Acknowledgment.—We thank Dr. J. H. Richards (personal communication) for drawing our attention to the existence of the quinone V (R = CH_3).

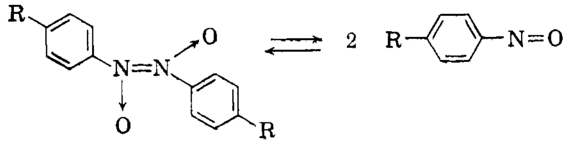
The Anomalous Behavior of *m*-Trifluoromethylnitrosobenzene Dimer[1]

L. A. ERREDE AND H. R. DAVIS

Contribution No. 244 from the Central Research Laboratories of Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota

Received December 10, 1962

It is well known that most aromatic nitroso compounds exist as colorless or pale yellow dimers in the crystalline state but dissociate to intensely green-colored monomers in the liquid state.[2,3]



para-Substituents such as R_2N—, I, Cl, and CH_3 increase the tendency for dissociation owing to electronic interaction with the aromatic system, thereby weakening the N-N bond.[3] In fact, the effect is so great with *p*-nitrosodimethylaniline and with *p*-iodonitrosobenzene that these compounds are monomeric even in the solid state. When electronic interaction is prevented by *ortho* substituents that preclude formation of a planar configuration, the nitroso molecule exists mostly as a dimer even in solution. Thus, in a 1% benzene solution, nitrosomesitylene is dimerized 77%[4,5] whereas *p*-nitro-, *p*-bromo-, *p*-methylnitrosobenzene, and nitrosobenzene are dimerized less than 4%.[4,5] *m*-Substituents are reported[5] to have little or no effect on the N-N bond.

In view of these generally accepted properties of aromatic nitroso compounds, we wish to report the anomalous stability of the *m*-trifluoromethylnitrosobenzene dimer. This dimer is a white crystalline compound that melts at 48.5–49.0° forming a light amber oil. It dissolves in organic solvents giving water white to light amber solutions. The compound can be distilled at atmospheric pressure (b.p. 295°). The vapor is light green and the distillate when recrystallized from methyl alcohol is obtained as light yellow needles (m.p. 44–46°). Unlike nitrosobenzene dimer, which must be stored in a refrigerator, *m*-trifluoromethylnitrosobenzene dimer is air and light stable at room temperature and can be kept on the shelf for at least ten years without decomposition. This nitroso compound could not be reoxidized to the nitro compound using potassium permanganate in acetone, potassium dichromate in sulfuric acid, or hydrogen peroxide in acetic acid. Neither could it be reduced with ferrous ammonium sulfate in aqueous hydroxide. Much stronger reducing systems such as zinc or tin in aqueous hydrochloric acid were required for reduction to the corresponding amine.

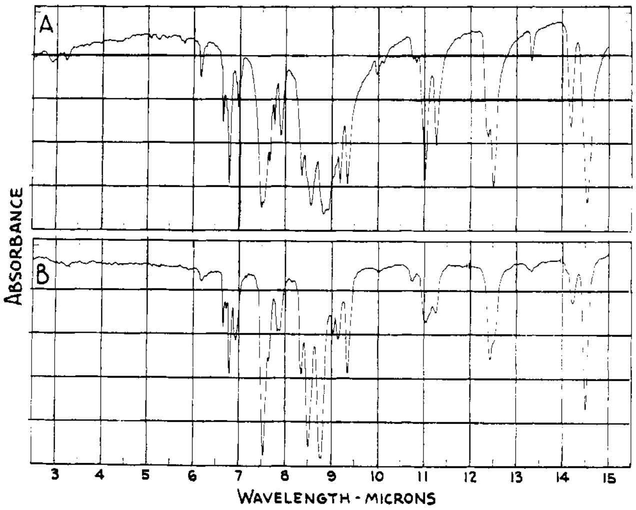


Fig. 1.—Infrared spectra of *m*-trifluoromethylnitrosobenzene dimer (A) in potassium bromide mull and (B) in carbon tetrachloride solution, 3–12 μ and 14–15 μ; in carbon bisulfide solution, 12–14 μ.

The empirical formula for *m*-trifluoromethylnitrosobenzene was established by elemental analysis. The molecular weight was determined cryoscopically using naphthalene and ebulloscopically using benzene. Both methods indicated that the compound was a dimer. The infrared spectra of this compound in its crystalline state and in solution are very similar as shown in Fig. 1, supporting the premise that no dissociation occurs at room temperature in solution. The ultraviolet absorption spectrum in ethanol [0.21 g./l.; peaks at 3150 Å., ε (l./g.-cm.) 42.9; at 2540 Å., ε 23.6; at 2320 Å., ε 30.8] also showed no evidence for the presence of the monomer. Dissociation in solution, however, begins to occur at temperatures above 100°.

N.m.r. data for this compound, summarized in Table I, are consistent with that anticipated for the symmetrical dimer as represented by the azodioxide structure.

Reduction of the dimer with zinc in aqueous hydrochloric acid gave *m*-trifluoromethylaniline which was identified by infrared analysis, and by conversion to its acetyl derivative.

m-Trifluoromethylnitrosobenzene dimer is prepared easily by reduction of *m*-trifluoromethylnitrobenzene with mild reducing systems such as ethylmercaptan in aqueous alkali, zinc in aqueous ammonium chloride, and even alcoholic sodium hydroxide. The reaction gives a mixture of reductive dimerization products from which the desired azodioxide can be isolated in 30–40% yield as described in Experimental.

Experimental

Reduction with Ethylmercaptan.—Ethylmercaptan (1.2 moles) was added dropwise to a chilled mixture of *m*-trifluoromethylnitrobenzene (0.3 mole), water (400 cc.), and sodium hydroxide

---

[1] Part of this work was completed in the laboratories of the M. W. Kellogg Co. The data were acquired by the Minnesota Mining and Manufacturing Co. with the purchase of the Chemical Division of the M. W. Kellogg Co. in March, 1957.

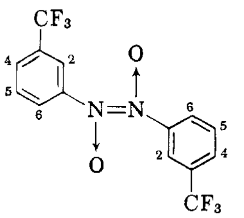
[2] N. V. Sidgwick, "Organic Chemistry of Nitrogen," Oxford Press, London, 1942, p. 204.

[3] B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, **12**, 321 (1958).

[4] N. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

[5] D. L. Hammick, *J. Chem. Soc.*, 3105 (1931).

TABLE I

N.M.R. DATA FOR 

H atom	τ^a	Mult.	J^b
2	1.57	b	...
4	2.39	s	...
5	2.38	AB	7.6
6	1.50	AB	7.6

ϕ^c for F atom of CF_3 = 63.62

b = broad

s = sharp

AB = type system[b]

[a] See ref. 6. [b] See ref. 7. [c] See ref. 8.

(2.5 moles) contained in a three-necked round-bottom flask fitted with a reflux condenser, stirrer, and dropping funnel. The dropping funnel was replaced by a thermometer and reaction was allowed to occur for an additional 24 hr. at 85°. The excess ethyl mercaptan and diethyl disulfide were removed by steam distillation. The residual aqueous alkaline mixture was extracted with benzene. The aqueous layer was discarded and the benzene layer was evaporated to dryness. The residue was dissolved in *n*-hexane and the solution passed through a 72 × 1 in. column filled with activated alumina. The column was developed with hexane. The first three 1-l. fractions contained 20 g. of sulfur-free white compound that melted at 48.5–49.0° after recrystallization from methanol. Fractions 4 and 5 contained 5 g. of a mixture of products, m.p. 45–60°. The infrared spectra of these fractions indicated that they were a mixture of the compound melting at 48.5–49.0° and the azoxy compound eluted next from the column. Fraction 6 contained 1.5 g. of a yellow compound (m.p. 127–129°). The compound was recrystallized from ethanol to give yellow crystals (m.p. 130–131°) that were identified as 4,4′-diethylmercapto-3,3′-ditrifluoromethylazoxybenzene by elemental analysis and by comparison of the infrared spectrum with those of similar azoxy compounds.[9] The compound gave a deep red-purple color when dissolved in concentrated sulfuric acid indicative of an aromatic azoxy containing alkyl mercapto-substituent in the *para* position.[9]

Anal. Calcd. for $C_{18}H_{16}ON_2S_2F_6$: C, 47.57; H, 3.55; S, 14.12. Found: C, 47.2; H, 4.0; S, 13.8.

Elemental analysis of the white compound melting at 48.5–49.0° indicated an empirical formula of $C_7H_4ONF_3$.

Anal. Calcd. for $C_{14}H_8O_2N_2F_6$: C, 47.98; H, 2.30; N, 8.00; O, 9.14; F, 32.55; mol. wt., 350. Found: C, 48.3; H, 2.49; N, 7.74; O, 8.98; F, 33.0; mol. wt., 356.

The molecular weight at 5° and at 80° was measured as 356 but the value decreased steadily when solvents of increasing boiling points were used, indicating that dissociation increased with temperature above 80°. The infrared spectrum and n.m.r. data for this compound are shown in Fig. 1 and Table I, respectively.

A sample of this compound (m.p. 48.5–49.0°) was distilled at atmospheric pressure (b.p. 295°) and showed no color formation in the vapor state or when melted. The distillate was crystallized from methanol in the form of long white thin needles (m.p. 44–46°), indicating that only little decomposition had occurred.

One gram of this compound (m.p. 48.5–49.0°) was reduced with zinc at reflux temperature for 4 hr. in 40 cc. of 10% aqueous hydrochloric acid. The solution was cooled to room temperature, made strongly alkaline, and then extracted with ether. The ether extract was dried with magnesium sulfate, separated by filtration, and evaporated to dryness. The residual oil was made to react with acetic anhydride to give the corresponding amide. The product was crystallized from aqueous methanol and then from hexane in the form of white platelets (0.9 g., m.p. 102.5–103.5°). The compound was identified as *m*-trifluoromethylacetanilide (no depression in melting point when mixed with an authentic sample).

Reduction with Zinc in Aqueous Ammonium Chloride.—Powdered zinc (0.46 mole) was added slowly to a cold mixture of *m*-trifluoromethylnitrobenzene (0.16 mole), water (500 cc.), and ammonium chloride (0.28 mole) contained in a 1-l. three-necked round-bottom flask fitted with a stirrer, reflux condenser, and an adapter for addition of solids. The mixture was allowed to react at room temperature for 6 hr. A small amount of *m*-$CF_3C_6H_4$-$NH_2 \cdot ZnCl_2$ precipitated from solution, and was removed by filtration. The mother liquor was acidified with dilute aqueous hydrochloric acid and then extracted with ether. The ether extract was evaporated to dryness. The residual oil was crystallized from a methanol–water solution and 10 g. (36%) of *m*-trifluoromethylnitrosobenzene was isolated in the form of tiny slightly orange needles, m.p. 44–46°.

The aqueous acid layer from which *m*-trifluoromethylnitrosobenzene was removed by extraction with ether was made alkaline and re-extracted with ether. The ether layer was evaporated to dryness and the residue treated with acetic anhydride. The acetylated product was recrystallized from water. The compound (7 g., 22%) was isolated in the form of white platelets (m.p. 87–88°). The compound resolidified when a crystal of *m*-trifluoromethylacetamide, m.p. 102–103°, was added to the melt. This white solid remelted at 102–103°.

Reduction with Alkaline Ethanol.—A mixture of *m*-trifluoromethylnitrobenzene (0.18 mole), water (100 cc.), sodium hydroxide (0.6 mole), and ethanol (0.5 mole) was allowed to react at reflux temperature for 24 hr. to give a deep red solution. The solution was diluted with water and extracted with benzene. The aqueous layer was discarded and the organic layer was evaporated to dryness. The red crystalline residue was dissolved in hexane and separated by chromatography as described previously to give *m*-trifluoromethylnitrosobenzene in the form of orange tinted delicate needles (10.5 g., m.p. 48.0–48.5°).

Acknowledgment.—The authors are indebted to Dr. G. V. D. Tiers for interpretation of the n.m.r. data. The elemental analyses and molecular weight determinations were done by the Carl Tiedke Laboratory of Teaneck, New Jersey, and by the Analytical Department of the M. W. Kellogg Company.

---

(6) G. V. P. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 119.

(8) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(9) H. R. Davis, J. W. Copenhaver, W. E. Hanford, and H. F. Lederle, 121st National Meeting of American Chemical Society, Buffalo, N. Y., March, 1952, p. 66-K.

On the Modified Oppenauer Oxidation

E. W. WARNHOFF[1] AND P. REYNOLDS-WARNHOFF

Laboratory of Chemistry of Natural Products,
National Heart Institute, National Institutes of Health,
Bethesda 14, Maryland

Received December 17, 1962

The use of acidic reagents for oxidation of a hydroxyl group to a carbonyl function has sometimes failed with compounds containing basic nitrogen atoms,[2] particularly if the nitrogen is in the immediate vicinity of the hydroxyl. The difficulty is not necessarily circumvented by oxidation under the basic conditions of the Oppenauer procedure since the aluminum alkoxide is capable of complexing with the nitrogen[3,4a] and in some

---

(1) Department of Chemistry, University of Western Ontario, London, Canada.

(2) *Inter alia* (a) quinine: P. Rabe, W. Naumann, and E. Kuliga, *Ann.* **364**, 345 (1909); (b) buphanamine: L. G. Humber and W. I. Taylor, *Can. J. Chem.*, **33**, 1268 (1955); codeine: F. Ach and L. Knorr, *Ber.*, **36**, 3070 (1903).

(3) (a) quinine: R. L. McKee and H. R. Henze, *J. Am. Chem. Soc.*, **66**, 2021 (1944); (b) 1,2-aminoalcohols: R. E. Lutz, R. H. Jordan, and W. L. Truett, *ibid.*, **72**, 4085 (1950); (c) *cis*- and *trans*-1-amino-2-indanols: R. E. Lutz and R. L. Wayland, *ibid.*, **73**, 1639 (1951).