2,2-Dichloro-3-(1-propyl)cyclobutanone (3).—A 50.0-g (0.22 mole) portion of freshly distilled trichloroacetyl bromide in 50 ml of dry ether was added dropwise to a stirred mixture of 250 ml of dry ether, 120 ml (1.11 moles) of 1-pentene and 57.5 g (0.88 mole) of zinc dust activated with copper. The mixture was cautiously warmed to initiate the exothermic reaction. The reaction solution was separated from the unreacted zinc and extracted with hexane. The solvents were evaporated to yield 8.0 g (31%) of 2,2-dichloro-3-(1-propyl)cyclobutanone at 69.5–70° (1.5 mm): infrared absorption smear, 1800 cm^{-1}. A pmr spectrum in $CDCl_3$ revealed a complex multiplet centered at τ 8.8 characteristic of the *n*-propyl group and another complex multiplet centered at τ 7.0 which had an area that was three-sevenths of the multiplet centered at τ 8.8.

Anal. Calcd for $C_7H_{10}Cl_2O$: C, 46.41; H, 5.52; mol wt, 181. Found: C, 46.66; H, 5.65; mol wt, 188.

10,10-Dichlorobicyclo[6.2.0]dec-4-en-9-one (4).—To a stirred refluxing solution containing 200 ml of dry hexane, 45.7 ml (0.33 mole) of triethylamine and 127 ml (1.04 moles) of 1,5-cyclooctadiene was added dropwise a solution of 50 g (0.26 mole) of freshly distilled dichloroacetyl bromide in 50 ml of dry hexane. The reaction mixture was refluxed 4 hr and the amine salt was removed by filtration. The filtrate was washed with water and dried over anhydrous magnesium sulfate. The solvent and excess olefin were removed by distillation and the residue was distilled to yield 24 g (53%) of 10,10-dichlorobicyclo[6.2.0]dec-4-en-9-one at 112° (1.0 mm): infrared absorption (smear), 1806 (s) and 1650 cm^{-1}; pmr spectrum ($CHCl_3$), complex multiplet centered at τ 7.9 (methylene protons), multiplet at τ 6.6 and 5.0 (methinyl protons), and multiplet centered at τ 3.3 (vinyl protons). The peak areas were in the ratio of 8:1:1:2.

Anal. Calcd for $C_{10}H_{12}Cl_2O$: C, 54.79; H, 5.48; mol wt, 219. Found: C, 55.04; H, 5.75; mol wt, 227.

2,2-Dichloro-3-ethoxycyclobutanone (5).—A solution of 54 g (0.28 mole) of freshly distilled dichloroacetyl bromide in 50 ml of dry ether was added dropwise to a stirred solution of 200 ml of dry ether, 70 ml (0.74 mole) of ethyl vinyl ether, and 41 ml (0.3 mole) of triethylamine at 0–5°. The reaction mixture was stirred 3 hr. The triethylammonium bromide was removed by filtration and the filtrate was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was distilled to yield 18.5 g (45%) of 2,2-dichloro-3-ethoxycyclobutanone at 91–94° (2.5 mm): infrared absorption (smear), 1806 cm^{-1}.

Anal. Calcd for $C_6H_8Cl_2O_2$: C, 39.34; H, 4.37. Found: C, 39.41; H, 4.64.

Registry No.—**1,** 13866-27-8; **2,** 13866-28-9; **3,** 13866-29-0; **4,** 13866-30-3; **5,** 13866-31-4; dichloroketene, 4591-28-0.

Free Radicals from the Irradiation of *o*-Nitrobenzyl Compounds

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Received May 22, 1967

Photochromism in nitrobenzyl compounds requires only the presence of a nitro and >C–H group *ortho* to each other.[2] The color change is believed to be due to formation (eq 1) of the *aci*-nitro structure.[2,3] We present here evidence which indicates that simple *o*-nitroalkylbenzenes undergo still another process when irradiated with ultraviolet light.

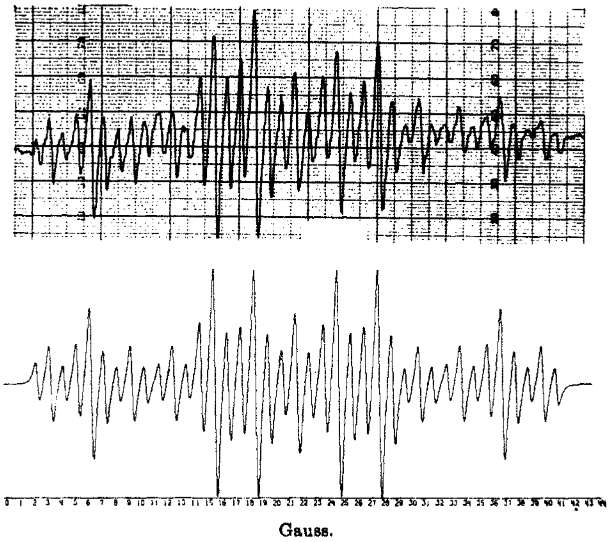


Figure 1.—Experimental spectrum obtained from irradiation of *o*-nitrocumene and simulated spectrum using splitting constants in text and a line width of 0.32 gauss.

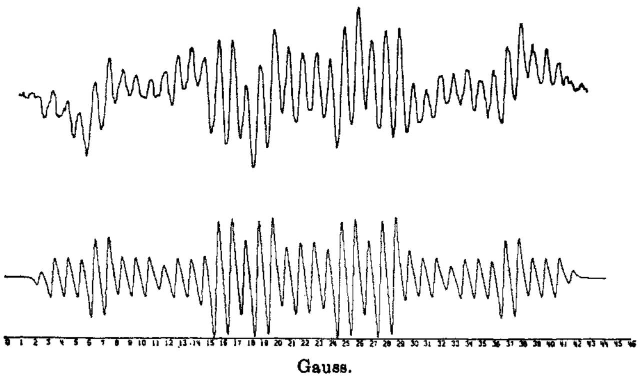
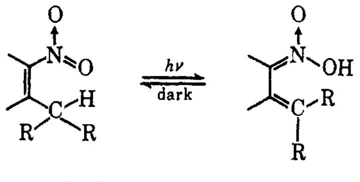


Figure 2.—Experimental spectrum obtained from irradiation of *o*-nitroethylbenzene and simulated spectrum using splitting constants in text and a line width of 0.32 gauss.



(1)

Irradiation of deoxygenated *o*-nitrocumene (neat) gave within 30 sec copious amounts of a single radical species. A 39-peak esr spectrum was recorded with the analysis as follows: A^N(1 N) = 9.1 ± 0.1 gauss, A^H(1 H) = 12.1 ± 0.1 gauss, A^H(2 H) = 3.0 ± 0.1 gauss, A^H(2 H) = 1.0 ± 0.1 gauss. The irradiation of neat *o*-nitroethylbenzene gave moderate amounts of a radical with a 40-peak esr spectrum. The splittings determined were A^N(1 N) = 9.1 ± 0.1 gauss, A^H(1 H) = 12.1 ± 0.1 gauss, A^H(2 H) = 3.0 ± 0.1 gauss, and A^H(3 H) = 1.0 ± 0.1 gauss. The experimental spectra together with theoretical spectra calculated from the above splitting constants are shown in Figures 1 and 2.[4] Continual irradiation of neat *o*-nitrotoluene gave only very small amounts of a radical with some hyperfine structure. An analysis could not be made because of the low radical concentration.

These radicals were stable for days and could also

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[2] A. L. Bluhm, J. A. Sousa, and J. Weinstein, *J. Org. Chem.*, **29**, 636 (1964).

[3] H. S. Mosher, C. Souers, and R. Hardwick, *J. Chem. Phys.*, **32**, 1888 (1960); R. Hardwick and H. S. Mosher, *ibid.*, **36**, 1402 (1962).

[4] Alternating line widths and a less well-resolved experimental spectrum in Figure 2 cause minor deviations in spectrum amplitudes.

TABLE I

SPLITTING CONSTANTS FOR AROMATIC NITROGEN-CONTAINING RADICALS

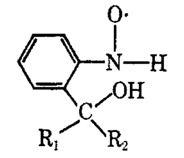
Radical	A^N	A_p^H	A_m^H	A_o^H	A^H (other)	Solvent	Ref
$PhNO_2\cdot^-$	10.32	3.97	1.09	3.39		CH_3CN	*d*
$PhNO\cdot^-$	7.90	3.90	1.01	3.90, 2.83		DMSO-*t*-BuOH	*e*
$\overset{O\cdot}{|}$ $PhNH$	9.10	3.00	1.14	3.00	11.90[a]	DMSO *t*-BuOH	*e*
$\overset{O\cdot}{|}$ $PhNOH$	15.00	3.1	1.08	3.1	0.38[b]	THF	*f*
$\overset{O\cdot}{|}$ $PhNCH_3$	11.00	2.9	1.0	2.9	10.4[c]	$PhNHCH_3$	*g*
$\overset{O\cdot}{|}$ $PhNPh$	10.5	1.94	.82	1.94		*t*-BuOOH	*h*
$\overset{O\cdot}{|}$ $PhNBz$	7.55	1.54	.64	1.54		PhH	*i*

[a] A_{NH}^H. [b] A_{OH}^H. [c] $A_{NCH_3}^H$. [d] D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960). [e] E. J. Geels, R. Konaka, and G. A. Russell, *Chem. Commun.*, 13 (1965). [f] R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963). [g] G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 3283 (1965). [h] J. Pannell, *Mol. Phys.*, **5**, 291 (1962). [i] H. G. Aurich and F. Baer, *Tetrahedron Letters*, 3879 (1965).

be formed in the presence of oxygen. Irradiation of 1 *M* solutions of the nitro compounds in benzene and ethanol gave the same radicals, although the splitting constants changed slightly as a result of solvent effects. No radicals were found when the corresponding pure *para*-substituted compounds were irradiated.

A consideration of the splitting constants in the radical derived from *o*-nitrocumene allows one to identify the type of radical present. The large splitting from a single hydrogen indicates that the hydrogen is attached to a nitrogen atom. The benzene ring is disubstituted, so the other four hydrogen splittings probably arise from the ring protons. The 3.0-gauss splitting is plausibly assigned to the two hydrogens *ortho* and *para* to the nitrogen function; the 1.0-gauss splitting then arises from the hydrogens *meta* to the nitrogen. Splitting constants are given in Table I for a series of aromatic nitrogen-containing radicals. The large hydrogen splitting, the equivalence[4a] of *ortho* and *para* hydrogens, the values of the ring hydrogen splitting constants, and the 9.0-gauss nitrogen splitting all indicate that the radical from *o*-nitrocumene is an *o*-alkylphenyl nitroxide. Nitroxides have been detected in a variety of photochemical reactions.[5]

o-Nitroethylbenzene has one more α hydrogen than *o*-nitrocumene and an additional 1.0-gauss splitting is found in the radical obtained by irradiation of this compound. This splitting must come from the side chain. Since two α hydrogens are present before irradiation, radical formation must entail the loss of an α hydrogen with the subsequent addition of a hydrogen to the nitrogen function. It is known that an aromatic nitro group is capable of light-induced hydrogen abstraction.[6] The relative amounts of radical with respect to side chain, *i*-Pr > Et > Me, is completely consistent with the reactivity of these groups toward hydrogen abstraction.[7] The radicals thus are probably of structure II, arising from intramolecular hydrogen abstraction and rearrangement, followed by hydrogen atom donation from another molecule.



IIa, $R_1 = CH_3$; $R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$

The effect, if any, of the radical-forming process on the photochromic reaction is presently being studied. It seems likely, however, that nitroxides are involved in some of the light-induced reactions of *o*-alkylnitrobenzenes.[8]

Experimental Section

o-Nitrocumene was synthesized by the procedure of Nelson and Brown.[9] The fraction boiling at 103–113° at 12 mm was redistilled at 4.5 mm with a 70-cm spinning-band column. *o*-Nitrocumene of bp 78° was obtained. The $n^{20}D$ was 1.5240 (lit.[10] $n^{20}D$ 1.5248). *o*-Nitrotoluene (Matheson Coleman and Bell) and *o*-nitroethylbenzene (Aldrich) were found to be pure.

Spectra were obtained with a Varian V-4500 epr spectrometer equipped with a 9-in. magnet. Samples were deoxygenated in the degassing apparatus previously described.[11] Irradiations were carried out in the cavity using a Bausch and Lomb SP 200W super pressure Hg lamp. Sweep rates were calibrated by the spectrum of *p*-benzosemiquinone in aqueous ethanol.[12] Theoretical spectra were calculated with the program of Stone[13] with minor changes in the print-out procedure to present the entire spectrum.

Registry No.—*o*-Nitrocumene, 6526-72-3; *o*-nitroethylbenzene, 612-22-6; *o*-nitrotoluene, 88-72-2.

Acknowledgment.—We wish to thank Mr. Robert Petkun for the synthesis of *o*-nitrocumene and Dr. Brinkley S. Snowden, Jr., and Mrs. Martha Nunn for aid in calculation of theoretical spectra.

(4a) NOTE ADDED IN PROOF.—Magnetic nonequivalance of *ortho* hydrogens in phenyl nitroxides has recently been demonstrated: Th. A. J. W. Wajer, A. Mackor, Th. J. de Boer, and J. O. W. van Voorst, *Tetrahedron Letters*, 1941 (1967).

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(6) See Table I, footnote *f*.

(7) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963); C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961); A. F. Trotman-Dickenson, *Quart. Rev.* (London), **7**, 198 (1953).

(8) For references, see P. de Mayo and S. T. Reid, *ibid.*, **15**, 393 (1961).

(9) K. L. Nelson and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 5607 (1951).

(10) H. C. Brown and W. H. Bonner, *ibid.*, **76**, 605 (1954).

(11) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

(12) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

(13) E. W. Stone, Ph.D. Thesis, Harvard University, 1962.