are much less stable in acetonitrile. Although cathodic waves can be obtained for DPA on reversal in cyclic voltammetry,[8] coulometric oxidation in acetonitrile shows a decay of the current to a high steady value and rapid disappearance of the radical as it is stirred away from the electrode surface. This lack of stability of the cation radical may be the reason for the past differences in results of different workers[3-6] and the poorer correlation of voltammetric potential data with energy levels calculated by molecular orbital theory.

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Received January 7, 1967

A Radical-Induced γ Elimination[1]

Sir:

We wish to report the observation of a radical-induced γ elimination from a carbon skeleton. The reaction involves treatment of 1,3-diiodopropane with a peroxide and results in formation of cyclopropane in high yield.[2] The highest conversions to cyclopropane obtained with benzoyl peroxide and *t*-butyl peroxide were "100" and 90%, respectively. Results are summarized in Tables I and II.

Table I. Reaction of 1,3-Diiodopropane with Benzoyl Peroxide

	Reaction conditions[a]			
	79°, 20 hr	98°, 14 hr	116°, 3.2 hr	116°, 1.5 hr
Reactants, mmole[b]				
$ICH_2CH_2CH_2I$	0.432	0.435	0.361	0.310
$(PhCO_2)_2$[c]	0.438	0.435	0.368	0.448
Products, mmole[d,e]				
Cyclopropane	0.32	0.36	0.29	0.31
$CH_3CH_2CH_2I$	0.003	0.003	Trace	Trace
$PhCH_2CH_2CH_2I$	0.02	0.02	0.02	Trace
$ICH_2CH_2CH_2I$	0.12	0.08	0.07	...
PhI	0.68	0.74	0.62	0.62

[a] No significance should be attached to the reaction time with the exception that it is long enough so that no detectable reaction occurred on further heating. [b] In benzene as solvent. [c] No reaction occurred in the absence of peroxide. [d] Yields were estimated by use of nmr spectroscopy and gas chromatographic analysis. [e] In addition, we observed a very small amount of a material which had the same retention time as 3-iodopropyl benzoate.

Table II. Reaction of 1,3-Diiodopropane with *t*-Butyl Peroxide

	Reaction conditions[a]			
	133°, 14 hr	148°, 12 hr	169°, 80 min	169°, 50 min
Reactants, mmole[b]				
$ICH_2CH_2CH_2I$	0.412	0.419	0.423	0.420
$(t\text{-BuO})_2$[c]	0.431	0.437	0.437	0.655
Products, mmole[d]				
Cyclopropane	0.24	0.26	0.31	0.38
$CH_3CH{=}CH_2$	0.02	0.02	0.01	0.01
$CH_3CH_2CH_2I$	0.02	0.03	0.02	0.02
$PhCH_2CH_2CH_2I$	0.002	0.002	0.003	Trace
$ICH_2CH_2CH_2I$	0.11	0.09	0.08	...
CH_3I	0.63	0.62	0.69	0.83
CH_3COCH_3	0.64	0.69	0.71	1.07
$(CH_3)_3COH$[e]	0.21	...	0.09	0.17
$(CH_3)_2C{=}CH_2$[e]	0.043	0.14	0.025	0.004
PhI	0.007	0.007	0.007	0.006
$PhCH_3$	0.018	0.012	0.017	0.068

[a-d] See the corresponding footnotes to Table I. [e] The effect of reaction time on the isobutylene:*t*-butyl alcohol ratio was not studied.

Although the mechanism of the reaction has not been established, the possibilities which one may envision are all such that our observation is likely to provide the opportunity to study one or more previously unreported free-radical processes such as carbon radical displacement on carbon,[6] formation and reactions of 1,3-bridged halo radicals, concerted radical-induced γ elimination, and neighboring group assistance by a carbon radical site in a radical displacement on halogen. Information is available for only one of these processes, formation of cyclopropane and iodine from the γ-iodopropyl radical. Benson has estimated the reaction to be exothermic by a few tenths of a kilocalorie per mole.[8]

Irrespective of mechanistic questions, the synthetic potential of such a cyclization reaction is clear.[9]

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Received January 11, 1967

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[1] This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] In possibly related reactions, cyclopropane has been produced by gas-phase pyrolysis of 1,3-diiodopropane (20% yield),[3] sodium flame reaction of 1,3-dibromopropane (57–87% gaseous products),[4] and reaction of phenylmagnesium bromide–ferric chloride with 1,3-dibromopropane (81% yield), 1-bromo-3-chloropropane (76% yield), or 1-bromo-3-phenoxypropane (26% yield).[5]

[3] R. A. Ogg, Jr., and W. J. Priest, *J. Chem. Phys.*, **7**, 736 (1939).

[4] C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938).

[5] M. S. Kharasch, M. Weiner, W. Nudenberg, A. Bhattacharya, T.-I. Wang, and N. C. Yang, *J. Am. Chem. Soc.*, **83**, 3232 (1961).

(6) In connection with the question of whether the formation of the β-(iodomethyl)cyclohexyl radical and its decomposition to iodine and norcarane is involved in the photolytic reaction of methylene iodide and cyclohexene, Simmons has reported some unsuccessful attempts to observe such a displacement.[7]

(7) D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, **30**, 959 (1965).

(8) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961). It was assumed that $D(ICH_2CH_2CH_2\text{–}H) = D(CH_3CH_2CH_2\text{–}H)$, *i.e.*, that the γ-iodopropyl radical is not appreciably stabilized by iodine bridging.

(9) We have also found that cyclopentane can be produced by reaction of 1,5-diiodopentane with a peroxide and that 1,1-diphenylcyclopropane is produced when methylene iodide, 1,1-diphenylethylene, and a peroxide are allowed to react. Details will be reported later.

Stereospecific Conversion of *cis–trans* Isomeric Aziridines to Open-Chain Azomethine Ylides

Sir:

Woodward and Hoffmann[1] predicted for the thermal isomerization of cyclopropyl anion to allyl anion a *conrotatory* ring opening, while the photochemical ring cleavage should take a *disrotatory* course. Our results with the isoelectronic aziridine system offer the first verification of this prediction.

We reported recently[2] that dimethyl 1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (I) is in equilibrium above 100° with a small concentration of the azomethine

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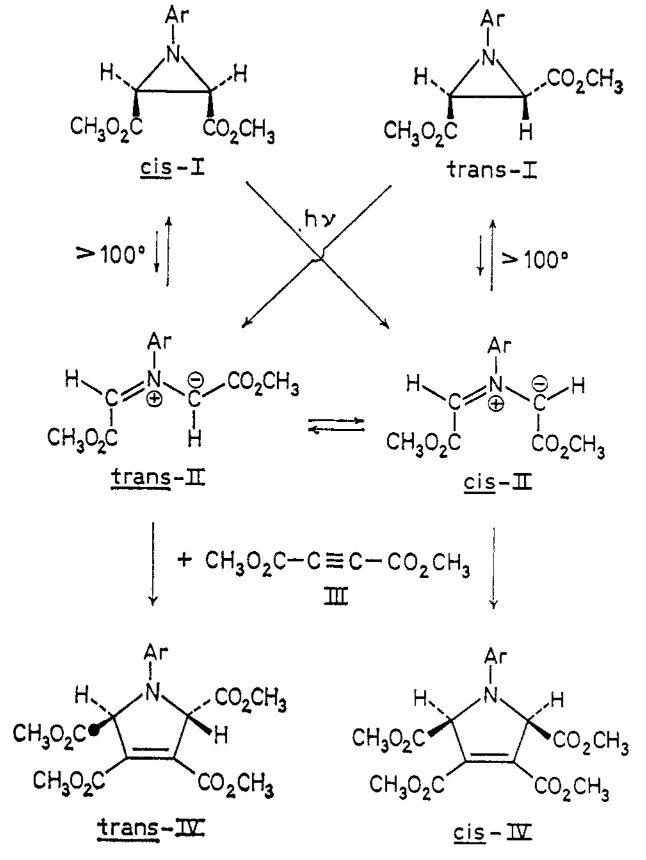
[1] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[2] R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *Tetrahedron Letters*, 397 (1966).

ylide II.[3] As a 1,3 dipole, II can be intercepted with suitable dipolarophiles to form five-membered rings.[4]

The separation of the *cis* and *trans* isomers of the dicarboxylic acid ester I was accomplished by thin-layer chromatography (2-mm layer, silica gel, Merck $PF_{254+366}$, benzene–ether, 85:15), giving *cis*-I, colorless, mp 76–78°; nmr (CCl_4):[5] two ring protons at τ 7.14 (s), two ester methyls at 6.25 (s), one ether methyl at 6.30 (s), four aromatic hydrogen at 3.21 (AB spectrum); *trans*-I, mp 66–67°; nmr (CCl_4): two *trans* ring protons at τ 6.69 (s), two ester methyls at 6.34 (s), one ether methyl at 6.28 (s), four aromatic hydrogens at 3.27 (s).[6] The structure assignment is based on the known influence of *cis,vic*- and *trans,vic*-CO_2CH_3 on the chemical shift of the ring protons and on the *cis–trans* ratio at equilibrium.



Ar = $-C_6H_4-OCH_3$ (4)

The thermal equilibration of *cis*- and *trans*-I in CCl_4 was followed by nmr at 100 and 120°. The equilibrium mixture was found to contain 20.0% *cis*-I at 100° and 21.5% at 120°; 10^5k_1 (100°) = 3.07 sec^{-1}; 10^6k_{-1} (100°) = 7.69 sec^{-1}; $\Delta H^{\neq}$(*cis* → *trans*) = 26 ± 3 kcal/mole. The stereoisomerization is assumed to take place *via cis*- and *trans*-II; it can easily be seen that two resonance structures contribute equally to the ground state of the azomethine ylides, *cis*- and *trans*-II.

The cycloaddition to dipolarophiles competes with the equilibration process. The more active the dipolarophile, the higher the stereoselectivity of the overall process. Only dialkyl azodicarboxylates, tetracyanoethylene, and dimethyl acetylenedicarboxylate (III) were found to be active enough to suppress completely the equilibration of *cis*- and *trans*-I; *i.e.*, *cis*- and *trans*-I combined with these dipolarophiles to yield diastereomeric cycloadducts without mutual admixture.

cis-I was heated with 10 equiv of III for 14 hr at 100°. After distillation of the excess dipolarophile, analysis by nmr revealed that the residue contained 98% tetramethyl 1-(4-methoxyphenyl)-3-pyrroline-2,3,4,5-tetracarboxylate (*trans*-IV), mp 140–141°. Dehydrogenation by chloranil in boiling xylene yielded 81% of 1-(4-methoxyphenyl)-pyrrole-2,3,4,5-tetracarboxylic acid tetramethyl ester, mp 110–112°, identical with an authentic specimen.[2] Only the 3-pyrroline structure is compatible with the nmr spectrum ($CDCl_3$) of *trans*-IV: τ 6.31 (s) for 2- and 5-CO_2CH_3, 6.16 (s) for 3- and 4-CO_2CH_3, 4.43 (s) for 2- and 5-H, 6.26 for ether methyl.

By the same procedure, *trans*-I was converted to the epimeric cycloadduct *cis*-IV, mp 132–133°, in 71% yield; nmr showed no contamination by *trans*-IV.[7] Nmr ($CDCl_3$) of *cis*-IV showed: τ 6.20 (s) for 2- and 5-CO_2CH_3, 6.12 (s) for 3- and 4-CO_2CH_3, 4.67 (s) for 2- and 5-H, 6.24 (s) for ether methyl. *cis*-IV was dehydrogenated by chloranil to the same pyrrole derivative (84%) that was obtained from *trans*-IV.

trans-IV possesses a twofold axis of symmetry, *cis*-IV a plane of symmetry. For obvious reasons, the chemical shift of the 2 and 5 protons in *cis*-IV is τ 0.24 higher than that in *trans*-IV (in benzene, $\Delta\tau$ 0.45). A similar phenomenon has been observed for the structurally unequivocal *cis,exo*- and *trans,exo*-cycloadducts of I to norbornene.[2] In the case of other pairs of *cis–trans* isomeric adducts of I, eight $\Delta\tau$ (*cis–trans*) for 2- and 5-H have been found to amount to τ 0.14–0.76. Thus, there is no doubt that *trans*-IV resulted from *cis*-I and III, while *cis*-IV originated solely from *trans*-I. Because 1,3-dipolar additions are known to proceed stereospecifically *cis*,[8] it must be the *conrotatory* ring opening I → II that is responsible for the over-all steric course.

Irradiation[9] of *trans*-I in III as solvent in a Jena glass apparatus for 24 hr at 10–15° effected a stereospecific conversion to *trans*-IV (40%),[7] corresponding to a photolytic *disrotatory* ring cleavage. The photolysis (quartz vessel, 3 hr) of *trans*-I in dioxane solution which contained 2% III yielded 69% *trans*-IV.[10]

The irradiation of *cis*-I, however, turned out to be less clear-cut. In III as solvent no photolysis took place; *cis*-I seems to be "in the shadow." In dioxane solutions of III, only part of *cis*-I was transformed to the cycloadduct IV by irradiation for 24 hr: % III in dioxane solution, 1.7, 7.8, 14.7, 30; % *cis*- + *trans*-IV, 78, 66, 41, *cis*-I unchanged; *cis*:*trans*, 53:47, 66:34, 71:29.

The trend to a higher percentage of *cis*-IV with increasing concentration of III pointed to a *photoreac-*

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(3) Other azomethine ylides: R. Huisgen, R. Grashey, and E. Steingruber, *Tetrahedron Letters*, 1441 (1963); R. Huisgen, H. Gotthardt, H. O. Bayer, and F. C. Schaefer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 136 (1964); H. Gotthardt, R. Huisgen, and F. C. Schaefer, *Tetrahedron Letters*, 487 (1964).

(4) Analogous cycloadditions of 1,2,3-triphenylaziridine: H. W. Heine, P. Peavy, and A. J. Durbetaki, *J. Org. Chem.*, **31**, 3924 (1966).

(5) Determined on a Varian A-60 spectrometer with TMS as internal standard; (s) denotes singlet.

(6) Satisfactory carbon, hydrogen, and nitrogen analyses have been obtained for all new compounds reported in this communication.

(7) The limit of nmr detection is 2–3%.

(8) Review: R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963).

(9) High-pressure mercury lamp (Q 81, Quarzlampen-Ges., Hanau).

(10) *cis*-IV and *trans*-IV turned out to be photostable.

tion[11] which competes with the 1,3-dipolar cycloaddition of *cis*-II with III. It was indeed shown that *cis*-I in dioxane (without III) was isomerized to 18% *trans*-I after 7 min of irradiation. On the other hand, *trans*-I in dioxane is slowly converted by irradiation to a mixture of diastereomeric dimers;[2] *cis*-I could not be detected. It may be justified to suppose that the photolysis of *cis*-I to *cis*-II is the eighth stereospecific process in the scheme, and that a secondary photoisomerization of *cis*-II becomes the more disturbing the lower the concentration of the dipolarophile III is.

[11] In the thermal reaction of *trans*-I with a 7.8% solution of III in boiling dioxane (24 hr), no lack of stereospecificity in the adduct formation was observed, although the same intermediate *cis*-II is involved. Nmr analysis disclosed 21% *trans*-I and 61% *cis*-IV, but no *trans*-IV. This rules out the possibility that the *thermal* isomerization *trans*-I → *cis*-I or *cis*-II → *trans*-II, respectively, is the cause of the nonstereospecificity of adduct formation in the photochemical reaction of *cis*-I.

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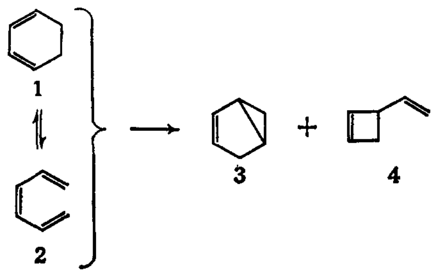
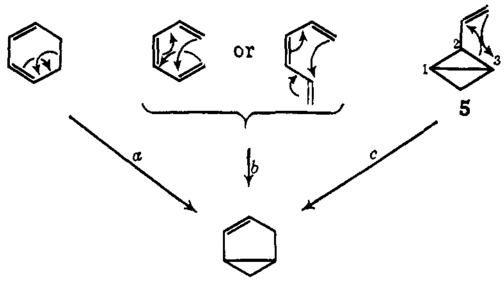
Studies on the Photochemistry of 1,3,5-Hexatrienes[1]

Sir:

Recently we reported that ultraviolet irradiation of 1,3-cyclohexadiene (**1**) leads initially to the formation of 1,3,5-hexatriene (**2**) and that extended irradiation yields a mixture (1:1) of bicyclo[3.1.0]hex-2-ene (**3**) and 3-vinylcyclobutene (**4**).[2] Many analogous photochemical bicyclo[3.1.0]hexene forming reactions have been reported.[3] These reactions have been discussed in terms of at least three mechanistic pathways: (1) a bond-switching process for cyclohexadiene (path a);[4] (2) an electrocyclic reaction of the hexatriene, formally analogous to an intramolecular Diels–Alder reaction (path b);[5] and (3) a vinylcyclopropane–cyclopentene rearrangement[6] of the hypothetical intermediate, 2-vinylbicyclo[1.1.0]butane (**5**) (path c).[5,7]

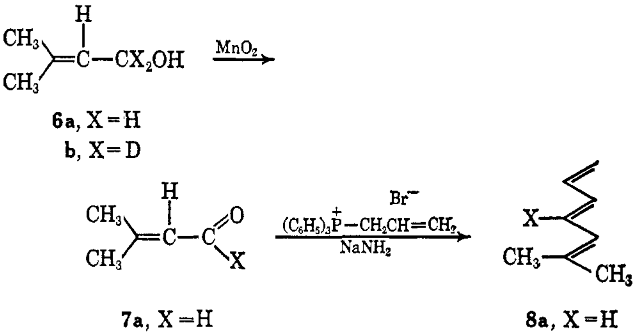

1
2
3
4

We wish to report the results of a tracer experiment which excludes the vinylbicyclo[1.1.0]butane hypothesis.



5

Our mechanistic study utilizes the fact that **5** has a plane of symmetry,[8] making C_1 and C_3 (*i.e.*, C_2 and C_3 of the original hexatriene) equivalent. Since this equivalence does not occur in paths a or b, photoisomerization of an appropriately labeled triene can provide mechanistic information. The triene chosen for this study was 6-methyl-1,3,5-heptatriene (**8**), prepared and characterized as described below.



6a, X = H
b, X = D
7a, X = H
b, X = D
8a, X = H
b, X = D

Reduction of methyl β-methylcrotonate with lithium aluminum hydride afforded 3-methyl-2-buten-1-ol[9] (**6a**), bp 77–79° (65 mm), in 73% yield.

Oxidation of **6a** with a 15:1 excess of manganese dioxide[10] gave β-methylcrotonaldehyde (**7a**), bp 72–76° (100 mm), in 52% yield. The infrared spectrum of **7a** showed maxima at 2900 (w), 2720 (w), 1670 (s), 1630 (w), 1440 (m), 1190 (m), 1120 (m), and 1040 (m) cm^{-1}. The nmr spectrum showed resonances at τ 8.29 and 8.09 (allylic methyl doublets, $J = 1.5$ cps), 4.5 (complex olefinic proton doublet), and 0.75 (aldehyde proton doublet, $J = 7$ cps). The mass spectrum showed its parent peak at m/e 84 with a strong peak at 83.[11]

Treatment of **7a** with the Wittig reagent prepared from allyltriphenylphosphonium bromide and sodamide afforded **8a** in 40% yield. The infrared spectrum of **8a** showed maxima at 2910 (m), 1800 (w), 1640 (w), 1620 (m), 1580 (w), 1440 (m), 1000 (s), 945 (m), and 895 (s) cm^{-1}. The nmr spectrum showed a broad methyl singlet at τ 8.25 and olefinic protons from 3.1 to 5.1 in the expected ratio of 1:1. The ultraviolet spectrum was typical of 1,3,5-hexatrienes,[12] showing $\lambda_{max}^{Et_2O}$ 261 mμ (ϵ 22,400), 269 (28,000), and 280 (25,000). The mass spectrum showed its parent peak at m/e 108.

Irradiation of **8a** gave a 27% yield of the expected 6,6-dimethylbicyclo[3.1.0]hex-2-ene (**9**) as the only important monomeric product. The structural assign-

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[1] The partial support of this research by the National Science Foundation is acknowledged with pleasure.

[2] J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **88**, 2850 (1966).

[3] For example, see R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

[4] R. J. Theis and R. E. Dessy, *J. Org. Chem.*, **31**, 4248 (1966).

[5] H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965).

[6] W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963), and references cited therein.

[7] For examples of the photochemical conversion of conjugated dienes to bicyclo[1.1.0]butanes, see W. G. Dauben, *Pure Appl. Chem.*, **9**, 539 (1964), and references cited therein.

[8] Only the *exo* isomer is shown. The same argument would apply to the *endo* isomer.

[9] H. Eggerer, *Chem. Ber.*, **94**, 174 (1961).

[10] R. J. Britter and T. J. Wallace, *J. Org. Chem.*, **24**, 1051 (1959).

[11] High voltage mass spectrum; ionizing potential = 70 v.

[12] G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **70**, 3394 (1948).