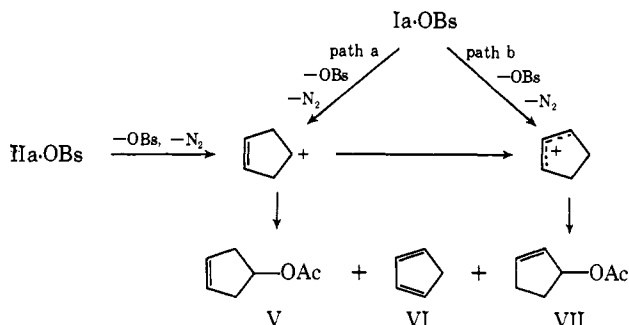


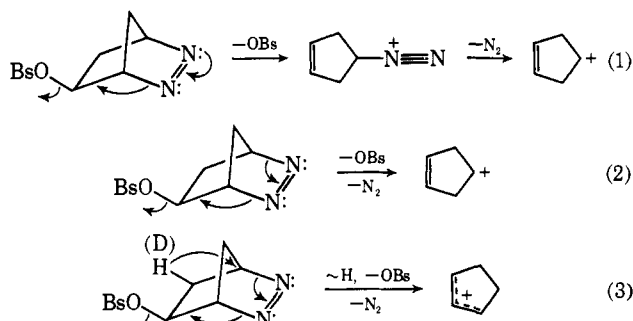
## Scheme I



intermediates. A mechanistic scheme which accounts for the results is formulated in Scheme I.

A comparison of the acetolysis rates shows that Ia-OBs reacts 117 times faster than Hla-OBs. The significantly higher reactivity of Ia-OBs can be attributed plausibly to anchimeric assistance to ionization at C<sub>5</sub> by the  $-N=N-$  group. In the case of Hla-OBs geometry is unfavorable for such assistance. Further support for assistance is found in the observation that  $\Delta S^\ddagger$  for Ia-OBs is 13.7 eu more positive than  $\Delta S^\ddagger$  for Hla-OBs. Such a difference is indicative of different modes of ionization for the two *p*-bromobenzenesulfonates. Others have reported solvolysis studies where  $\Delta S^\ddagger$  was found to be 10–14 eu more positive for systems showing neighboring group participation.<sup>19</sup>

The question of the nature of the ionization–nitrogen elimination step(s) for Ia-OBs is extremely interesting. Three attractive possibilities are illustrated by eq 1–3.



We have found that  $k_H/k_D$  is  $1.1 \pm 0.1$  at 75° for Ia-OBs and Ia-OBs-*exo*-6-*d*.<sup>20</sup> This precludes the completely concerted process 3 and thus one of the possibilities for path b proposed in the above mechanistic scheme. At present there is not sufficient information to allow for a distinction to be made between processes 1 and 2, and perhaps other possibilities. In the case of Hla-OBs we presume that ionization precedes nitrogen elimination. These questions are currently under investigation. Results with other azo systems will be reported later.

**Acknowledgment.** We express appreciation to the National Science Foundation for support of this work with Grant GP-9478.

(19) M. G. Jones and J. L. Coke, *J. Amer. Chem. Soc.*, **91**, 4284 (1969); D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963); S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

(20) E. L. Allred and R. L. Smith, *J. Org. Chem.*, **31**, 3498 (1966).

(21) National Institutes of Health Predoctoral Fellow, 1968–1970.

Evan L. Allred, Charles R. Flynn<sup>21</sup>

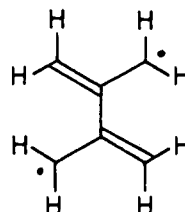
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Received December 13, 1969

## Tetramethyleneethane

Sir:

Tetramethyleneethane (I) is predicted by simple theory to be a ground-state triplet.<sup>1</sup> This molecule has long been assumed to be the central reactive in-



I

termediate in the dimerization of allene leading to the major product 1,2-dimethylenecyclobutane. Indeed, reaction of allene with  $Fe_3(CO)_{12}$ <sup>2a</sup> and  $Fe_2(CO)_9$ <sup>2b</sup> has resulted in the isolation of a compound which has been suggested to be a bis(iron carbonyl) complex of I. X-Ray structure determinations of organonickel and -palladium complexes of tetramethyleneethane have also been reported recently.<sup>3</sup> The stable, highly substituted diradical bisgalvinoxyl<sup>4</sup> is a derivative of tetramethyleneethane. Tetramethyleneethane (possibly in its singlet state) has been shown to be an intermediate in the thermal, degenerate rearrangement of 1,2-dimethylenecyclobutane.<sup>5</sup> The anion radical of tetramethyleneethane has been observed recently.<sup>6</sup>

As a consequence of the above results and the theoretical interest in this molecule and also in order to learn more about the mechanism of allene dimerization, it became attractive to attempt the direct observation of the diradical I using electron spin resonance spectroscopy.<sup>7</sup> That is, it was hoped that the knowledge gained in attempting to generate I at low temperatures might be used in the development of trapping reactions. These might then be applied to an investigation of the possible intermediates present in the allene dimerization reaction.

The necessary precursor to tetramethyleneethane (I) was prepared as follows: the known<sup>8</sup> *trans*-3,4-cyclopentanedicarboxylic acid (II) was allowed to react with phosphorus pentachloride in ether at 0°. The resulting bis(acid chloride) III was not isolated but was allowed to react directly with dimethylamine yielding the N,N,N',N'-tetramethyl-3,4-cyclopentanedicarboxamide (IV); ir (CHCl<sub>3</sub>) carbonyl bands at 5.7 and 6.1  $\mu$ ; nmr (CDCl<sub>3</sub>) two-proton multiplet at  $\tau$  6.2, two three-proton methyl singlets at 6.8 and 7.0, and a

(1) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

(2) (a) A. Nakamura, *Bull. Chem. Soc. Japan*, **39**, 543 (1966); (b) R. Ben-Shoshan and R. Pettit, *Chem. Commun.*, 247 (1968).

(3) W. Keim, *Angew. Chem.*, **80**, 968 (1968).

(4) E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 1263 (1964).

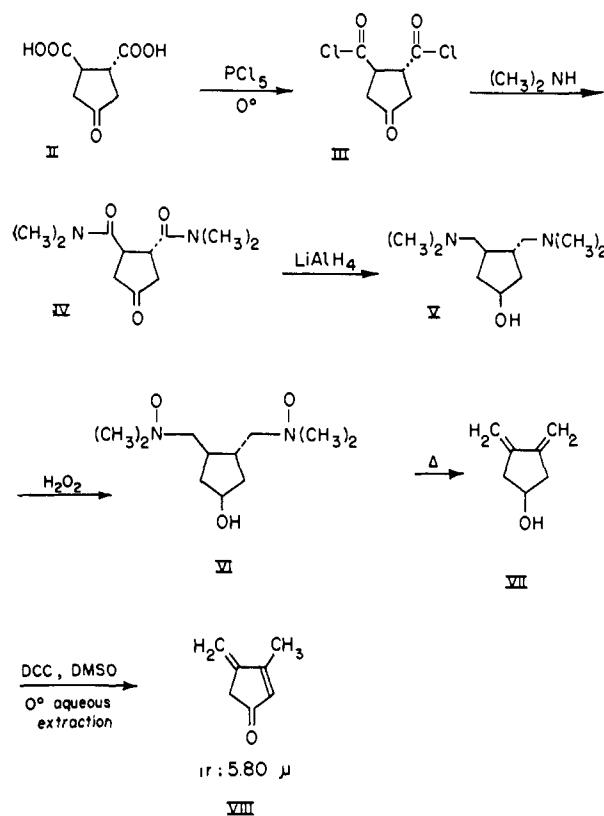
(5) W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967); J. J. Gajewski and C. N. Shih, *ibid.*, **89**, 4532 (1967).

(6) N. L. Bauld and G. R. Stevenson, *ibid.*, **91**, 3675 (1969).

(7) C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **34**, 908 (1961); J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959); **3**, 190 (1960); W. A. Yager, E. Wasserman, and R. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

(8) R. Giuliano, M. Artico, and V. Nacci, *Ann. Chim. (Rome)*, **51**, 491 (1961); K. Auwers, *Ber.*, **26**, 364 (1893); K. Auwers and A. Jacob, *ibid.*, **27**, 1114 (1894); C. K. Ingold, *J. Chem. Soc.*, 119, 341 (1921).

(9) Cf. J. H. Muller, M. N. Doniss, W. E. Behnke, and K. Hoffmann, *J. Am. Chem. Soc.*, **73**, 2487 (1951); W. Doering, M. Farber, and A. Sayigh, *ibid.*, **74**, 4379 (1952).

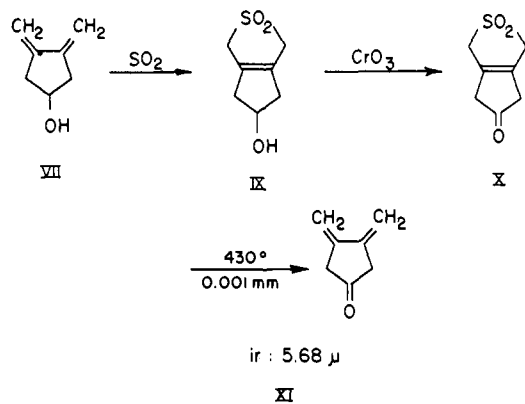


four-proton multiplet at 7.4. The diamide IV was reduced with lithium aluminum hydride to the diamino alcohol V; nmr ( $\text{CCl}_4$ ) one-proton singlet at  $\tau$  5.2, one-proton broad single peak at 5.8, twelve-proton methyl singlet at 7.8, broad ten-proton aliphatic multiplet at 7.6–8.8. Treatment of the diamino alcohol V with 30% hydrogen peroxide yielded the bis(amine oxide) VI which was pyrolyzed at  $170^\circ$  (0.001 mm) to the very unstable 3,4-dimethylenecyclopentanol (VII);<sup>10</sup> nmr ( $\text{CCl}_4$ ) two-proton exocyclic methylene multiplet at  $\tau$  4.7, three-proton exocyclic methylene and hydroxyl multiplet at 5.1, one-proton quintuplet ( $J = 5$  cps) corresponding to the hydrogen adjacent to the hydroxyl group at 5.8, and four-proton aliphatic multiplet at 7.0, in 70% yield. An attempted oxidation of this alcohol using dicyclohexylcarbodiimide–dimethyl sulfoxide<sup>11</sup> yielded only the rearranged ketone VIII: ir ( $\text{CCl}_4$ ) carbonyl at 5.8, double bonds at 5.92, 6.1, and  $11.2\ \mu$ ; nmr ( $\text{CCl}_4$ ) one-proton vinyl singlet at  $\tau$  3.9, two-proton exocyclic methylene at 4.65 and 4.8, aliphatic methylene at 7.1, and methyl group at 7.8; uv (isohexane)  $\lambda_{\text{max}}$   $260\ \text{m}\mu$  ( $\epsilon$  14,000) with shoulders at  $250$  ( $\epsilon$  12,800) and  $270\ \text{m}\mu$  ( $\epsilon$  10,000). Thus, the dimethylenecyclopentanol was allowed to react with sulfur dioxide<sup>10</sup> yielding the crystalline sulfone alcohol IX; ir ( $\text{CHCl}_3$ ) hydroxyl at 2.7 and sulfone bands at 7.6 and  $8.5\ \mu$ ; nmr ( $\text{CDCl}_3$ ) one-proton septet at  $\tau$  5.3 ( $J_{\text{cis}} = 3$ ,  $J_{\text{trans}} = 6$  cps) corresponding to the hydrogen adjacent to the hydroxyl, four-proton multiplet at 6.2 due to the sulfone protons,

(10) Cf. A. T. Blomquist, J. Walmsky, Y. C. Meinwald, and D. T. Langone, *J. Am. Chem. Soc.*, **78**, 6057 (1956), who first prepared and studied the reactivity of 1,2-dimethylenecyclopentane.

(11) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5661 (1965). The experimental procedure used in this reaction was that described in P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967), for the oxidation of 3-methylenecyclobutanol. The latter reaction did not require an aqueous work-up, whereas in the present instance an aqueous work-up is necessary in order to remove the dimethyl sulfoxide. The use of water is presumed responsible for the isomerization of the ketone.

and five-proton multiplet at 7.3 due to the aliphatic and hydroxyl hydrogens. This was readily oxidized under Jones conditions to the  $\beta,\gamma$ -unsaturated ketone X: ir ( $\text{CHCl}_3$ ) carbonyl at 5.67, sulfone bands at 7.7 and  $8.6\ \mu$ ; nmr ( $\text{CDCl}_3$ ) four-proton sulfone multiplet at  $\tau$  6.1 and four-proton cyclopentenone multiplet at 6.9. Pyrolysis at  $430^\circ$  (0.001 mm) then yielded the desired 3,4-dimethylenecyclopentanone (XI): ir ( $\text{CCl}_4$ ) carbonyl at 5.68, exocyclic methylene at  $11.2\ \mu$ ; nmr ( $\text{CCl}_4$ ) two-proton exocyclic methylene triplet ( $J = 2$  cps) at  $\tau$  4.4, two-proton narrow exocyclic methylene



multiplet at 5.0, and four-proton aliphatic multiplet at 6.9; uv (isohexane)  $\lambda_{\text{max}}$   $255\ \text{m}\mu$  ( $\epsilon$  5500) containing less than 1% of the conjugated ketone (VIII). Photolysis of this material at the boiling point of liquid nitrogen with light of wavelength 270–300  $\text{m}\mu$  yielded an epr spectrum consisting only of a single very broad line. No evidence for the presence of a triplet-state molecule could be found here.<sup>12</sup> This result was inconclusive since the possibility still remained that the triplet spectrum was present but obscured by the presence of a strongly absorbing monoradical. If one assumes that the broadness of the observed single line is due, in part, to hyperfine interaction with the protons of the substrate, then the situation should be subject to improvement and the line narrowed by the substitution of deuterium for hydrogen on the starting ketone. This was accomplished by exchange (pyridine– $\text{D}_2\text{O}$ )<sup>13</sup> at the cyclopentanonedicarboxamide (IV) stage followed by reduction with lithium aluminum deuteride to the  $d_9$ -diamino alcohol XII. From this point the synthesis was carried out as outlined above, leading ultimately to 3,4-dimethylenecyclopentanone- $d_8$  (XIII) (Figure 1).

Photolysis of the perdeuterated ketone XIII led to the spectrum shown in Figure 1 in which it was now possible to discern the elements of the desired triplet spectrum. The experimental  $D$  value obtained from the spectrum is  $0.012\ \text{cm}^{-1}$ . One may calculate, on the basis of simple Hückel molecular orbital theory, a value of  $0.030\ \text{cm}^{-1}$  for (planar) tetramethyleneethane.<sup>14</sup>

This is a relatively unstable species as indicated by its half-life at the boiling point of liquid nitrogen of *ca.* 20 min. Thus, the spectrum shown in Figure 1 is the strongest which is presently available and was obtained while irradiating continuously at 290–310  $\text{m}\mu$  and ob-

(12) The same result was obtained from the irradiation of 1,2-dimethylenecyclobutane at low temperature.

(13) J. E. Baldwin and R. G. Pudussery, *Chem. Commun.*, 408 (1968).

(14) The integrals used here were those of M. Godfrey, C. W. Kern, and M. Karplus, *J. Chem. Phys.*, **44**, 4459 (1966). The author is indebted to Professor Martin Karplus for helpful discussion on this calculation.

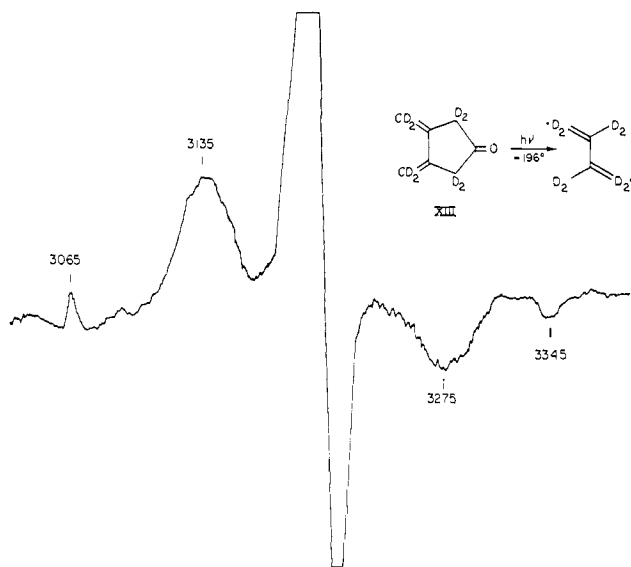


Figure 1. Epr spectrum of tetramethyleneethane- $d_8$ .

servicing the epr spectrum simultaneously. The instability of the molecule may also be responsible for the lack of resolution of the  $x,y$  lines whose presence is indicated by the broadness of the inner two lines. The central line is a distinct, more stable radical as indicated by the fact that the intensity of this line is undiminished on standing for a period of time at  $-196^\circ$ .

The above results constitute the first direct observation of a 1,4 diradical by physical means.<sup>15</sup> Efforts to trap this species chemically are currently in progress.

**Acknowledgment.** This work was generously supported by the National Science Foundation (Grant No. GP 6667).

(15) Strong evidence for the intermediacy of 1,4 diradicals in cycloaddition reactions has been presented by P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964). See also subsequent papers in that series.

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Received January 5, 1970

### Stereochemically Nonrigid Six-Coordinate Hydrides

Sir:

We report the first unambiguous example of stereochemically nonrigid behavior in six-coordinate complexes. Barriers to intramolecular rearrangement in such complexes are usually relatively high<sup>1</sup> as exemplified by  $C_6H_5SF_5$  whose  $AB_4$   $^{19}F$  nmr spectrum we find is unaltered at  $215^\circ$ .

Rapid intramolecular rearrangements have been established for  $H_2Fe[P(OC_2H_5)_4]_2$  (1) and  $H_2Fe[C_6H_5-P(OEt)_2]_4$  (2) by analysis of the temperature-dependent  $^{31}P$  and  $^1H$  nmr spectra. The 220-MHz  $^1H$  nmr spectra at  $-50^\circ$  for the hydride regions of complexes 1 and 2 are shown in Figure 1, together with spectra simulated on a Calcomp plotter. Spectra for both compounds

(1) E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968), and references therein.

(2) W. Kruse and R. H. Atalla [*Chem. Commun.*, 921 (1968)] incorrectly assign a distorted *trans* ground-state structure (see Figure 3).

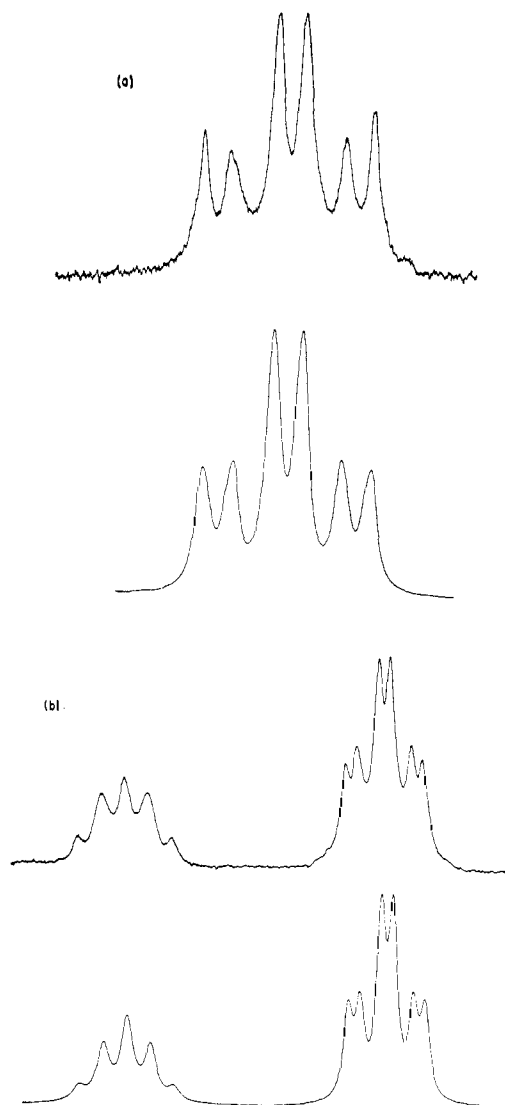


Figure 1. Observed and simulated 220-MHz  $^1H$  nmr spectra of hydride region of complex 1 (a) and complex 2 (b) ( $-50^\circ$ ).

show pronounced line-shape effects as the temperature is increased, and at  $+50^\circ$  both give rise to simple quintet resonances. Similarly, the 40.5-MHz  $^{31}P$  nmr spectra of compound 2 at low temperatures with and without proton noise decoupling are shown in Figure 2. The  $^{31}P$  nmr spectra for both complexes at  $+50^\circ$  show a simple triplet structure with the same splitting as the high-temperature proton quintets. Nuclear resonance data are given in Table I.

Averaging of nuclear environments and retention of H-P spin-spin coupling at the high temperatures operationally defines these molecules as stereochemically nonrigid. Consistently, the temperature-dependent hydride spectra are invariant to concentration changes and to addition of free phosphite. Also the high-temperature apparent coupling constants are equal to the average of the assigned low-temperature coupling constants.

At high temperatures the molecules are nonrigid and the four phosphorus atoms appear magnetically equivalent. As the temperature is lowered, specific *cis* and *trans* forms become apparent. For compound 2, the two isomers have similar energies at  $-50^\circ$ . One isomer is clearly the *trans* dihydride (Figure 3) with a sym-