with nearly pure **1** (R = *t*-butyl; R′ = CH_3). Signals were observed for *t*-butyl (δ 1.10), α-methyl (1.87), and NH (4.7, 8.8, and 9.7).[9] Very weak signals at δ 0.95 and 1.21 were probably due to the presence of cyclic isomer.

The nmr spectra of other ketone derivatives were determined with crude and recrystallized samples. The observed mixtures contained 55–95% cyclic isomer, the remainder being the linear form.

As seen in Table I, consistencies in the ultraviolet (uv) spectra supported cyclic structures for all derivatives shown except those of pinacolone and benzaldehyde.[10] The spectra of the latter two closely resembled those of propionaldehyde and benzaldehyde thiosemicarbazone, respectively (see Experimental Section).

An infrared (ir) band at 6.15 μ was present in the spectrum of the pinancolone derivative, resulting from NH_2 in-plane bending as well as C=N stretching. The benzaldehyde analog produced a band of similar shape and intensity at 6.21 μ, although phenyl ring absorption is also expected in this region. Surprisingly, the acetone derivative gave a band at 6.08 μ.[11] Similar bands were absent in the spectra of other derivatives, an observation consistent with the cyclic structure.[12]

Experimental Section

General.—The nmr spectra were determined in DMSO-d_6 on a Varian A-60 instrument. Double-resonance experiments were carried out on a Varian HA-100 spectrometer. Ir spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer using KBr disks. Band positions given in the text were confirmed with a Baird-Atomic NK-1 instrument. Uv spectra were determined in methanol on a Perkin-Elmer Model 202 spectrophotometer.

Monoisovaleraldehyde Thiocarbohydrazone, *i.e.*, **1,4,5,6-Tetrahydro-6-isobutyl-3(2H)-*s*-tetrazinethione.**—Thiocarbohydrazide (10.6 g, 0.10 mol) was dissolved in 200 ml of hot water. The solution was stirred magnetically without further heating and treated dropwise over 15 min with 8.6 g (0.10 mol) of isovaleraldehyde in 30 ml of ethanol. The product began to precipitate during the course of addition. The mixture was allowed to stand overnight and then was filtered. After the product was washed with dilute ethanol and air dried, it weighed 17.1 g, mp 178–179° dec.

Other derivatives were similarly prepared. Less soluble carbonyl compounds required higher dilutions and longer addition times. The *n*-heptaldehyde derivative was prepared at steam-bath temperature with vigorous mechanical stirring. The use of 1 *N* acetic acid in place of water improved the yield and the appearance of the crude material in some cases, especially that of the pinacolone derivative, but did not alter the structure of the products.

Thiosemicarbazones of Propionaldehyde and Benzaldehyde.—Thiosemicarbazide was heated in ethanol containing an excess of the aldehyde until solution was complete. The products crystallized on cooling and were purified by recrystallization from ethanol. The propionaldehyde derivative had mp 158–159° (lit.[13] mp 159°), uv max (methanol) 270 mμ (ϵ 22,400). The benzaldehyde derivative had mp 162–163° (lit.[14] mp 160°), uv max (methanol) 311 mμ (ϵ 32,800).

Registry No.—**1** (R = $PhCH_2$; R′ = H), 18801-46-2; **1** (R = Ph; R′ = H), 5351-58-6; **1** (R = *t*-Bu; R′ = H; *syn*), 18801-48-4; **1** (R = *t*-Bu; R′ = H; *anti*), 18801-49-5; **1** (R = *t*-Bu; R′ = Me), 18801-50-8; **1** [RR′ = $-(CH_2)_4-$], 18801-51-9; **1** (R = Et; R′ = Me), 18801-52-0; **1** (R = *i*-Pr; R′ = Me), 18801-53-1; **2** (R = Et; R′ = H), 18801-54-2; **2** (R = *i*-Bu; R′ = H), 18801-55-3; **2** (R = *n*-hexyl; R′ = H), 18801-56-4; **2** (R = $PhCH_2$; R′ = H), 18801-57-5; **2** (R = *t*-Bu; R′ = H), 18801-58-6; **2** [RR′ = $-(CH_2)_5-$], 18801-59-7; **2** [RR′ = $-(CH_2)_4-$], 18801-60-0; **2** (R = Et; R′ = Me) 18801-61-1; **2** (R = *i*-Pr; R′ = Me), 18801-62-2.

Acknowledgment.—The author is indebted to Dr. T. H. Regan and Mr. R. L. Young for nmr spectra and to Dr. T. H. Regan for helpful discussions throughout the course of this work.

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[10] On standing, the very dilute solutions used for uv determinations often showed such changes as broadening, shifting, and diminution of maxima. The tendency to shift toward a 267-mμ limit paralleled the tendency to exist as isomeric mixtures, as shown by nmr. The observed changes in the uv spectra were probably caused by isomerization and decomposition.

[11] The material was insoluble in DMSO-d_6. A solution was obtained by warming in DMSO-d_6–D_2O and the nmr spectrum was then recorded. A signal was observed at δ 1.08 (methyl groups of **2**, R = R′ = CH_3). Two weaker signals at δ 1.81 and 1.89 were ascribed to **1**, indicating an isomeric mixture containing *ca.* 80% **2**. Signals at δ 1.20 and 2.05, one-fourth the area of the adjacent methyl signals, indicated the introduction of other products during solution of the sample.

[12] The crude 3-methyl-2-butanone derivative had mp 114–116°. Rapid recrystallization from ethanol (ice bath) gave material of varying melting point in poor recovery. The ir spectra of the original crude product and recovered material differed significantly, the latter showing, in particular, a weak but distinct band at 6.15 μ. The recovered material had uv max 264 mμ (ϵ *ca.* 16,000). A sample softening at 117° and melting at 139–141° gave analytical values shown in Table I. The nmr spectrum of this sample showed 55% **2**.

[13] Staff of Hopkin and Williams Research Laboratories, "Organic Reagents for Organic Analysis," Chemical Publishing Co., Brooklyn, N. Y., 1946, p 123.

[14] Reference 13, p 121.

Radical Coupling in the Photoreduction of an Aromatic Nitro Compound in Ether

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Photochemical excitation of nitroaromatic compounds frequently leads to products derived from hydrogen abstraction by an oxygen of the nitro group.[2] Such abstractions may be intramolecular from an *ortho* substituent, as in many well known photochromic and related systems, or it may be intermolecular, usually from the solvent. Several studies of the latter type of reaction have appeared recently.[3-5] Mechanistic studies[3,5] indicate that these reductions involve both photochemical and thermal steps; the first of these is hydrogen abstraction, probably by the $n \rightarrow \pi^*$ triplet state of the nitro compound. Nitrobenzene is photoreduced to phenylhydroxylamine[3] in isopropyl alcohol, and the resulting acetone has been identified; in

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[1] A National Science Foundation Undergraduate Summer Research Participant, 1967.

[2] Other processes, such as the nitro → nitrite rearrangement, are also possible; see O. L. Chapman, D. C. Heckert, D. W. Reasoner, and S. P. Thackaberry, *J. Amer. Chem. Soc.*, **88,** 5550 (1966). For leading references to other nitroaromatic photochemistry, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 477. For preparative uses, see A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, Inc., New York, N. Y., 1968, p 266.

[3] R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88,** 4330 (1966); R. Hurley and A. C. Testa, *ibid.*, **89,** 6917 (1967).

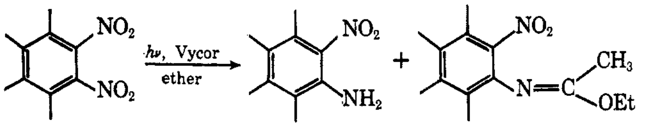
[4] R. A. Finnegan and D. Knutson, *ibid.*, **90,** 1670 (1968).

[5] J. A. Barltrop, N. J. Bunce, and A. Thomson, *J. Chem. Soc.*, *C*, 1142 (1967); J. A. Barltrop and N. J. Bunce, *ibid.*, 1467 (1968).

reductive condensations of di- and trinitrobenzenes in ethanol, acetaldehyde from the ethanol oxidation was identified.[6] Ethanol was effective in reducing esters of 4-nitrobenzoic acid to the corresponding amino acid, whereas *t*-butyl alcohol, a poor hydrogen donor, was not.[4] Ether and aliphatic amines were good solvents for photoreducing nitrobenzene to aniline.[5]

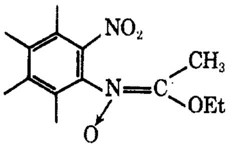
Although the final oxidation products from the hydrogen donor in the photoreduction of aromatic nitro compounds have been identified in two instances,[3,6] we are unaware of any experiment in which a coupling product has been observed, formed from a radical derived from the nitro compound and a radical derived from the hydrogen donor. We wish to describe here a result which is best rationalized in that way.[7]

Irradiation of an approximately 0.5% solution of dinitroprehnitene (**1**) in anhydrous ether through Vycor proceeded rapidly. The major product was identified as 2-nitro-3,4,5,6-tetramethylaniline (**2**). It was obtained as red crystals, mp 115–116°, whose elemental analysis and ir, nmr, and uv spectra were consistent with the assigned structure. Hydrogenation of either **1** or **2** gave the known 3,4,5,6-tetramethyl-*o*-phenylenediamine,[8] thus proving the structure of **2**.



1 2 3

The second photoproduct (yellow crystals, mp 79.5–81.0°) analyzed well for $C_{14}H_{20}N_2O_3$. The ir spectrum showed a C=N stretching absorption at 1660 cm^{-1} and a nitro group (1520 and 1380 cm^{-1}). The nmr spectrum showed an ethoxy group (triplet, τ 8.68, 3 H, and quartet, τ 5.85, 2 H) and five methyl groups at τ 7.76 (6 H), 7.86, 8.00, and 8.27. The first four of these are assigned to aromatic methyl groups, whereas the fifth is due to the allylic methyl group. These spectral data are consistent with structure **3**, or possibly with the N-oxide **4**; elemental analysis, however, clearly eliminated the latter possibility.

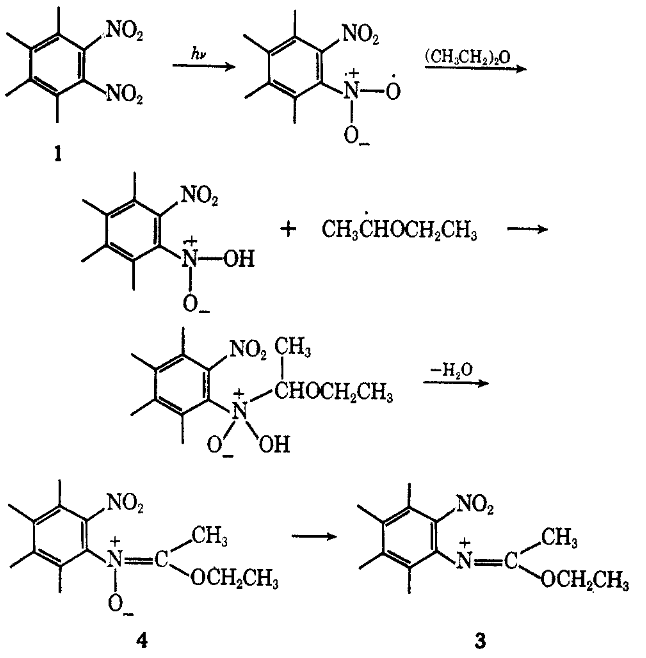


4

The isolated of **3** from the photolysis of **1** can be rationalized in terms of Scheme I. The required reduction step, shown here in the final stage (**4** → **3**), may occur earlier in the sequence. Additional reductions are required to account for the major product, **2**.

The isolation of **3** lends further support to the free radical nature of these reactions.

SCHEME I



Experimental Section

Ultraviolet (uv) spectra were measured with a Unicam Model SP-800 spectrophotometer. Infrared (ir) spectra were obtained on a Unicam Model SP-200 infrared spectrometer and were calibrated with polystyrene. Nmr spectra were measured with a Varian A-60 spectrometer using tetramethylsilane as an internal reference. The mass spectra were carried out by Mr. Michael Petschel with a Consolidated Electrodynamic Corp. 21-103C instrument operating at an ionizing potential of 56 V. Elemental analyses are by Spang Microanalytical Laboratories, Ann Arbor, Mich. Melting points are uncorrected.

Dinitroprehnitene (1).—The procedure of Smith and Harris[9] was followed. From 10 g of pentamethylbenzene there was obtained 9.5 g (63%) of **1**: white needles; mp 175.5–176.5° (lit.[9] mp 176–177°); uv $\lambda_{\max}^{Et_2O}$ 260 mμ (log ϵ 4.26) and 215 (4.52); ir ($CHCl_3$) 1560 and 1360 cm^{-1} (NO_2); nmr [$(CD_3)_2CO$] τ 7.64 (s, 6 H) and 7.70 (s, 6 H); mass spectrum *m/e* 224.

Irradiation of 1.—A solution of dinitroprehnitene (0.4 g, 1.79 mmol) in 130 ml of anhydrous ether was irradiated through Vycor using a 450-W Hanovia Type L mercury lamp. The solution being irradiated was 2–4 cm from the center of the mercury arc and was maintained at 2–6°. Nitrogen was bubbled through the solution for 15 min before and also during the photolysis. The reaction was monitored by uv and was complete in 1.5 hr.

Removal of the solvent on a rotary evaporator afforded a residue of colored crystals and a little dark oil. The crude product was dissolved in a minimum amount of hot solvent (10% chloroform in benzene) and chromatographed on a 21 cm column of F-20 Alcoa alumina using the above solvent mixture. Three fractions were eluted (followed by tlc); the second and third were combined and, after evaporation of the solvent, yielded red crystals which were sublimed [90° (2 mm)]. The product was **2-nitro-3,4,5,6-tetramethylaniline** (**2**): mp 115–116°; ir (CCl_4) 3500 (doublet, ν_{NH_2}) and 1520 and 1360 cm^{-1} (ν_{NO_2}); uv $\lambda_{\max}^{MeOH}$ 404 mμ (log ϵ 3.0), 273 (3.31), 232 (4.02), and 209 (4.31); nmr (CCl_4) τ 7.90, 7.86, 7.82, 7.80 (s, each 3 H), and 5.68 (br, NH_2). The compound gave a positive test for a nitro group.[10]

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.85; H, 7.21; N, 14.36.

The first fraction from the chromatographic separation, after evaporation of solvent, yielded a yellow crystalline material. This mixture was purified further using "dry column" chroma-

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[6] V. I. Stenberg and D. J. Holter, *J. Org. Chem.*, **29**, 3420 (1964).

[7] Irradiation of nitrobenzene in certain alcohols gave esr signals assigned to species derived from coupling of $PhNO_2H\cdot$ with solvent-derived radicals [C. Chacarty and A. Forchioni, *Tetrahedron Lett.*, 307 (1968)]; esr spectra observed on irradiation of several aryl nitro compounds in ethers are thought to arise from species obtained through attack of solvent-derived radicals on the ground state of the nitro compound [D. J. Cowley and L. H. Sutcliffe, *Chem. Commun.*, 201 (1968)].

[8] L. I. Smith and L. R. Hac, *J. Amer. Chem. Soc.*, **56**, 477 (1934).

[9] L. I. Smith and S. A. Harris, *ibid.*, **57**, 1289 (1935).

[10] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 4th ed, 1956, p 163.

tography. The crystalline material was dissolved in a small amount of hot chloroform and adsorbed on a small amount of silica gel, after which the solvent was evaporated (air stream). The silica gel was then added to the top of a 20-cm column of dry silica gel and covered with an additional 3 cm of fresh dry silica gel. The column was packed tightly with glass wool and inverted into a 250 ml graduate cylinder containing chloroform. After 2 hr the solvent level had reached the top of the inverted column. The column was removed and again inverted, and two fractions (already partially separated) were eluted with further addition of solvent. This procedure allowed efficient separation of two materials with very similar retention times. The first fraction from this separation was identified as unreacted **1**. The second fraction gave yellow crystals of the **imino ethyl ether of 2-nitro-3,4,5,6-tetramethylacetanilide** (**3**): mp 79.5–81.0°; ir (CCl_4) 1660 ($\nu_{C=N}$) and 1520 and 1380 cm^{-1} (ν_{NO_2}); uv λ_{max}^{MeOH} 208 mμ (log ϵ 4.42); nmr (CCl_4) τ 8.68 (t, 3 H, J = 7 Hz), 8.27, 8.00, and 7.86 (s, 3 H each), 7.76 (6 H, br s), and 5.85 (q, 2 H, J = 7 Hz).

Anal. Calcd for $C_{14}H_{20}N_2O_3$: C, 63.62; H, 7.63; N, 10.60. Found: C, 63.46; H, 7.53; N, 10.57.

The yields were not determined precisely, but for purified, sublimed material were about 25% for **2** and 5% for **3**. Initial yields before purification were probably appreciably higher, but some tars were produced.

Irradiation of **1** in ethanol gave a fair yield of **2** but no **3**.

Diaminoprehnitene. From 1.—Catalytic hydrogenation of a solution of 0.2 g (0.894 mmol) of **1** in 10 ml of absolute ethanol over 5% Pd/C catalyst (25 mg) at 20 psig and room temperature for 2.5 hr afforded, after filtration and evaporation of the solvent, an essentially quantitative yield of diaminoprehnitene as white crystals: mp 142–144° (lit.[8] mp 144°); nmr (CCl_4) τ 7.86 and 7.92 (s, 6 H each) and 6.83 (br, 4 H). The compound darkened on standing in air.

From 2.—Hydrogenation of **2** as described for **1** gave the same product (melting point, mixture melting point, and nmr).

Registry No.—**1**, 18801-63-3; **2**, 18801-64-4; **3**, 18801-65-5.

The Reaction of SF_5Br with Fluoro Olefins

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SF_5Cl will add to fluoro olefins[3] at elevated temperatures and in the presence of free radicals to produce 2-chloropolyfluoroalkylsulfur pentafluorides.

Also, S_2F_{10} will react with olefins and fluoro olefins under pressure and elevated temperatures to give small amounts of SF_5 addition products.[4,5]

No report has appeared in the literature dealing with the SF_5Br addition to fluoro olefins.[6]

We have found that SF_5Br, produced from the reaction of S_2F_{10} and Br_2 at elevated temperatures (eq 1),

$$S_2F_{10} + Br_2 \xrightarrow{\Delta} 2SF_5Br \qquad (1)$$

Table I

2-Bromopolyfluoroalkylsulfur Pentafluorides

Compd	Bp,[a] °C	Mol wt Calcd	Mol wt Found	Yield,[b] %	Calcd, % C	Calcd, % H	Calcd, % Br	Calcd, % Cl	Calcd, % S	Found, % C	Found, % H	Found, % Br	Found, % Cl	Found, % S
SF_5CH_2CHFBr	99.5–100.5	253	255	70	9.49	1.20	31.58	0.00	12.67	9.88	1.31			12.41
$SF_5CH_2CF_2Br$	86–87	271	270	70	8.86	0.74	29.49	0.00	11.83	9.15	0.76			11.01
SF_5CHFCF_2Br	74–75	289	288	46	8.31	0.35	27.65	0.00	11.10	8.25	0.38			10.88
$SF_5C_2F_3ClBr$	94–95	323.4	323	60	7.43	0.00	24.71	10.96	9.91	7.45	0.00	25.29	11.94	9.53

[a] Boiling points were recorded at 766 ± 1 mm of Hg. [b] The yield was based on the assumption that only SF_5Br was added. However, we have found that SF_6, SF_4, and S_2F_{10} transferred over with the SF_5Br. Therefore, the actual yields are higher than the ones given here. Note: The boiling point of $SF_5CH_2CH_2Br$ is 109.5° at 760 mm of Hg. Thus, replacing the hydrogens with fluorines in $SF_5CH_2CH_2Br$ causes the boiling point to drop approximately 10° per hydrogen atom.

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[1] Taken from a M. S. thesis to be submitted to Portland State University.

[2] To whom inquiries should be addressed.

[3] J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 2070 (1961).

[4] M. Tremblay, *Can. J. Chem.*, **43**, 219 (1965).

[5] H. L. Roberts, *J. Chem. Soc.*, 3183 (1962).

[6] C. Merrill found that SF_5Br added to ethylene giving $SF_5CH_2CH_2Br$. See C. Merrill, Ph.D. Thesis, University of Washington, Seattle, Wash., 1962.