of the by-product, $Et_3NH^+ ClO_4^-$, with ether followed by vacuum distillation: yellow liquid; bp 84° (0.2 mm); ir 5.52 μ; nmr δ 1.40 (s, 9), 6.38–7.15 (m, 4); mass spectrum, P 175.0999 (calcd 175.0997) (*Anal.* Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.59; H, 7.38). To our knowledge VIIId is the first isolated benzoazetinone, though definitive spectroscopic and chemical evidence for the intermediacy of the *N*-phenyl derivative in the photolysis of benzotriazinones has been published[12] and a similar photochemical experiment has produced *N*-phenylnaphtho[2,3-*b*]azetinone.[13]

We believe that the reaction of Et_3N with I begins not with the usual nucleophilic addition but instead with proton abstraction at C_3 and concerted ring scission to the iminoketene (VII) which subsequently cyclizes to VIII. The ring opening has precedent in the reactions of 3-unsubstituted isoxazolium[14] and benzisoxazolium salts[15] with nucleophiles, but the ketoketenimines generated from the former do not close to the cyclic iminoethers, even when constrained in an s-cis conformation,[14] whereas the intermediates generated from the latter system are too reactive for structural characterization.[15,16]

It is not yet known whether the formation of III from VIII involves attack of the nucleophile at the carbonyl of VIII or at the electrophilic carbon of VII, possibly present as a minor equilibrium component in solution. Also, although the adduct II can be excluded (reaction rate, temperature data) as an intermediate on the pathway from VIII to III, it is not yet clear whether the rearrangement, II → III, always proceeds by a direct route or sometimes involves a reversion to I (X = R′), followed by generation of VIII (*i.e.*, II $\rightleftharpoons$ I (X = R′) → VII and VIII + R′H → III), but experiments designed to solve these problems are under way. The intriguing question of the relationship between VIII and benzocyclobutadiene (is VIII an amide with significant amide resonance stabilization or is it an amino ketone?) has not yet been answered, but further chemical studies are in progress as are attempts to prepare a crystalline analog of VIIId which would allow the resolution of this issue by X-ray crystallography.[17]

Acknowledgment. We are grateful to the U. S. Public Health Service for a grant (GM-13980) to support this research.

[12] E. M. Burgess and G. Milne, *Tetrahedron Lett.*, 93 (1966); G. Ege, *Chem. Ber.*, **101**, 3079 (1968); G. Ege and F. Pasedach, *ibid.*, **101**, 3089 (1968).

[13] G. Ege and E. Beisiegel, *Angew. Chem., Int. Ed. Engl.*, **7**, 303 (1968).

[14] R. B. Woodward and R. A. Olofson, *Tetrahedron Suppl.*, No. 7, 415 (1966); R. A. Olofson and Y. L. Marino, *Tetrahedron*, **26**, 1779 (1970), and references therein

[15] D. S. Kemp and R. B. Woodward, *ibid.*, **21**, 3019 (1965); D. S. Kemp, *ibid.*, **23**, 2001 (1967).

[16] This statement is also true for *N*-*tert*-butylbenzisoxazolium ClO_4^-, mp 165–166°.

[17] Here just the angle of the N–R bond with the plane of the ring system (is stereochemistry at N trigonal or pyramidal?) should provide a first level answer.

* Address correspondence to this author at The Pennsylvania State University.

R. A. Olofson,* Robert K. Vander Meer, Stamoulis Stournas
Chemistry Department, The Pennsylvania State University
University Park, Pennsylvania 16802
Chemistry Department, Harvard University
Cambridge, Massachusetts 02138

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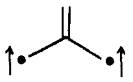
2-Isopropylidenecyclopentane-1,3-diyl. Preparation, Properties, and Reactions of a Distorted Trimethylenemethane. Direct Evidence for a Triplet Reaction[1]

Sir:

Dowd's work[2] has shown that the unsubstituted trimethylenemethane molecule (**1**) has a triplet ground state. It is a plausible and widely held[3a] but so far unproven assumption that this species is an intermediate in the formation of the dimeric product, 1,4-dimethylenecyclohexane. An unsymmetrically substituted trimethylenemethane (**2**) provides the means to test the effect of symmetry on the ordering of the singlet and triplet energy levels. Moreover, because dimerization is expected to lead to mixtures resulting from four modes of combination (aa + aa, ab + ab, ab + ba, aa + ab), the product composition can be used to test the postulate that various methods of generation of the species lead to a common intermediate. The present study of 2-isopropylidenecyclopentane-1,3-diyl (**3**) bears on these two problems. It also provides direct evidence that at least part of the dimeric products from **3** arise from reactions of a triplet species.



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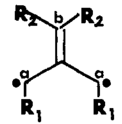

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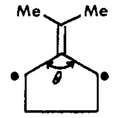
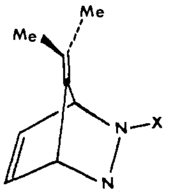
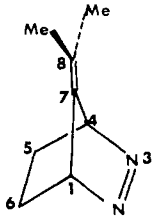


3

Dimethyl azodicarboxylate and 6,6-dimethylfulvene in 1:1 ether–pentane at 0° react to give 96% of adduct **4**,[4] mp 100–101°, which by successive selective hydrogenation[4] of the endocyclic double bond (10% Pd/C, EtOAc), saponification (KOH, aqueous EtOH), oxidation (HgO), and sublimation (40° (<0.1 mm)) is converted in 65% yield to the azo compound **5**, an unstable white solid: nmr ($CDCl_3$) τ 4.63 (2 H, broad q, J = 1.5 Hz, H_1, H_4), 8.3–9.0 (4 H, m, H_5, H_6), 8.37 (6 H, s, Me).



4: X = CO_2Me



5

Pyrolyses of azo compound **5** in sealed tubes in the gas phase (80°, 2 hr, naphthalene internal standard) give four hydrocarbon products (dimers of **3**) in total yields that increase from 68 ± 4% at an initial pressure

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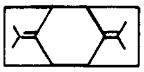
[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We are also grateful to the National Science Foundation (GP-11017X) and the National Institute of General Medical Sciences (GM 15166) for partial support.

[2] (a) P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966); (b) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967); (c) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

[3] (a) For a review, see F. Weiss, *Quart. Rev., Chem. Soc.*, **24**, 278 (1970). (b) See the additional pertinent observations of G. Köbrich and H. Heinemann, *Chem. Commun.*, 493 (1969). We thank Professor H. R. Ward for this reference.

[4] J. J. Tufariello and J. J. Spadaro, Jr., *Tetrahedron Lett.*, 3935 (1969).

of 1.1 atm to 103 ± 4% at 1.2 × 10^{-3} atm. The dimers, separated by preparative vapor chromatography on a Varian FFAP column, each have elemental compositions and mass spectra consistent with $C_{16}H_{24}$. The nmr spectra show that one of them, **6**, has no vinylic protons, one, **7**, has one, and two, **8** and **9**, each have two. Other features of the spectra confirm the assigned gross structures, although the stereochemical details presently are not known.



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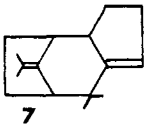

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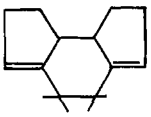

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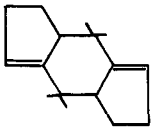

9

Photolysis of 1–2% ether solutions of azo compound **5** (0°, Hanovia lamp, Pyrex filter) gives the same four dimeric hydrocarbons **6–9** in yields of 75–85%.

Generation of dimethylvinylidene (**10**) or its equivalent[5] by the action of lithium β-ethoxyethoxide on (a) 0.05 and (b) 1.2 *M* solutions of *N*-nitroso-5,5-dimethyloxazolidone (**11**) in refluxing cyclobutene[6] leads to a complex mixture of products, but among these are the same four dimers **6–9**, formed in yields of 2.7 and 4.9% from a and b, respectively, and isolated for spectroscopic identification by vpc. The simplest pathway for dimer formation would involve initial carbenoid addition to give 5-isopropylidenebicyclo-[2.1.0]pentane (**12**) followed by rupture of the bridge bond to give the diyl **3**.

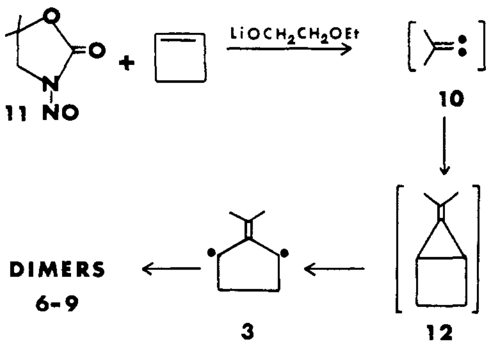

Table I shows that within experimental error, the distribution of dimeric products **6–9** formed by the three described methods is identical. This is a necessary but insufficient condition for the intervention of a common intermediate.

When a 1 *M* solution of azo compound **5** in perfluoro(methylcyclohexane) is degassed at 10^{-6} mm and irradiated for 3 hr at 77°K with a 200-W Hg lamp in the cavity of a Varian electron spin resonance (esr) spectrometer, a triplet spectrum[7a] attributable to **3** appears. This consists of a strong six-line absorption centered near 3250 G and a weak absorption due to the half-field ($\Delta m = 2$) transition near 1625 G. The zero-field splitting parameters for **3**, $D = 0.027$ cm^{-1} and $E = 0.0023$ cm^{-1}, are to be contrasted with those for trimethylenemethane itself, **1**, which shows $D = 0.024$ cm^{-1} and $E = 0$. The nonzero value for the parameter E of **3** is reasonably ascribed to distortion of the π-electron system from the D_{3h} symmetry of **1** to C_{2v} symmetry. On the simplifying assumptions that the spatial part of the total wave function for **3** can be acceptably constructed from Hückel molecular orbitals and that despite the angular distortion, the orbital coefficients do not differ from those calculated for **1**, the observed E value for **3** is consistent with an internal angle θ of about 108°. A reasonably close model for the geometry of a five-membered ring with three contiguous trigonal carbons is acenaphthene, for which the corresponding angle is 112.4°.[7]

Table I. Composition of Dimeric Hydrocarbon Products from Three Different Methods of Generation of 2-Isopropylidenecyclopentane-1,3-diyl (**3**)

Reaction	Rel yield, %[a]			
	6	**7**	**8**[f]	**9**[f]
Pyrolysis of azo compd **5**[b]	22	43	20	14
Photolysis of azo compd **5**[c]	22	45	19	15
Cyclobutene + **11**[d]	22	44	19	15
"Statistical"[e]	11	45	22	22

[a] All values are based upon duplicate or multiple vpc analyses on a Ucon capillary column at 120° and are estimated to be accurate to ±1%. [b] In the vapor phase at 80° and at 0.1 atm initial pressure. The product composition from pyrolysis of a neat liquid sample, although not carefully analyzed, was similar. [c] In ether solution at 0°. [d] In excess of refluxing cyclobutene. [e] Disregarding stereochemistry. [f] The assignments of structure to **8** and **9** are presently somewhat arbitrary and could be reversed without affecting the argument.

There remains the question whether the common intermediate(s) implied by the dimerization results involves the same entity as the triplet species observed in the esr spectrum. *A priori*, dimerization might involve the combination of two triplets, of two singlets, or of a singlet and a triplet.

Evidence on this point is provided by scans of the nmr spectrum of the product mixture during the first 1–2 min after insertion of a tube containing a solution of azo compound **5** in *m*-dichlorobenzene into the preheated probe of a Varian A-60 spectrometer. In several runs conducted at temperatures between 63.5 and 112°, strong nuclear polarization emission signals appear at positions corresponding to those of nonpolarized absorption lines of the product dimers. The spectra permit identification of emission lines for nearly all the product protons, including not only those at carbons directly involved in the dimerization but also many of those at other sites. Enhanced absorption lines are not observed.

According to recent theory,[8] a one-step reaction between two trimethylenemethane triplets can give product with a nuclear polarization spectrum, but the corresponding singlet–singlet combination cannot. If

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(5) *Cf.* M. S. Newman and A. O. M. Okarodudu, *J. Amer. Chem. Soc.*, **90**, 4189 (1968); *J. Org. Chem.*, **34**, 1220 (1969); M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **91**, 6461 (1969).

(6) We thank Mr. G. B. Ellison for a generous sample of this substance.

(7) (a) *Cf.* E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964); (b) H. W. W. Erlich, *Acta Crystallogr.*, **10**, 699 (1957).

(8) See the accompanying paper by G. L. Closs, *J. Amer. Chem. Soc.*, **93**, 1546 (1971).

the reaction occurs in two steps, the singlet–triplet combination can give polarized product as a result of triplet–singlet transitions in the intermediate diradical. In either case, however, the part of the dimerization that leads to polarized product must involve at least one triplet reaction partner.

Acknowledgment. We thank Professor G. L. Closs for an advance copy of his paper and for instructive comments on the nuclear polarization spectra.

[9] Supported by a NATO Research Fellowship administered by the Science Research Council of Great Britain, 1969–1970.

[10] Proctor and Gamble Fellow, 1969–1970; IBM Fellow, 1970–1971.

Jerome A. Berson,* Richard J. Bushby[9]
J. Michael McBride, Michael Tremelling[10]
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received December 31, 1970

On the Origin of Nuclear Spin Polarization in Triplet Dimerizations[1]

Sir:

Recently Berson, *et al.*,[2] observed chemically induced dynamic nuclear spin polarization (CIDNP) in the dimers derived from trimethylenemethane derivatives. Since the monomers are known to have triplet ground states,[2,3] it appeared of interest to examine whether the previously proposed radical-pair model of CIDNP[4] can be extended to cover triplet reactions.

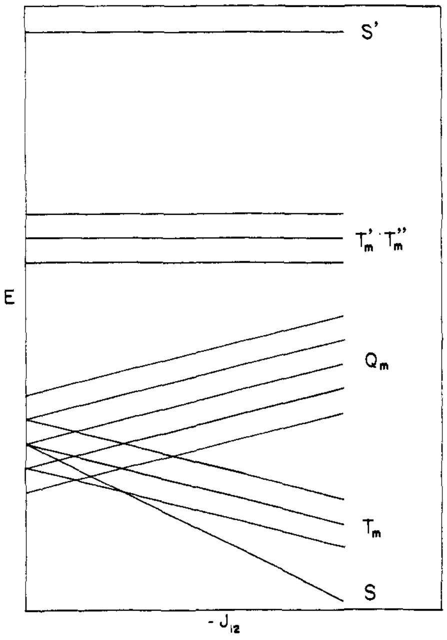

Figure 1. Eigenvalues of $\mathcal{H}_0$ as function of J_{12}. Note: to conserve space, J, given by the separation of T_0' from S' and S at J_{12} = 0, has been made unrealistically small compared to the Zeeman splitting.

A four-electron spin system with D_2 symmetry serves as a model for a *weakly* interacting pair of identical triplet molecules. A schematic representation is given in eq 1, where S_1,S_1' and S_2,S_2' represent the electron spins on components 1 and 2 of the triplet pair, respectively.[5] The scalar electron exchange coupling within each triplet molecule is denoted by J, while the intermolecular exchange coupling is given as J_{12}. The nuclei, $i,j, \ldots$ on component 1 with nuclear spins I_i, I_j, ... are coupled only to the electron spins S_1 and S_1' with the isotropic hyperfine coupling constants A_i, A_j, ..., whereas the corresponding coupling on component 2 is denoted with subscripts k, l, ... Neglecting the nuclear Zeeman term and all anisotropic interactions, the spin Hamiltonian describing the stationary system in a strong magnetic field may be formulated as $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{hyp}}$, where the first term describes the isotropic interactions of the electrons with the magnetic field and with themselves and the the second term represents the isotropic hyperfine interactions. For the case of $|J| \gg |J_{12}|$ these terms are given in units of $\hbar$ by

$$\begin{tikzcd}
 & & S_1 & & S_2 & & \\
I_i & A_i \arrow[l] \arrow[r] & J \arrow[u] \arrow[d] & J_{12} \arrow[l] \arrow[r] & J \arrow[u] \arrow[d] & A_k \arrow[l] \arrow[r] & I_k \\
 & & S_1' & & S_2' & &
\end{tikzcd} \qquad (1)$$

$$\mathcal{H}_0 = g\beta H_0 S_z - J(\mathbf{S}_1 \cdot \mathbf{S}_1' + \mathbf{S}_2 \cdot \mathbf{S}_2') - J_{12}(\mathbf{S}_1 + \mathbf{S}_1') \cdot (\mathbf{S}_2 + \mathbf{S}_2') \qquad (2)$$

$$\mathcal{H}_{\text{hyp}} = \sum_i A_i I_i (\mathbf{S}_1 + \mathbf{S}_1') + \sum_k A_k I_k (\mathbf{S}_2 + \mathbf{S}_2') \qquad (3)$$

where g and S_z are the isotropic g factor and the z component of electron spin of the triplet pair, respectively.

Of the 16 zero-order symmetrized electron spin functions,[6] 9 are derived from the combination of two triplet molecules and can be factored into a quintet, Q_m, a triplet, T_m, and a singlet, S. Two additional degenerate triplet states, T_m' and T_m'', originate from the two combinations of one triplet with one singlet molecule and the remaining singlet state S' is obtained from the combination of two singlet molecules. The symmetries and eigenvalues of these states are listed in Table I, and Figure 1 shows the energies as a function

Table I. Eigenstates of $\mathcal{H}_0$ for a Four-Electron System with D_2 Symmetry

$(\rho)_{S,m}$	Eigenvalue of $\mathcal{H}_0$	m
$(\mathfrak{A})_{2,m} \equiv Q_m$	$g\beta H_0 m - J/2 - J_{12}$	2, 1, ..., −2
$(B_1)_{1,m} \equiv T_m$	$g\beta H_0 m - J/2 + J_{12}$	1, 0, −1
$(B_2)_{1,m} \equiv T_m'$	$g\beta H_0 m + J/2$	1, 0, −1
$(B_3)_{1,m} \equiv T_m''$	$g\beta H_0 m + J/2$	1, 0, −7
$(\mathfrak{A})_0 \equiv S$	$- J/2 + 2J_{12}$	
$(\mathfrak{A})_0' \equiv S'$	$+ 3J/2$	

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[1] Supported by National Science Foundation Grant No. GP 18719X.

[2] J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Amer. Chem. Soc.*, **93**, 1544 (1971).

[3] P. Dowd, *ibid.*, **88**, 2587 (1966).

[4] (a) G. L. Closs, *ibid.*, **91**, 4552 (1969); (b) R. Kapstein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969); (c) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183, 2186, 7227 (1970); (d) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970); (e) H. Fischer, *Chem. Phys. Lett.*, **4**, 511 (1970).

[5] Instead of using a basis set of four $S = {}^1/_2$ functions, the problem can also be treated with a basis set of $S = 1$ and $S = 0$ functions.

[6] For a review of the procedure of symmetrization of basis vectors, see P. L. Corio, "Structure of High-Resolution NMR Spectra," Academic Press, New York, N. Y., 1966, Chapter 8.