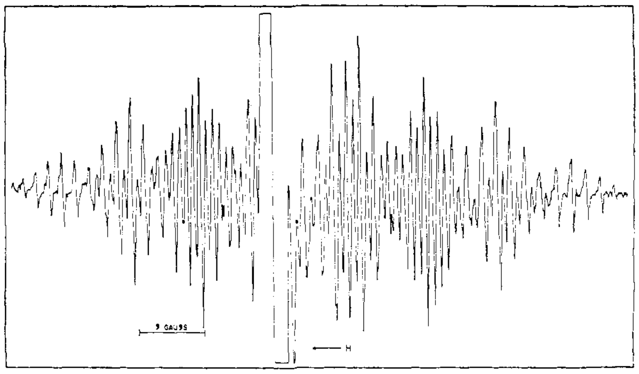

Figure 1. Esr spectrum of R_1, with that of E superimposed.

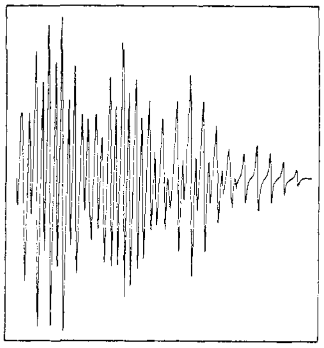

Figure 2. Calculated esr spectrum of Ia. Lines are assumed Lorentzian with a half-width of 0.15 gauss.

monia.[10,11] With further increase in current the spectrum of R_1 decreased in intensity, and that of a new radical, R_2 (superimposed by E), became visible, increased in intensity, and finally vanished, leaving only E. When the current was turned off E disappeared in 5 min and subsequently the signal of R_2 reappeared.

Table I. Esr Spectral Parameters of Ia

Position assignment[a]	No. of protons	Spin density, ρ_i[b]	Splitting constants a_i gauss This work	Ref 9
1,8	2	+ 0.194	5.24 ± 0.1[c]	6.7
2,7	2	+ 0.038[a]	1.02 ± 0.05	0.9
3,6	2	+ 0.194	5.24 ± 0.1[c]	4.5
4,5	2	+ 0.075[a]	2.04 ± 0.05	1.1
9a	1		4.80 ± 0.1	2.0
9b	1		12.00 ± 0.1	16.8

[a] Based on HMO and McLachlan calculations. [b] $\rho_i = a_i/\sum_1^8 a_i$. [c] The constants used to derive Figure 2 are 5.19 and 5.29 gauss. The intensities suggest that the two sets differ by an unresolved 0.1 gauss.

The spectrum of R_1 (Figure 1) is believed to be that of the cyclononatetraene anion radical (Ia). A set of coupling constants that account for the spectrum is recorded in Table I, and the spectrum calculated shown in Figure 2.

The radical R_2 was identified as the methylcyclooctatetraene anion radical by the similarity of its esr spectrum and spectral parameters, $a_1 = 1.42 \pm 0.05$ gauss (4 H), $a_2 = 5.03 \pm 0.05$ (3 H), $a_3 = 5.51 \pm 0.05$ (3 H), with those reported: 1.6 gauss (4 H), 4.8 (3H), 5.1 (3H).[12] For R_1, $Q = \sum_1^8 a_i = 27.1$ gauss, similar to the 26.26 found for $C_7H_8\cdot^-$[6]. The spin densities, ρ_i ($i = 1, \ldots, 8$), evaluated[13] as a_i/Q, are given in the table. The dissimilarity in the splittings a_i ($i = 1, \ldots, 8$) does not provide a strong basis for believing that the electronic structure of Ia resembles that of the cyclooctatetraene anion radical.

The spectrum of R_1 implies that reduction is accompanied by valence tautomerism, for otherwise the olefin proton couplings would have been similar to those in cycloheptatriene (7.64, 0.59, 4.90 gauss),[6] and coupling to the distant C_9 protons a magnitude smaller.[7,14,15] But all the carbons do not lie in one plane because the two C_9 protons are not equivalent. If the hyperfine splittings of these two have as their origin a hyperconjugative interaction of the C–H bonds with adjacent 2p orbitals, then the dihedral angles subtended by the plane containing H_9, C_9, and C_8 and that containing C_9 and the axis of the 2p orbital on C_8 might be estimated as $\cos^{-1} [a_9/(40)(4)\rho_8]^{1/2}$,[5,7,16] or 52 and 67° for H_{9a} ahd H_{9b}. Since the dihedral angle between the planes H_{9a}–C_9–C_8 and H_{9b}–C_9–C_8 must be approximately 120° (for sp^3 hybridization), the two C–H bonds at C_9 presumably flank the adjacent 2p orbitals as in III.

The formation of methylcyclooctatetraene anion radical may have its origin in the reduction of Ia to Ib, isomerization to methylcyclooctatetraene dianion, and loss of an electron to the solvent to yield the corresponding anion radial.

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[12] A. Carrington and P. F. Todd, *Mol. Phys.*, **7**, 533 (1964).

[13] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958); A. D. McLachlan, H. H. Dearman, and R. Lefebvre, *ibid.*, **33**, 65 (1960).

[14] E. Strom, G. A. Russell, and R. D. Stephens, *J. Phys. Chem.*, **69**, 2131 (1965).

[15] But long-range splittings are known: (a) G. A. Russell and K. Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965); (b) G. A. Russell, K. Y. Chang, and C. W. Jefford, *ibid.*, **87**, 4383 (1965).

[16] (a) S. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, **41**, 994 (1964); (b) J. R. Morton, *ibid.*, **41**, 2956 (1964); (c) C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960); (d) G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 774 (1964); (e) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Wiener, *ibid.*, **88**, 1998 (1966); (f) K. Morokuma and K. Fukui, *Bull. Chem. Soc. Japan*, **36**, 534 (1963).

[17] We thank the National Institutes of Health and the Alfred P. Sloan Foundation for support and J. C. Carnahan, Jr., for assistance.

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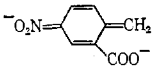
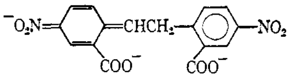
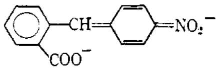
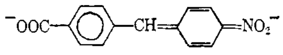
New Photochromic Compounds with *p*-Nitrobenzyl Structures

Sir:

Four new photochromic compounds are described in Table I. They each contain an aromatic nitro group only in the position *para* to an alkyl substituent. Previously, only nitrobenzyl derivatives containing *o*-

Table I. Photochromic Compounds in Aqueous Base

Compound	Unexposed solutions $\lambda_{\max}$, mμ	Transient species from ultraviolet photolysis[a]		
		Possible *aci*-nitro structure	$\lambda_{\max}$,[b] mμ	τ at pH 7,[c] sec
5-Nitro-*o*-toluic acid (I)	284		362	7.8
4,4′-Dinitrobibenzyl-2,2′-dicarboxylic acid (II)	286		372	65
2-(4-Nitrobenzyl)benzoic acid (III)	287		400	0.44
4-(4-Nitrobenzyl)benzoic acid (IV)	283		425	75

[a] Xenon flash lamp exposures filtered with Corning CS 7-54 filter. [b] From photolyses in the pH range 10–12. [c] Measured with 2 × 10^{-5} *M* solutions, near 25°, in phosphate buffer, outgassed on a vacuum line. The lifetime $\tau = 1/k_{app}$, where k_{app} is the apparent first-order rate constant at pH 7.

nitro groups had been found to be photochromic.[1-4] The new photochromic reactions occur most readily with *p*-nitrobenzyl structures also containing a carboxylate ion *ortho* to the alkyl substituent. As indicated in Table I, this reaction occurs with the *p*-nitro group and the *o*-carboxylate ion either on the same or on different aromatic rings.

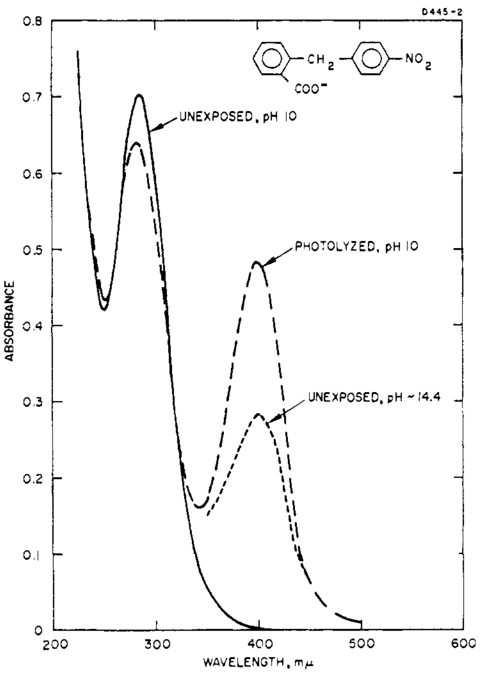


Figure 1. Photochromism of 2-(4-nitrobenzyl)benzoate ion. (Using 7 × 10^{-5}*M* nitrogen-bubbled solutions. Photolyzed in pH 10.0 buffer with a 366-mμ source, then spectrum recorded with a fast scan on a Cary 14. High pH spectrum recorded 30 min after making an unbuffered solution 2.5 *M* in NaOH).

Our observations are in general consistent with an over-all reaction process of the type

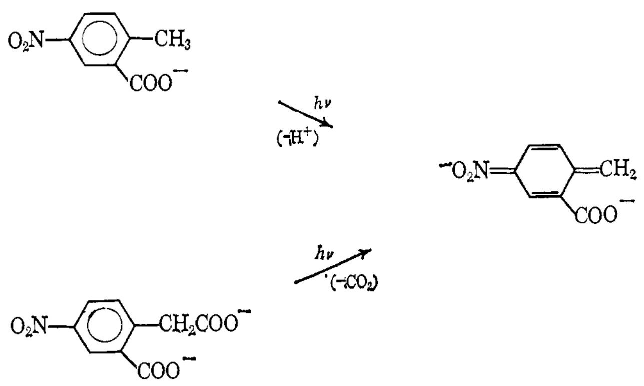
$$\text{nitro} \underset{}{\overset{h\nu}{\rightleftharpoons}} aci\text{-nitro}^- + H^+$$

The spectra of the transients from photolysis of compounds III and IV in dilute base are nearly identical with the spectra obtained from these compounds, without ultraviolet exposure, in the presence of a high concentration of hydroxyl ions (pH >14). Such a comparison is shown in Figure 1. This is interpreted as evidence that the same *aci*-anion species is formed by the photolysis reaction as is formed by the following reaction of strong base with the ground state of the nitro compound.

$$\text{nitro} + OH^- \rightleftharpoons aci\text{-nitro}^- + H_2O$$

Photolysis of the carboxylate ions of I, II, III, and IV in unbuffered solutions results in temporary increases in acidity. Conversely, the lifetime of the photolysis transients decreases with increased acidity of the solutions. The lifetimes in Table I pertain only to pH 7; they are shorter at lower pH's and longer at higher pH's. This behavior is consistent with the photolysis mechanism given above.

The transient observed from photolysis of I in base has the same spectrum and lifetime as a transient intermediate observed in the photodecarboxylation of 4-nitrohomophthalate ions.[5] Presumably the same transient *aci*-nitro structure is formed by two different photolysis mechanisms.



The photochromic reactions are strongly dependent upon the structure of the compounds. Thus, flash photolysis of matched solutions of III and IV produces only 4% as much absorption due to a transient species

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(1) R. Hardwick, H. S. Mosher, and P. Passailaigne, *Trans. Faraday Soc.*, **56**, 44 (1960).

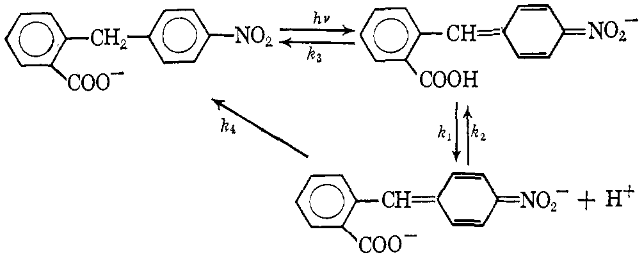
(2) J. D. Margerum, L. J. Miller, E. Saito, M. S. Brown, H. S. Mosher, and R. Hardwick, *J. Phys. Chem.*, **66**, 2434 (1962).

(3) G. Wettermark, *Nature*, **194**, 677 (1962).

(4) A. L. Bluhm, J. Weinstein, and J. A. Sousa, *J. Org. Chem.*, **28**, 1989 (1963).

(5) J. D. Margerum, *J. Am. Chem. Soc.*, **87**, 3772 (1965).

from the *p*-carboxylate structure (IV) as from the *o*-carboxylate structure (III). Also, the undissociated carboxylic acid form of III yields very little transient species compared to the carboxylate ion form; photolysis at pH 2 yields only about 1% as much transient absorption as is formed at pH 7 or greater. These observations indicate that the photochromic reaction is probably favored by an intramolecular reaction mechanism in which a six-membered ring pathway facilitates hydrogen transfer[6] from the methylene group to the carboxylate ion and then into solution.



In O_2-free solutions the kinetics of the decay of the transient species from III is consistent with this mechanism over seven orders of magnitude (milliseconds to hours) in the pH range 3 to 11. If values typical[7] of aromatic carboxylic acids are assumed for k_1 and k_2, then $K = k_1/k_2 \cong 10^{-4}$, where $k_1 \cong 5 \times 10^6$ sec^{-1} and $k_2 \cong 5 \times 10^{10}$ M^{-1} sec^{-1}. The intramolecular proton-transfer back-reaction represented by k_3 is probably the dominant transient decay process, and $k_3 \cong 2.5 \times 10^3$ sec^{-1} if $k_4 < 10^3 k_3$. On the other hand, if $k_4 > 10^5 k_3$ the intermolecular proton-addition back-reaction (k_4) would be dominant, with $k_4 \cong 2.5 \times 10^7$ M^{-1} sec^{-1}. In either case the equilibrium process represented by k_1 and k_2 would be about 10^3 more rapid than the transient decay reaction.

The rate of decay of the photolysis transients from I, II, III, and IV is dependent upon the presence of oxygen in the solutions as well as on the pH. Oxygen increases the fading rate markedly in the more basic solutions, while it has only a small effect in the lower pH range. Since the photochromic repeatability is better in the absence of oxygen and in less basic solutions, it appears that oxygen enhances nonreversible reactions of the *aci*-nitro anions, and that these compete with the reversible protonation reaction. Our attempts to check the photochromic mechanism by carrying out photolyses in D_2O have as yet been inconclusive because of analytical difficulties in the infrared analysis of the C–H and C–D bands in these acids. However, the starting material has been recovered in high yield after long periods of photolysis in the lower pH range.

Acknowledgment. The authors are indebted to the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1264, for financial support.

[6] It is convenient to consider this as a proton transfer in an excited-state acid–base reaction, but a hydrogen atom transfer could give the same results.

[7] A. F. Scott, Ed., "Survey of Progress in Chemistry," Vol. 2, Academic Press Inc., New York, N. Y., 1964, p 81.

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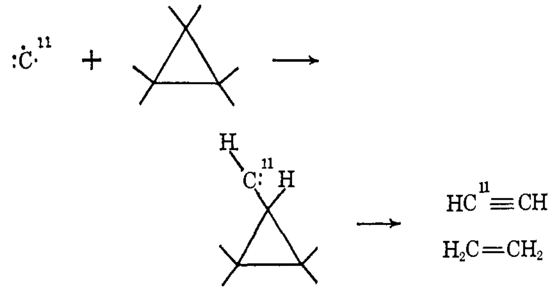
The Reactions of Cyclopropylcarbinyl Carbene Produced Photolytically in the Gas Phase[1]

Sir:

The reactions of energetic carbon atoms with cyclopropane produce acetylene and ethylene as major products.[2] It was suggested[2] that the carbon atom in colliding with a cyclopropane molecule inserts in a C–H bond yielding a short-lived cyclopropylcarbinyl carbene which by simple electronic rearrangement decomposes to give acetylene and ethylene.

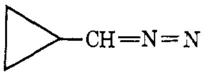


(1)

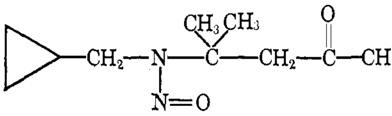
The cyclopropane system is particularly well suited for energetic carbon atom studies because the yields of products are high and the numbers of products produced are small.[3] In particular, bond reorganization reactions[4] and pressure dependence studies[5] have been and are still being carried out on this sytem.

In a recent communication Engel and Skell[6] have reported on the products of reaction between carbon atoms and cyclopropane when these are simultaneously "condensed" on a cold surface. No acetylene or ethylene was obtained as product. Since both the reaction at low temperatures involving carbon atoms on a cold surface and the gas-phase reactions of energetic and discrete carbon atoms presume the intermediacy of cyclopropylcarbinyl carbene, we chose to prepare cyclopropylcarbinyl carbene by a chemical method in which the geometric structure of this intermediate is perhaps less questionable.

Accordingly we have prepared cyclopropyldiazomethane (I)[7] *via* N-nitroso-N-(isobutyl methyl ketone)-N-cyclopropylmethylamine (II). Cyclopropylamine hydrochloride was prepared by the method of Mazur,



I



II

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

[3] For a review of energetic carbon atom reactions, *cf.* (a) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 202 (1964); (b) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 99 (1965).

[4] H. J. Ache and A. P. Wolf, "Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna, 1964, pp 107–120.

[5] H. J. Ache and A. P. Wolf, *J. Am. Chem. Soc.*, **88**, 888 (1966).

[6] R. R. Engel and P. S. Skell, *ibid.*, **87**, 4663 (1965).

[7] H. A. Moss and F. C. Shulman, *Chem. Commun.*, **12**, 373 (1966), have recently reported the preparation of this compound *via* the nitrosourethan.