

Fig. 1.— γ -Radiolysis of 0.1 and 0.5 M benzophenone in 2propanol; effect of phenyl disulfide on reduction of benzophenone: ---, 0.1 M benzophenone; -O-O-, 0.5 M benzophenone.

Experimental

Materials.—Benzophenone (Fisher) was crystallized from ethyl alcohol; m.p. 47° . 2-Propanol (Fisher spectroscopic or reagent grade) was found free from impurity by gas chromatographic analysis and used without further treatment. Naphthalene (Fisher) and phenyl disulfide (Eastman) were used as received; m.p. 78–79 and 59°, respectively.

Preparation and Irradiation of Solutions.—Standard solutions of 0.1 and 0.5 *M* benzophenone in 2-propanol were prepared. For the experiments with naphthalene and phenyl disulfide these materials were weighed into a volumetric flask and made up to the mark with standard benzophenone solution. Aliquots (2 ml.) of the reaction mixture were placed in 150×12 mm. Pyrex tubes and degassed by the freeze-thaw method (three cycles) on a vacuum line at 0.02 mm. The tubes were then irradiated with a nominal 1.25-Mc. cobalt-60 source. The radiation doses received by the solutions were determined with a ferrous-copper dosimeter¹⁵ (a solution of 10^{-3} N ferrous sulfate and 10^{-2} N copper sulfate in 10^{-2} N sulfuric acid, taking $G_{\rm Fe^{3-}(Cu^{2-})} = 0.66$). The dose rate at the commencement of the experiments was 4.06 Mrads hr.⁻¹ dropping to 3.91 Mrads hr.⁻¹ at the end. The electron densities of the dosimeter and 2-propanol are 0.554 and 0.432 electron mole ml.⁻¹, respectively. To calculate the dose received by the reaction solutions, the dose received by the same volume of the ferrous-copper dosimeter was multiplied by a factor 0.432/0.554 = 0.780.

Analysis .- After the irradiation period the reaction tube was opened and 0.5 ml. of the reaction mixture was removed and mixed with a weighed (1 mmole) amount of 2-butanol. This solution was gas chromatographed on an Aerograph A700. A 6-ft. column of 10% polymeric butyl glycol adipate (Rubber Corporation of America B.G.A.) on 80-100 Chromosorb-W (Johns Manville) was used at 40°. The carrier gas was helium and a thermal conductivity detector was used. The acetone formed was identified by its retention time and infrared spectrum of a sample collected at the exit port of the gas chromatograph. Acetaldehyde was identified by its retention time and typical odor at the exit port. The concentration of acetaldehyde was determined by comparison of its peak area with that of the added 2-butanol, while acetone was determined by comparison with both 2-butanol and 2-propanol peaks. From calibration curves the mole ratios of 2-propanol/acetone, 2-butanol/acetone, and 2-butanol/ acetaldehyde were found to be 1.00, 0.90, and $0.76 \times \text{peak}$ area ratio, respectively. Benzophenone was estimated by removing a 1-ml. aliquot, diluting with 2-propanol, and measuring the absorption at 333, 340, 350, and 360 m μ on a Perkin-Elmer Model 202 spectrophotometer. Extinction coefficients at these wave lengths were 150, 140, 108, and 68, respectively.

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(15) E. J. Hart and P. D. Walsh, Radiation Res., 1, 342 (1954).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASS.]

Oxidative Decarboxylation¹

By Louis F. Fieser and Makhluf J. Haddadin

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A convenient synthesis of *p*-terphenyl reported in the literature from the adduct 1 of *trans,trans*-1,4-diphenylbutadiene and dimethyl acetylenedicarboxylate involves a hitherto unrecognized alkaline isomerization of 1 to 2 prior to saponification to 3. Elucidation of the true structure of 3 provides the basis for a rational interpretation of the ready decarboxylation of this bisallylic diacid to *p*-terphenyl by alkaline ferricyanide $(6 \rightarrow 7 \rightarrow 4)$. Further examples of the reaction with diacids of the dihydronaphthalene and dihydrobenzene series are recorded.

Lohaus² briefly reported the synthesis of *p*-terphenyl (4) by Diels-Alder addition of *trans,trans*-1,4-diphenylbutadiene to diethyl acetylenedicarboxylate (5 hr. at 150°), saponification, and oxidation with potassium ferricyanide in sodium carbonate solution. McDonald and Campbell³ repeated the synthesis without isolation of intermediates and extended the scheme to the synthesis of a number of polyphenyls, including *p*-

 $(1)\,$ This work was supported by National Institutes of Health Grant CA-01696-12.

(2) H. Lohaus, Ann., 516, 295 (1935).

(3) R. N. McDonald and T. W. Campbell, J. Org. Chem., 24, 1969 (1959).

quinquephenyl.⁴ These authors formulated each oxidation as involving a diacid corresponding in structure to the diester adduct saponified, for example 1. Such an oxidative decarboxylation seemed to us surprising enough to call for a reinvestigation.

We prepared *trans*,*trans*-1,4-diphenylbutadiene by a simplified version of the phosphate modification of the Wittig reaction,⁵ particularly as developed by Seus

(4) T. W. Campbell and R. N. McDonald, Org. Syntheses, 40, 85 (1960).
(5) L. Horner, H. Hoffmann, and H. G. Wippel, Ber., 91, 61 (1958);
L. Horner, H. G. Wippel, and G. Klahre, *ibid.*, 92, 2499 (1959); W. S. Wadsworth, Jr., and W. D. Emmons, J. Am. Chem. Soc., 83, 1733 (1961).



and Wilson,⁶ and found that the Diels-Alder reaction with dimethyl acetylenedicarboxylate can be conducted more conveniently than previously $^{2-4}$ at the reflux temperature of phenol (b.p. 181°, 1 hr.) or of triethylene glycol dimethyl ether (b.p. 222°, 0.5 hr.); phenol is preferred because it is more easily removed from an ethereal extract. Lohaus² saponified both the dimethyl ester 1 (m.p. 98°) and the diethyl ester (m.p. 88°) by refluxing with ethanolic potassium hydroxide for 11 hr., and in the second instance isolated a small amount of an unidentified neutral substance melting at 111°. We found that when the ester 1 is warmed on the steam bath with methanolic potassium hydroxide for 15 min. it is transformed in high yield to a much less soluble isomeric ester melting at 170°. Saponification of the isomerized ester by prolonged refluxing with methanolic potassium hydroxide or by brief heating with potassium hydroxide in triethylene glycol dimethyl ether at 140° gave a high-melting diacid corresponding to that used previously^{2,3} in the synthesis of p-terphenyl. Re-esterification with diazomethane regenerated the isomerized ester, to which we assign the formula 2 on the basis of chemical and spectroscopic evidence. Ozonolysis of 2 in ethyl acetate at -50° afforded dimethyl 1,2-dibenzoylsuccinate⁷ (5). An ultraviolet maximum for 2 at 335 m μ (ϵ 22,400) is consistent with the presence of a cisoid diene system conjugated with two phenyl groups. The n.m.r. spectrum exhibits a singlet at 3.45τ corresponding to two vinylic protons, a singlet at 5.53 τ corresponding to two allylic protons α to carboxyl groups, as well as peaks corresponding to the methoxyl and aromatic protons. The fact that acid 3 was obtained as a product of vigorous basic hydrolysis as well as the high melting point suggest the trans configuration. Spectroscopic characterization of the initial product of Diels-Alder addition (infrared, ultraviolet, n.m.r.) all support structure 1.

(6) E. J. Seus and C. V. Wilson, J. Org. Chem., 26, 5243 (1961).

(7) K. Alder and M. Günzl-Schumacher, Ber., 92, 822 (1959).

Elucidation of the true structure of the diacid **3** makes it easy to account for its ready oxidative decarboxylation in alkaline solution. Potassium ferricyanide in alkaline solution functions as a complex electron-abstracting ion,⁸ here represented as Fe⁺³, and abstraction of two electrons from the dianion **6**



gives a diradical (7) which expels two molecules of carbon dioxide from the allylic carboxylate groups to give p-terphenyl (4). Contrary to a suggestion of Walker and Scott⁹ that oxygen is involved in such oxidative decarboxylations, we found that decarboxylation proceeds as well in an oxygen-free nitrogen atmosphere as in the presence of air.

Walker and Scott reported observations on the oxidative decarboxylation of dihydronaphthalene-1,2and -1,4-dicarboxylic acids obtained by carbonation of the complex formed by reaction of sodium with naphthalene in special solvents, but it is now known that this reaction gives a complicated mixture of isomers.^{10,11} One of six components characterized by Lyssy¹¹ is the Δ^2 -trans-1,4-diacid **8**. Jiang¹⁰ showed that acid **8** is isomerized by alkali to the Δ^1 -1,4-diacid **9** and that



the isomerized acid was the precursor of α -naphthoic acid in the Walker-Scott experiment. We have found that both 8 and 9 are oxidized by ferricyanide in alkaline solution and that 8 is decarboxylated much faster than it is isomerized by alkali. Thus decarboxylation of 8 at room temperature is complete in 2 hr., with no detection of any 9, whereas 9 is recovered unchanged under the same conditions. In 8 the carboxyl group is both allylic and benzylic, that is, it is activated by both a double bond and a benzene ring. In isomer 9 the carboxyl eliminated is activated only by a benzene ring, and oxidative decarboxylation at room temperature requires about 30 hr. The oxidation of 9 evidently follows the anion \rightarrow radical course analogous

(9) J. F. Walker and N. D. Scott, J. Am. Chem. Soc., 60, 951 (1938).

(11) T. M. Lyssy, J. Org. Chem., 27, 5 (1962).

⁽⁸⁾ B. S. Thyagarajan, Chem. Rev., 58, 439 (1958).

⁽¹⁰⁾ S. H-K. Jiang, Hua Hsüch Pao, 23, 351 (1957) [Chem. Abstr., 52, 15,481 (1958)].

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to $6 \rightarrow 7 \rightarrow 4$. The oxidation of 8 to α -naphthoic rather than to naphthalene indicated that the oxidant abstracts the hydrogen at C-1 of the relatively stable¹² anion radical $10 \leftrightarrow 11$ rather than an electron from the carboxylate anion group.

The Δ^{3} -1,2-*trans*-diacid **13**, prepared according to Lyssy,¹¹ is oxidized slowly by alkaline ferricyanide to give β -naphthoic acid (**17**). Since the Δ^{1} -diacid is known to undergo prototropic shift in a basic medium



to the Δ^2 -diacid 14, it seemed to us possible that the isomerized acid 14 is the precursor of 2-naphthoic acid. Trial indeed showed that 14 is oxidized by alkaline ferricyanide more rapidly than 13 and that the product is β -naphthoic acid. In acid 14 the carboxyl group at C-1 is activated by both the benzene ring and the double bond at C-2 and hence is preferentially attacked by the oxidant to give the radical 15 \leftrightarrow 16, which then affords β -naphthoic acid.

A further example of the oxidative elimination of an allylic carboxyl group is the nearly quantitative conversion of Baeyer's $\Delta^{3.6}$ -cyclohexadiene-*trans*-1,2-dicarboxylic acid¹³ (18) into benzoic acid. *meso*-1,2-Diphenylsuccinic acid and *trans*-1,4-tetralindicarbox-



ylic acid¹¹ proved to be resistant to alkaline ferricyanide under forcing conditions; the former belongs to a group of acids known to undergo decarboxylation on oxidation with tetravalent lead.¹⁴

Experimental¹⁵

trans,trans-1,4-Diphenyl- $\Delta^{1,3}$ -butadiene.^{6,16}—A mixture of 5 ml. of benzyl chloride and 7.7 ml. of triethyl phosphite was refluxed in a test tube under a cold finger condenser for 1 hr. and the phosphonate ester was cooled and dissolved in 40 ml. of dimethylformamide. After addition of 2.4 g. of sodium methoxide the mixture was chilled thoroughly and swirled in an ice bath while running in 5 ml. of cinnamaldehyde. The mixture turned deep red and crystalline hydrocarbon soon started to separate. After 2 min. at 0° and 10 min. at room temperature, water (20 ml.) and methanol (10 ml.) were added and the

(13) A. Baeyer, Ann., 269, 189 (1892).

product was collected and washed with water until the red color was all replaced by yellow. Brief washing with methanol removed the yellow color and gave 5.7 g. (67%) of faintly yellow hydrocarbon (m.p. 150–151°) suitable for the next step. Dimethyl 3,6-Diphenyl- $\Delta^{1,4}$ -cyclohexadiene-1,2-dicarboxylate

Dimethyl 3,6-Diphenyl- $\Delta^{1,4}$ -cyclohexadiene-1,2-dicarboxylate (1).--A mixture of 1.5 g. of 1,4-diphenylbutadiene, 1.5 ml. of dimethyl acetylenedicarboxylate, and 15 g. of phenol was refluxed for 1 hr. and the yellowish solution was cooled and poured into water in a separatory funnel. After extraction with ether the ether layer was washed thoroughly with 5% potassium hydroxide solution, dried, and evaporated. The residue was a yellowish oil which solidified on cooling; 2.2 g. (87%). Recrystallization from methanol afforded colorless prisms, m.p. 97–98° (lit. 96°,¹⁷ 101°²); infrared spectrum (Nujol): 1740, 1650, 1610, 1500, 1450–1400, 1265, 1150, 1000, 855, 795, 760, 750, 740, 700 cm.⁻¹; ultraviolet: λ_{max} 240, 262, 270 m μ (ϵ 3310, 1910, 1400); n.m.r.: 5.54 τ (J = 3 c.p.s.), 4.23 τ (J = 3 c.p.s.).

Anal. Calcd. for $C_{22}H_{20}O_4$ (348.38): C, 75.84; H, 5.79. Found: C, 75.88; H, 5.61.

Dimethyl 3,6-Diphenyl- $\Delta^{8,6}$ -cyclohexadiene-1,2-trans-dicarboxylate (2).---A solution of 2 g. of dimethyl 3,6-diphenyl- $\Delta^{1,4}$ -cyclohexadiene-1,2-dicarboxylate in 10 ml. of 5% methanolic potassium hydroxide was warmed on the steam bath for 15 min. A reddish brown color soon disappeared with separation of the isomerized ester as a white solid which was collected after cooling, washed with chilled methanol to remove brown mother liquor, and dried. The yield of colorless product, m.p. 165-167°, was 1.75 g. (87%). Recrystallization from methanol gave fluorescent, shiny needles, m.p. 169-170°; infrared (Nujol): 1720, 1455, 1230, 1000, 840, 770, 750, 690 cm.⁻¹; ultraviolet: λ_{max} 335, 230 (shoulder) m μ (ϵ 22,400, 10,000); n.m.r.: 5.53 τ (2 allylic protons α to a carboxyl group), 3.45 τ (2 vinylic protons).

Anal. Calcd. for $C_{22}H_{20}O_4$ (348.38): C, 75.84; H, 5.79. Found: C, 75.86; H, 5.85.

Dimethyl 1,2-Dibenzoylsuccinate (5).—For ozonolysis, a solution of 3 g. of the above dimethyl ester in 1 l. of ethyl acetate was cooled to -50° and a stream of ozone (2 equiv.) was passed into it. Evaporation of the solvent left a yellowish oil which was dissolved in 25 ml. of acetic acid. Zinc dust (5 g.) was added and the mixture stirred on the steam bath for 1 hr. Filtration and dilution with water gave a yellowish, gummy solid which was collected and dried. Digestion with methanol gave 1.3 g. of a white solid, m.p. 140–145°. Elution from a column of neutral alumina with ether containing 2% of methanol and crystallization from methanol gave dimethyl 1,2-dibenzoylsuccinate, m.p. 184–186°; a recrystallized sample melted at 186–188° (lit.⁷ 182°); infrared (KBr): 1735, 1675, 1600, 1445, 1430, 1300, 1260, 1200, 1156, 1000, 980, 880, 778, 730, 685 cm.⁻¹; ultraviolet: $\lambda_{max} 252 \, \text{m}\mu$ (e 27,600).

Anal. Calcd. for $C_{20}H_{18}O_6$ (354.34): C, 67.79; H, 5.12. Found: C, 67.58; H, 5.11.

3,6-Diphenyl- $\Delta^{3,5}$ -cyclohexadiene-1,2-trans-dicarboxylic Acid (3).—A suspension of 0.8 g. of the ester 2 in 15 ml. of 5% methanolic potassium hydroxide was refluxed until the solid was all dissolved (4 hr.), excess methanol was evaporated, and the concentrated solution was poured into water. Filtration and acidification with dilute hydrochloric acid gave a milky precipitate, which was collected, washed with water, and dried; yield 0.63~g.~(86%). Crystallization from methanol gave hard prisms, m.p. 257–259° dec. (lit.² 255°). Repeated recrystallization raised the m.p. to 267–268° dec. with previous yellowing. The acid is fluorescent in methanol solution and in the crystalline Hydrolysis of the hindered ester can be accomplished form. also by heating a mixture of 2 g. of ester, 0.7 g. of potassium hydroxide, and 5 ml. of triethylene glycol dimethyl ether at 140° for 5 min.; infrared (KBr): 3000-2500, 1685, 1590, 1485, 1440, 1400, 1278, 1190, 1027, 930-900, 845, 765-755, 695-690, 680-670 cm. -1.

Anal. Calcd. for $C_{20}H_{16}O_4$ (320.33): C, 74.99; H, 5.03. Found: C, 74.74; H, 4.93.

Methylation of the acid with ethereal diazomethane gave the ester 2 in high yield.

p-Terphenyl (4).—A stream of oxygen-free nitrogen¹⁸ was passed through a solution of 1.2 g. of the diacid **3** in 30 ml. of 1 N sodium hydroxide at room temperature long enough to re-

⁽¹²⁾ Compare the known naphthalene carbanion radical: D. E. Paul, D. Lipkin, and S. I. Weissman, J. Am. Chem. Soc., 78, 116 (1956).

^{(14) (}a) W. von E. Doering, M. Farber, and A. Sayigh, J. Am. Chem. Soc.,
74, 4371 (1952); (b) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, Helv.
Chim. Acta, 41, 1191 (1958); (c) E. J. Corey and J. Casanova, Jr., J. Am.
Chem. Soc., 85, 165 (1963).

⁽¹⁵⁾ All melting points are corrected. Infrared spectra were taken on a Perkin-Elmer 21 double beam spectrophotometer; ultraviolet spectra were determined in methanol using a Cary 14 recording spectrophotometer; n.m.r. spectra were run in deuterated chloroform with hexamethyldisiloxane as an internal standard on a Varian A-60 n.m.r. spectrometer.

⁽¹⁶⁾ Procedure developed (L. F. F.) as a student experiment

⁽¹⁷⁾ K. Alder and M. Schumacher, Ann., 571, 87 (1950).

⁽¹⁸⁾ L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p. 299.

move all oxygen. On addition of 6 g. of potassium ferricyanide the solution turned milky at once from separation of *p*-terphenyl. The flow of nitrogen was continued for 20 min. and the white solid was collected, washed, and dried; yield 0.84 g. (95.5%), m.p. 211-212°. Crystallization from dioxane or methanol gave shiny flakes, m.p. 212° (lit.²212°).

No change in speed of reaction or yield was observed when the reaction was run without nitrogen. If potassium ferricyanide is added to a solution of the acid in alkali (25°) and the mixture is swirled on a hot plate, the oxidation can be completed in about 5 min.

Oxidation of Δ^2 -Dihydronaphthalene-trans-1,4 dicarboxylic Acid¹¹ (8).—A solution of 100 mg. of the diacid and 0.5 g. of potassium ferricyanide in 10 ml. of 1 N sodium hydroxide was prepared at room temperature and let stand for 2 hr. Acidification with dilute hydrochloric acid liberated carbon dioxide and precipitated 75 mg. (96%) of α -naphthoic acid. Crystallization from methanol-water afforded colorless needles, m.p. 161-162°; a mixture melting point determination with an authentic sample showed no depression.

Oxidation of Δ^1 -Dihydronaphthalene-1,4-dicarboxylic Acid¹¹ (9).—A solution of 100 mg. of the diacid and 0.5 g. of potassium ferricyanide in 10 ml. of 1 N sodium hydroxide was heated on the steam bath for 3 hr. and acidified. The product that precipitated (65 mg., 83%) after crystallization melted at 161–162° and did not depress the m.p. of authentic α -naphthoic acid.

When the oxidation was conducted as above but at room temperature for 11 hr., acidification precipitated starting material; α -naphthoic acid was obtained after a reaction period of 30 hr.

Oxidation of Δ^3 -Dihydronaphthalene-trans-1,2-dicarboxylic Acid¹¹ (13).—A solution of 200 mg. of the diacid in 10 ml. of 1 N sodium hydroxide was flushed with a stream of oxygen-free nitrogen, treated with 2 g. of potassium ferricyanide, and heated on the steam bath for 1.5 hr. in a nitrogen atmosphere. The yellow solution was cooled and acidified, and the product that precipitated (135 mg., 86%) on crystallization from *n*-hexane melted at 185–186° and gave no depression when mixed with β -naphthoic acid.

The oxidation proceeded equally well when air was not excluded. β -Naphthoic acid was obtained under the same conditions but at room temperature for 4 days.

Oxidation of Δ^2 -Dihydronaphthalene-1,2-dicarboxylic Acid¹¹ (14).—A solution of 150 mg. of the diacid and 0.6 g. of potassium ferricyanide in 8 ml. of 1 N sodium hydroxide was warmed on the steam bath for 30 sec. and let stand at room temperature for 4 hr. Acidification with hydrochloric acid gave a white solid and ether extraction afforded 105 mg. of β -naphthoic acid, identified by m.p. and mixture m.p. determinations.

Oxidation of $\Delta^{3,5}$ -Cyclohexadiene-trans-1,2-dicarboxylic Acid (18).—This acid was prepared according to Baeyer¹³ except that glacial acetic acid was used instead of 50% acetic acid; the yield rose from 56 to 80%.

A solution of 1 g. of the diacid and 5 g. of potassium ferricyanide in 30 ml. of 1 N sodium hydroxide was heated on the steam bath for 15 min., cooled, and acidified. After collection of precipitated benzoic acid, a further crop was isolated by ether extraction; total yield 0.68 g. (98%); identification by m.p. and mixture m.p.

Attempted Oxidations.—Samples of *meso-1,2-diphenylsuc*cinic acid and *trans-1,4-tetralindicarboxylic* acid were refluxed; the starting materials were recovered unchanged.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

The Diazene-Hydrazone Rearrangement

By DAVID M. LEMAL, FREDRIC MENGER, AND EUGENE COATS

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The course of thermal decomposition of a series of 1,1-dialkyl-2-benzenesulfonylhydrazine sodium salts has been found to be highly solvent dependent. Tetrazenes are the major products when the solvent is tetraglyme, but rearrangement to hydrazones occurs competitively with or to the exclusion of tetrazene formation with diethylene glycol the solvent. In contrast to the dialkyl analogs, 1,1-diphenyl-2-benzenesulfonylhydrazine sodium salt yields diphenylamine in both solvents, and no rearrangement product (azobenzene) was isolated. Mechanistic implications of these observations are discussed and certain of them are tested experimentally.

Aminonitrenes (1), called diazenes, have been proposed as intermediates in the oxidation of 1,1-disubstituted hydrazines,¹⁻³ in the thermal decomposition of 1,1-disubstituted 2-sulfonylhydrazine salts,^{4,5} in the base-catalyzed decomposition of 1,1-disubstituted 2chlorohydrazines,^{1b} in the reduction (particularly by

(1) See, for example: (a) L. A. Carpino, A. A. Santilli, and R. W. Murray, J. Am. Chem. Soc., **82**, 2728 (1960); C. G. Overberger and L. P. Herin, J. Org. Chem., **27**, 417 (1962); (b) C. G. Overberger and B. S. Marks, J. Am. Chem. Soc., **77**, 4104 (1955); C. G. Overberger, Record Chem. Progr., **21**, 21 (1960).

(2) C. G. Overberger, N. P. Marullo, and R. G. Hiskey, J. Am. Chem. Soc., 83, 1374 (1961); C. G. Overberger and L. P. Herin, J. Org. Chem., 27, 2423 (1962).

(3) (a) W. R. McBride and H. W. Kruse, J. Am. Chem. Soc., 79, 572 (1957);
(b) W. H. Urry, H. W. Kruse, and W. R. McBride, *ibid.*, 79, 6568 (1957);
(c) W. R. McBride and E. M. Bens, *ibid.*, 81, 5546 (1959).

(4) (a) L. A. Carpino, Chem. Ind. (London), 172 (1957); J. Am. Chem. Soc., 79, 4427 (1957); 84, 2196 (1962); 85, 2144 (1963); R. L. Himman and K. L. Hamm, *ibid.*, 81, 3294 (1959); W. Baker, J. F. W. McOmie, and D. R. Preston, Chem. Ind. (London), 1305 (1960); J. Chem. Soc., 2971 (1961); (b) D. M. Lemal, T. W. Rave, and S. D. McGregor, J. Am. Chem. Soc., 85, 1944 (1963).

(5) P. Carter and T. S. Stevens, J. Chem. Soc., 1743 (1961).

(6) C. G. Overberger, L. G. Lombardino, and R. G. Hiskey, J. Am. Chem. Soc., **80**, 3009 (1958); C. G. Overberger and N. P. Marullo, *ibid.*, **83**, 1378 (1961).

(7) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *ibid.*, **85**, 97 (1963).

sodium hydrosulfite) of nitrosamines,^{2,6,7} and most recently in the reaction of secondary amines with difluoroamine.⁷ Tetrazenes have been the usual products of reactions which proceed *via* diazenes, whether the substituent groups were aryl or alkyl.⁸ Special features

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in the substituents can lead to cleavage of the carbon-nitrogen bond of the intermediate, however, with the formation of molecular nitrogen accompanied by disproportionation, coupling, and/or fragmentation products.^{1–7}

Among representatives of a single type of diazene intermediate, arylbenzyl- or arylallyldiazenes, rearrangement to hydrazones has been observed. Thus Carter and Stevens⁵ recently discovered that decomposition in aqueous or ethanolic alkali of a series of 1aryl-1-benzyl-2-sulfonylhydrazines (2) leads to the corresponding hydrazones **3**, and earlier Busch and Lang⁹ had shown that oxidation of a 1-aryl-1-benzylhydrazine (**4**) gave either the hydrazone or the tetrazene **5** or both. Carter and Stevens concluded that the rate-determining

(8) An interesting exception is discussed in footnote 17.

(9) M. Busch and K. Lang, J. prakt. Chem., 144, 291 (1936).