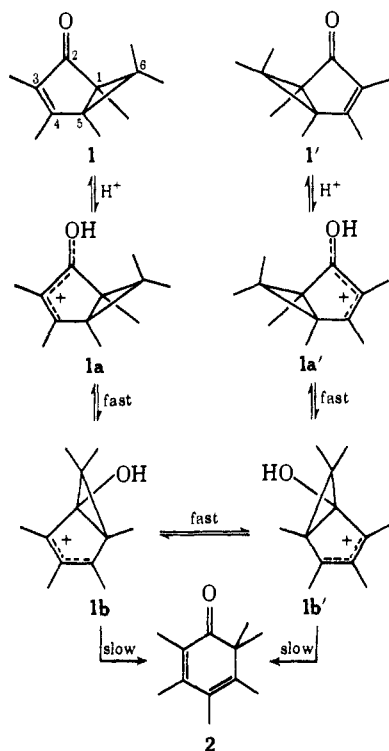
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Stereochemistry of the Rapid Equilibration of Protonated Bicyclo[3.1.0]hexenones

Sir:

We recently demonstrated¹ that protonation of hexamethylbicyclo[3.1.0]hexenone (**1**) by 97% sulfuric acid results in rapid successive migrations of C₆, leading to the enantiomer **1'**. The equilibrium $\mathbf{1} \rightleftharpoons \mathbf{1}'$ is rapid compared with ring opening to dienone **2**, which occurs

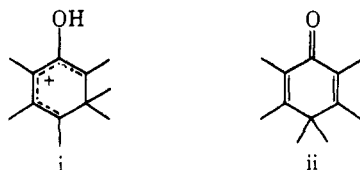
(1) D. W. Swatton and H. Hart, *J. Am. Chem. Soc.*, 89, 5075 (1967).



only from **1b** (or **1b'**).²⁻⁶

It was recognized earlier¹ that these interconversions can have stereochemical consequences for substituents on C₆. We now wish to present chemical evidence that these substituents maintain their positions (*endo* or *exo*) relative to the five-membered ring.⁷

(2) Opening of **1a** should afford **i** which, when generated other ways,³ gives cross-conjugated dienone **ii**, not **2**. No **ii** was formed under the present reaction conditions.



(3) H. Hart and D. W. Swatton, *J. Am. Chem. Soc.*, **89**, 1874 (1967).

(4) Ions **1a**, etc., are written without depicting charge delocalization into the three-membered ring. This is for convenience in representation only, since such delocalization must be important.⁵

(5) R. F. Childs, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7144 (1968).

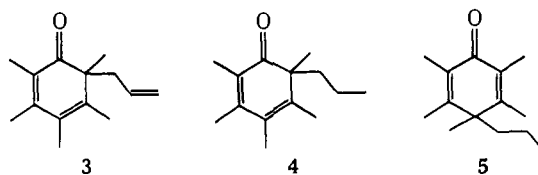
(6) For the possible involvement of ion **1c**, see ref 1, footnote 8.



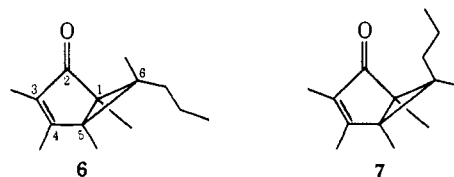
(7) Nmr evidence for a similar conclusion in scrambling of the heptamethylbicyclo[3.1.0]hexenyl cation **iii** has recently been disclosed: R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7146 (1968).



The isomeric bicyclo[3.1.0]hexenones **6** and **7** were used as probes. Sodium pentamethylphenoxide and allyl bromide in toluene gave mainly dienone **3**, which was hydrogenated (Rh-C, cyclohexane) to a mixture of dienones **4** and **5** and pentamethylphenol (4:1:2). Irradiation of the crude hydrogenation product in methylene chloride through Pyrex (Hanovia 650-W



lamp), followed by evaporation, replacement of the solvent with methanol, and further irradiation through quartz at 2537 Å, converted **4**, then **5**, to a mixture of **6** and **7**. These were separated and purified by preparative vpc; **7** has the shorter retention time.^{8,9}



The isomers had similar ir and uv spectra, and the chemical shifts (Table I) of methyls at C₁, C₃, C₄, and C₅

Table I. Chemical Shifts (τ) of Protons in **6** and **7**

Protons	6	7	1'
Methyl at			
C ₁	8.90	8.91	8.90
C ₃	8.46 ^a	8.46 ^b	8.45 ^b
C ₄	8.15 ^a	8.12 ^b	8.12 ^b
C ₅	8.78	8.78	8.78
C ₆	9.13	8.96	8.90, 9.08
Propyl	8.55-8.70 ^c 8.90-9.15 ^c	8.80-8.95 ^c 9.05-9.40 ^c	

^a Quartet, $J = 1.0$ Hz, due to homoallylic coupling. ^b Quartet, $J = 0.93$ Hz; see footnote a. ^c Broad multiplets with the approximate ranges shown.

appeared at essentially identical positions as those established for **1**.¹ The isomers were readily distinguished, however, by the chemical shifts of the C₆ substituents, which appear at appreciably higher field when *endo* than when *exo*.³

Treatment¹⁰ of either **6** or **7** with 98% sulfuric acid at 4° for 2 min, followed by quenching on ice, gave recovered ketone (85-90%) and dienone **4** (10-15%). In each case, none of the isomeric ketone was formed (detection limit 0.5%). Thus, under conditions where **6** and **7** rearrange to **4**, their stereochemical identity is preserved.

Ketones **6** and **7** labeled with CD₃ at C₄ were prepared by exchange in excess CH₃ONa-CH₃OD. In each

(8) Differences in retention time of 2-3 min (in 13-19 min) were readily achieved using SE-30 or DEGS on Chromosorb W.

(9) All new compounds gave satisfactory elemental analyses and had ir, uv, and nmr spectra consistent with the assigned structures.

(10) Ketone (0.10 g) was added to 5 ml of acid.

case, the τ 8.12 (8.15) peak was absent, and the peak at τ 8.46 sharpened to a singlet. After separate treatment of each labeled ketone with acid as above, the recovered ketone showed return of 1.5 H at τ 8.12 (8.15) and a decrease in the intensity of the τ 8.78 peak to 1.5 H.^{11,12}

These experiments establish that equilibrations of the type $1a \rightleftharpoons 1b \rightleftharpoons 1b' \rightleftharpoons 1a'$ occur without interchange in the positions of substituents at C₆; the endo group remains endo, and the exo group remains exo. The result can be rationalized readily in terms of the Woodward-Hoffmann rules for sigmatropic rearrangements;¹³ inversion occurs at C₆ as the bond to C₅ is displaced by one to C₂, etc. The chemical evidence presented here is consistent with the conclusion⁷ based on nmr evidence.^{14,15}

(11) Control experiments showed that vpc purification was without effect on label distribution.

(12) With 6, integration of the τ 8.78 peak was unambiguous and gave the result described. With 7 the τ 8.78 peak overlapped those of the propyl methylenes (Table I). The entire peak was integrated and showed a decrease from 7.0 to 5.5 H; we assume the deuterium entered the C₃ methyl.

(13) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(14) We are indebted to the National Science Foundation for financial support of this research.

(15) After this paper was submitted, two related papers appeared in which similar stereochemical conclusions were reached. The reactions involved a single migration of C₆, under conditions which are probably not equilibrating. See H. E. Zimmerman and D. S. Crumrine, *J. Am. Chem. Soc.*, **90**, 5612 (1968); T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968).

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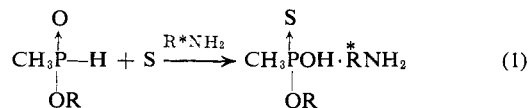
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Evidence of Phosphino Radical from Alkyl Alkylphosphinates

Sir:

The addition of elemental sulfur to trivalent phosphorus compounds has been studied previously and has been considered to proceed *via* an ionic mechanism.¹ We wish to report a sulfur addition to pentavalent phosphorus which appears to proceed by a predominantly radical mechanism.

During the investigation of sulfur addition to alkyl methylphosphinates in the presence of an optically active base, *d*- or *l*- α -methylbenzylamine (eq 1), the

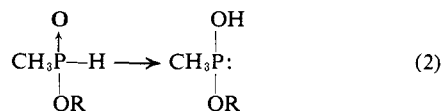


racemic acid obtained and the facile manner under which this reaction took place could not be readily explained by a simple prototropy to an "enol" form² as shown in eq 2.

Evidence of a radical mechanism was first noted by the inhibition of the above sulfur addition when 1

(1) P. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956); P. Bartlett, E. Cox, and R. Davis, *ibid.*, **83**, 103 (1961).

(2) A. Kirby and S. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing New York, N. Y., 1967, pp 21-23.



equiv of hydroquinone was added. In the absence of hydroquinone the above reaction was rapid and highly exothermic. In the presence of hydroquinone the reaction was essentially inhibited.

The presence of radicals in mixtures of certain amines with elemental sulfur has been studied previously by Hodgson, *et al.*,³ and Poziomek⁴ using esr technique. They believe the radical present to be the result of homolytic scission of N,N'-polythiobisamine with localization of the odd electron around the terminal sulfur atom with $g = 2.030$.

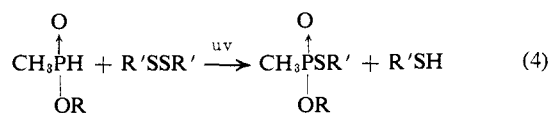
When a mixture of excess α -methylbenzylamine and elemental sulfur in a quartz tube was placed in a Varian 4500 esr instrument, no evidence of radicals was found. One drop of alkyl methylphosphinate was added to this mixture, resulting in a deep red coloration, and radicals were detected with approximate concentration of 5×10^{-4} spin/mol and a g value of 2.0289.

It is clear from the behavior of all possible combinations of the reagents in the esr that it is necessary to have all three components, phosphorus acid, amine, and elemental sulfur, present to produce the stable free radicals.

In order to obtain additional support for the radical mechanism of this reaction, advantage was taken of the alkyl and aryl disulfide radical reaction with trialkyl phosphites induced by ultraviolet light, as studied by Walling, *et al.*⁵ (eq 3).



When a neat sample of alkyl methylphosphinate and phenyl disulfide was exposed to ultraviolet light and distillation, a 63% yield of S-phenyl isopropyl methylphosphonothiolate was obtained with 45% of phenyl mercaptan (eq 4). A 0.2 M solution of this reaction



mixture in spectral grade benzene was studied under the influence of uv radiation using a uranyl oxalate actinometer.⁶ A quantum yield of 18.6 was obtained, indicating a relatively short chain length. The yield of phenyl mercaptan after 5 hr with uv light was 27.5%; bp 95-97° (0.10mm) (lit.⁷ 78° (0.010 mm)); ir (film on CsI), no P-H at 4.2-4.4, 6.32 (Ar), 7.7 (CH₃-P), 8.11 (P-O), 10.1 (P-O-R), 18.6 μ (P-S-Ar) (the ir is consistent with the ir of the corresponding ethoxy compound); nmr (neat), σ 1.27 (m, 3, $J = 6$ Hz, CCH₃), 1.37 (m, 3, $J = 6$ Hz, CCH₃), 1.63 (d, 3, $J = 16$ Hz,

(3) W. Hodgson, S. Buckler, and E. Peters, *J. Amer. Chem. Soc.*, **85**, 543 (1963).

(4) E. Poziomek, *Chemist-Analyst*, **55**, 78 (1966).

(5) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957); **81**, 1243 (1959).

(6) A. Weissenberger, "Techniques of Organic Chemistry," Vol. II, Interscience Publishing Co., New York, N. Y., 1948, p 105.

(7) G. Schrader, Farbenfabriken Bayer AG., U. S. Patent 3,032,580 (May 1, 1962).