When the temperature reached 175°, heating was stopped, and the condenser set for refluxing. A single addition of 14.0 g. (0.1 mole) of 3-thienylacetone was made and the temperature was maintained at 160-170° for seven hours. The reaction mixture was cooled, and upon adding 60 ml. of water, the formyl derivative of the amine separated as an oil. The mother liquor was extracted with benzene, the benzene evaporated, and the two portions of the formyl derivative were mixed. This formyl derivative was refluxed with 100 ml. of 3 N sodium hydroxide for 20 hours, and the amine extracted with benzene. The benzene solution was made alkaline with concd. ammonia, and the amine was again extracted with benzene. The solvent was removed under reduced pressure and the product was vacuum distilled, b.p. 64-71° (3 mm.), to yield 1.6 g. (11%). B. Reduction of 1-(3-Thienyl)-2-nitropropene.—1-(3-Thienyu) 2 sitercorcene (32.8 c. 0.2 mole) was reduced in

B. Reduction of 1-(3-Thienyi)-2-nitropropene.—1-(3-Thienyi)-2-nitropropene (33.8 g., 0.2 mole) was reduced in ether solution with 22.8 g. (0.6 mole) of lithium aluminum hydride. After isolation of the amine, it was vacuum distilled, b.p. 79° (12 mm.) to 85° (5 mm.), to yield 23.9 g. (85%). Fractionation through a short column gave a product, b.p. 70-74° (7 mm.), n²⁰D 1.5349, d²⁶, 1.037.

Anal. Calcd. for $C_7H_{11}NS$: S, 22.70. Found: S, 23.03. The hydrochloride was recrystallized from absolute ethanol, m.p. 135–136°.

Anal. Calcd. for C_7H_{12} CINS: N, 7.88. Found: N, 7.91. The benzamide was recrystallized from ethanol, m.p. 118-118.5°.

Anal. Calcd. for C₁₄H₁₆NOS: C, 68.53; H, 6.16; S, 13.07. Found: C, 68.54; H, 5.88; S, 13.07.

The phenylthiourea derivative was recrystallized from ethanol, m.p. 110.5-111°.

Anal. Calcd. for $C_{14}H_{16}N_2S_2$: N, 10.14. Found: N, 10.07.

N-Methyl-1-(3-thienyl)-2-propylamine (Id).—From 25.5 g. (0.5 mole) of 90% formic acid, 54 ml. (0.5 mole) of 9.34 M methylamine solution and 14.0 g. (0.1 mole) of 3-thienyl-acetone, 7.5 g. (48%) of an amine fraction, b.p. 89–92° (9 mm.), was obtained via the Leuckart procedure previously described. Redistillation gave a product, b.p. 67–69° (3 mm.), n^{20} D 1.5233, d^{20} , 1.009.

Anal. Calcd. for $C_8H_{13}NS$: S, 20.65. Found: S, 20.35. The hydrochloride was recrystallized from a mixture of absolute alcohol and dry ether, m.p. 97–98°.

Anal. Calcd. for C₈H₁₄ClNS: C, 50.11; H, 7.36; S, 16.72. Found: C, 50.65; H, 7.55; S, 16.28.

The phenylthiourea derivative was recrystallized from ethyl alcohol, m.p. 122-122.5°.

Anal. Calcd. for $C_{15}H_{18}N_2S_2;$ N, 9.65; S, 22.08. Found: N, 9.36; S, 22.39.

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Triphenylmethyl Nitrate¹

By Stanley J. Cristol and John E. Leffler Received March 29, 1954

One of the possible modes of organic nitrate ester decomposition or reduction involves oxygennitrogen fission leading to the formation of alkoxy free radicals. We have been interested in the reductive denitration of nitrate esters with alkaline hydrosulfides,² and wished to conduct experiments to determine the possibility of free-radical intermediates. Although mixtures of *n*-butyl nitrate and sodium hydrosulfide with the radical detectors acrylonitrile and methyl methacrylate failed to

(1) This research was supported by a contract between the University of Colorado and the U. S. Naval Ordnance Test Station, Inyokern, U. S. Navy Bureau of Ordnance.

(2) R. T. Merrow, S. J. Cristol and R. W. Van Dolah, TRIS JOURNAL, **75**, 4259 (1953).

give any polymer, *n*-butyl nitrate appeared to inhibit the benzoyl peroxide-catalyzed polymerization of acrylonitrile. It was of interest to obtain triphenylmethyl nitrate for use in similar experiments, since the triphenylmethoxy free radical, if formed, should reveal itself by β -cleavage to benzophenone or by the Wieland rearrangement.³

Attempts to make triphenylmethyl nitrate from the chloride and silver nitrate in dimethylformamide as a solvent gave only triphenylcarbinol. A similar experiment in acetonitrile gave N-triphenylmethylacetamide by way of an intermediate, probably the nitrate of the imidol form of this amide. Even in benzene the reaction gave only the carbinol, by decomposition at higher temperatures or by hydrolysis on exposure of the solution to air at lower temperatures. The nitrate appeared to be inordinately sensitive to hydrolysis. When prepared in carbon tetrachloride, only the carbinol was isolated when the solvent was allowed to evaporate in air. Vacuum-line technique, using carbon tetrachloride as the solvent, gave a solid which melted with decomposition at 73° and resolidified at a higher temperature.

Exposure of this solid to the laboratory air even for a few minutes converted it almost entirely to the carbinol. We therefore heated freshly prepared solutions of the nitrate in sealed ampoules and isolated the decomposition products without any further attempt to purify the nitrate itself. In carbon tetrachloride and in nitrobenzene the decomposition products were benzophenone, triphenylcarbinol, picric acid and oxides of nitrogen. These products are consistent with β -cleavage of some of the triphenylmethoxy radicals to phenyl radicals and benzophenone, nitration and oxidation of the cleaved phenyl radical by nitrogen dioxide and reduction of some of the triphenylmethoxy radicals by hydrogen atoms supplied in the nitration reaction. In addition some of the alcohol may have resulted from hydrolysis.

Experimental

Formation and Decomposition of Triphenylmethyl Nitrate in Carbon Tetrachloride.—To 5 g. of silver nitrate and 2.0 g. of triphenylmethyl chloride in an ampoule was added 50 ml. of carbon tetrachloride by distillation from phosphorus pentoxide. The mixture was frozen, degassed, sealed, shaken overnight, then heated to 110° for 15 minutes. The filtrate was concentrated and put onto an alumina column with ordinary chloroform. There was isolated a trace of benzophenone, 1.44 g. of triphenylcarbinol, m.p. and mixed m.p. 162–164°, and 0.4 g. of triphenylmethyl ethyl ether (evidently from alcohol in the chloroform), m.p. and mixed m.p. 483–84°, and 40 mg. of pictic acid. From a second experiment in which the heating period was three hours, there was obtained 250 mg. of benzophenone, m.p. and mixed m.p. 47–49° (oxime, m.p.é 141–142°), 1.38 g. of carbinol, and 140 mg. of pictic acid, m.p. and mixed m.p. 119–121°. Similar results were obtained when the triphenylmethyl nitrate solution was decanted into an ampoule of calcium oxide before sealing. A mixture of carbon tetra-chloride and styrene as solvent gave polymer, benzophenone, carbinol and nitrophenols.

Nitrobenzene.—A similar experiment in which the product of the reaction in nitrobenzene was decanted, sealed and decomposed at 110–125° gave oxides of nitrogen, benzophenone, carbinol and picric acid.

(3) J. E. Leffler, Chem. Revs., 45, 385 (1949); H. Wieland, Ber., 44, 2550 (1911).

(4) J. Herzig and P. Wengraf, Monatsh., 22, 601 (1901).

(5) A. Janny, Ber., 15, 2718 (1882); E. Bamberger and R. Seligmann, *ibid.*, 36, 685 (1903). Triphenylmethyl Nitrate.—For the preparation of solid triphenylmethyl nitrate the reaction mixture with carbon tetrachloride as the solvent was stirred magnetically for four hours, the supernatant liquid was decanted into a receiver, and the solvent distilled back into the reaction flask at room temperature. The entire operation was done in a closed system. Part of the residual pale yellow solid was removed for a melting point and the rest was decomposed *in vacuo* without solvent. It gave (from 2.0 g. of triphenylmethyl chloride) 200 mg. of benzophenone, 600 mg. of carbinol and a mixture of highly colored substances. The solid melted at 73° when heated rapidly, became red, and evolved a gas. When heating was continued, the mixture resolidified (with lightening of color) and remelted to a light orange liquid at $145-160^\circ$.

N-Triphenylmethylacetamide.—A solution of 16 g. of triphenylchloromethane in acetonitrile was added to a solution of 10 g. of silver nitrate in acetonitrile. After a short while, the precipitated silver chloride was removed by filtration, and the solvent was removed. The residue was crystallized from toluene giving about 12.5 g. of solid, m.p. 95-125° (dec. with formation of nitrogen oxides). When this material was recrystallized from commercial acetone or from 95% ethanol, it was converted to N-triphenylmethylacetamide,⁶ m.p. 214–218°.

Anal. Calcd. for C₂₄H₁₉ON: C, 83.69; H, 6.35. Found: C, 83.84; H, 6.52.

When this compound was submitted to hydrolysis in aqueous acetic acid, using a trace of hydrochloric acid catalyst, triphenylcarbinol, m.p. and mixed m.p. 162-163° was obtained.⁶

NOTE ADDED IN PROOF.—G. W. H. Cheeseman, *Chem. and Ind.*, 281 (1954), recently has noted the high reactivity of triphenylmethyl nitrate.

(6) W. Hemelian and H. Silberstein, Monatsh., 17, 741 (1884).

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On the Expansion of the Sulfur Octet¹

By G. CILENTO AND WOLFGANG FERDINAND WALTER RECEIVED DECEMBER 8, 1953

As reported in previous papers,² the ultraviolet absorption spectra of fully aromatic esters and thiolesters show that the three main electronic transitions expected in these compounds are largely independent of one another and strongly indicate that in certain of these thiolesters, in an activated state, the sulfur atom uses a 3d-orbital, expanding its valence shell to a decet.

In the light of these results, it was expected that an indication of expansion would also be found in the spectra of certain partially aromatic thiolesters, such as p-anisyl thiolacetate. The spectra of this compound, of the analogous ester and of both corresponding unsubstituted compounds have been investigated and are shown in Fig. 1.

It can be seen that introduction of a methoxyl in the ring of phenyl acetate produces essentially the same spectral changes which are to be observed on passing from benzene to anisole. However, the same substitution in the case of phenyl thiolacetate produces a very strong absorption maximum at around 240 m μ . This almost certainly indicates

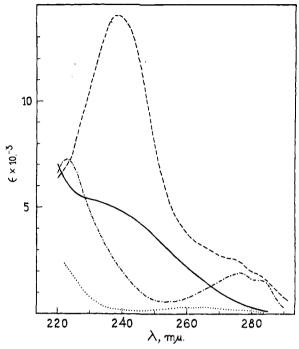


Fig. 1.—Absorption spectra in C_2H_5OH of: $CH_3-CO-O-C_6H_5$; $CH_4-CO-S-C_6H_5$; $CH_4-CO-S-C_6H_5$; $CH_2-CO-O-C_6H_4-OCH_2$; $CH_3-CO-S-C_6H_4-OCH_2$

that the sulfur atom participates in the electronic transition corresponding to this band by using a 3d-orbital

$$\xrightarrow{\Theta}$$
 $\xrightarrow{\Theta}$ $\xrightarrow{\Theta}$

It is pertinent to note that there seems to exist a counterpart of this finding in chemical reactivity. Thus, Tarbell and Herz³ have connected the failure of aryl thiolesters to undergo the Fries rearrangement with deactivation of the aromatic nucleus by resonating structures in which sulfur expands its octet.³

As suggested by chemical or physicochemical evidence, this peculiarity of the sulfur atom to enlarge the outer shell presents itself in various other classes of compounds.⁴ Nonet structures also have been formulated.⁵ Very probably this peculiarity is involved also in the explanation of the behavior of triphenylmethyl radicals in liquid sulfur dioxide. These radicals transfer their unpaired electron to the solvent, most likely to a d-orbital of the sulfur atom.

It would not be going too far to suggest that the ability of sulfur to use a d-orbital might, in certain cases, be of significance—or at least should not be overlooked—in the elucidation of the biological role of certain sulfur-containing groups or molecules. Such a suggestion would in a way remind one of the importance of vacant d-orbitals in the activity of certain cations in some biological systems.⁶

(3) D. S. Tarbell and A. H. Herz, ibid., 75, 1668 (1953).

(4) Several references are given by D. S. Tarbell and D. P. Harnish, Chem. Revs., 49, 1 (1951).

- (5) C. C. Price and J. Zomlefer. This JOURNAL, 72, 14 (1950).
- (6) See, for instance, A. L. Lehninger, Physiol. Rev., 30, 393 (1950)

⁽¹⁾ Presented at the 5th Meeting of the "Sociedade Brasileira para o Progresso da Ciência," Curitiba, November, 1953.

⁽²⁾ G. Cilento, Experientia, 8, 421 (1952); THIS JOURNAL, 75, 3748 (1953).