C. With Ammonium Hydroxide.—Addition of 67 ml. of a butyl ether solution of 30 g. of trichloromethyltrichlorosilane to 50 ml. of concentrated ammonium hydroxide in the cold gave a curdy, white precipitate. This material was filtered, washed with butyl ether, dried, washed with 5% aqueous ammonia to remove ammonium chloride, and finally dried at 130° for three hours. The resulting 6.3 g. of tan powder was free of bound halogen and gave 80% residue on ashing; thus it was apparently partially hydrated silica.

From the butyl ether layer and washings was isolated 11 g. of material b. p. 56–58° at 730 mm., $n^{20}D$ 1.444. This product was heavier than water, gave a positive Beilstein test, was inert to hot 95% ethanolic silver nitrate, and had a chloroform odor.

Anal. Calcd. for $CHCl_3$: Cl, 89.1. Found: Cl, 87.5.

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THE SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA RECEIVED JUNE 3, 1948

The Photodecomposition of Nitrobenzene

BY S. H. HASTINGS[1a] AND F. A. MATSEN

Nitrobenzene exhibits in the vapor phase a strong continuous absorption in the 2600 Å. region[1] in contrast to most other monosubstituted benzenes which yield discrete spectra in the same region. On the long wave length shoulder of the nitrobenzene continuum are four relatively weak bands. In Fig. 1 is a microphotometer tracing of the vapor spectrum of nitrobenzene. The occurrence of the continuum suggests that photodecomposition takes place, evidence for which was obtained by Shelegova[1] in the form of a yellow tarnish on the walls of the reaction chamber. The following reactions were postulated by Shelegova.

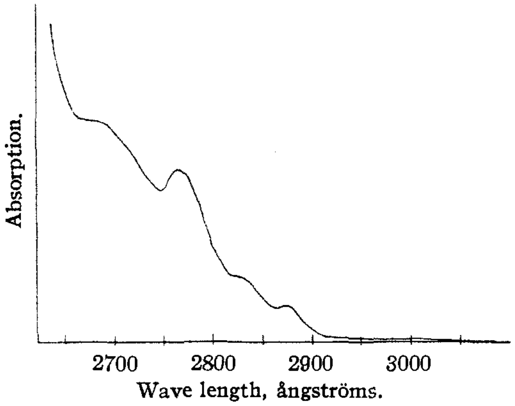

Fig. 1.—Microphotometer tracing of near ultraviolet absorption spectrogram of nitrobenzene vapor.

$$C_6H_5NO_2 + h\nu \longrightarrow C_6H_5 + NO_2$$

$$2C_6H_5 \longrightarrow (C_6H_5)_2$$

$$NO_2 + C_6H_5NO_2 + C_6H_4(NO_2)_2 + H \text{ (and tri-nitro compounds)}$$

No evidence was offered for the formation of nitrogen dioxide or polynitrated benzenes.

The suggestion that the aromatic nitro compounds split off oxygen in the photodecomposition process frequently has been made. Aniline and nitrobenzene in the liquid state when irradiated produce *p*-aminophenol and other products some of which require the formation of nitrosobenzene as an intermediate.[2] *o*-Nitrobenzaldehyde forms *o*-nitrosobenzoic acid.[3] The NO_2 molecule itself is known to decompose into nitric oxide and atomic oxygen.[4] It seemed worthwhile in view of these facts to reinvestigate the photodecomposition of nitrobenzene in the vapor phase.

Nitrobenzene with nitrogen as a carrier was passed through a quartz cell irradiated by two 220 v. d.c. arcs with brass negative electrodes[4a] and iron positive electrodes. The exhaust vapor

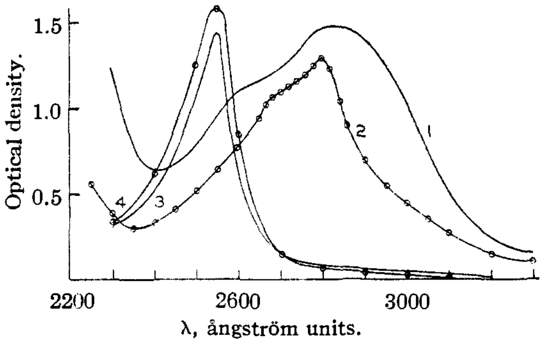

Fig. 2.—Ultraviolet spectra in cyclohexane solution of: 1, unknown cyclohexane-soluble product; 2, nitrosobenzene; 3, oxidation product of 1; 4, nitrobenzene.

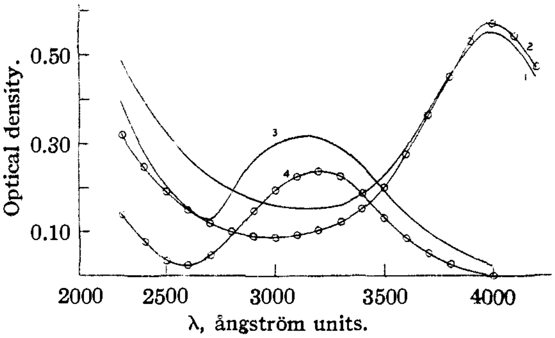

Fig. 3.—Ultraviolet spectra of: 1, 1 *N* NaOH solution of base-soluble product; 2, 1 *N* NaOH solution of *p*-nitrophenol; 3, 4.5 *N* HCl solution of base-soluble product; 4, 4.5 *N* HCl solution of *p*-nitrophenol.

(1a) Humble Oil and Refining Company Fellow.

(1) O. N. Shelegova, *J. Exp. Theoret. Phys. U. S. S. R.*, IX, 1527 (1939).

(2) L. Vecchiotti and C. Piccinini, *Gazz. chim. ital.*, **61**, 626 (1931).

(3) (a) F. Weigert and L. Kummerer, *Ber.*, **46**, 1207 (1913); (b) P. A. Leighton and F. A. Lucy, *J. Chem. Phys.*, **2**, 756, 760 (1934).

(4) R. G. Dickinson and W. P. Baxter, THIS JOURNAL, **50**, 774 (1928).

(4a) Zinc and copper emit strongly in the wave length region of the nitrobenzene continuum.

was passed through a cold trap and a sodium hydroxide scrubber.

No evidence of nitrogen dioxide was found in the reaction chamber or in the caustic scrubber by any of the well-known nitrate tests. On the walls of the reaction chamber a white crystalline deposit was formed which slowly turned yellow, approximately 2–3 mg. of product being obtained per hour. To prevent the formation of appreciable amounts of secondary products the reaction was never allowed to run for more than thirty minutes.

Following a run, the cell was pumped for thirty minutes to remove unreacted nitrobenzene. The cell was then rinsed with cyclohexane which dissolved part of the product and then with sodium hydroxide which removed the remainder. The spectrum obtained on the cyclohexane solution of the product is shown as curve 1 in Fig. 2. The absorption spectrum of nitrosobenzene is curve 2. Since the unknown appeared to be nitrosobenzene a confirmation by oxidation to nitrobenzene was undertaken. Curve 3 is the absorption spectrum of the unknown after oxidation with hydrogen peroxide. The absorption spectrum of nitrobenzene in cyclohexane solution is curve 4. On the basis of these data it is concluded that nitrosobenzene is one of the primary products.

In Fig. 3, curve 1 is the spectrum obtained on the sodium hydroxide solution of the sodium hydroxide soluble portion of the product. Curve 2 is a sodium hydroxide solution of *p*-nitrophenol. Upon acidification of these solutions curves 3 and 4 were obtained. From these data it is concluded that *p*-nitrophenol is also a product. The ultraviolet absorption curves obtained on these two fractions did not resemble the curves for any of the polynitrobenzenes. It appears that the primary reaction postulated by Shelegova is not an important reaction.

The presence of nitrosobenzene and *p*-nitrophenol in the product in relatively high concentrations and the apparent absence of poly nitrobenzenes suggest that the predominating reactions are:

$$C_6H_5NO_2 + h\nu \longrightarrow C_6H_5NO + O$$
$$O + C_6H_5NO_2 \longrightarrow p\text{-}HOC_6H_4NO_2$$

The presence of para rather than meta nitrophenol is in accord with the fact that the nitro group is ortho–para directing for free radical substituents.[5]

Since photolysis takes place through the rupture of an N–O bond, it seems probable that most of the near ultraviolet absorption of nitrobenzene is due to excitation partially localized in the NO_2 chromophore as has been suggested by Leighton and Lucy[3b] and others instead of in the ring as is the case for most monosubstituted benzenes. See, however, G. Kortüm.[6]

DEPARTMENTS OF CHEMISTRY AND PHYSICS
THE UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS

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[5] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944. p. 262.

[6] G. Kortüm, *Z. physik. Chem.*, **B42**, 53 (1939).

Preparation of Diphenylacetonitrile

BY WM. BRADLEY REID, JR., AND JAMES H. HUNTER

The preparation of diphenylacetonitrile in relatively large quantities became necessary in connection with certain semi-pilot scale operations in This Laboratory.

Diphenylacetonitrile has been prepared by a variety of methods,[1] but generally in small amounts only or under conditions which resulted in low yields. However, Rupe and Gisige[2] reported a 57% yield of this nitrile from diphenylacetic acid by treatment of the corresponding amide with the calculated quantity of phosphorus pentachloride in an equal weight of phosphorus oxychloride.

It has now been found that the preparation of diphenylacetonitrile can be accomplished smoothly in 72% yield from diphenylacetic acid by dehydration of its amide with phosphorus oxychloride alone. Substitution of thionyl chloride for phosphorus oxychloride lowered the over-all yield approximately 6%. The foregoing method affords certain advantages over the Friedel–Crafts reaction of α-bromophenylacetonitrile and benzene since it requires less attention and avoids the use of the undesirable lachrymal bromo-compound.

Experimental[3]

Diphenylacetamide.—A mixture of 318 g. (1.5 moles) of diphenylacetic acid (Lemke) and 730 g. (6.1 moles, 445.7 ml.) of thionyl chloride was stirred mechanically and warmed on a steam-bath for three hours. Excess thionyl chloride was removed *in vacuo* and the residue poured with stirring into 4 liters of 28% ammonium hydroxide. The precipitate was collected, washed free from ammonium chloride, and crystallized from 95% alcohol; yield of white, crystalline product, 247.5 g. (78.2%); m. p. 165–166°. The literature[4] reports 165–166°.

Diphenylacetonitrile.—To 115.9 g. (0.55 mole) of diphenylacetamide was added 46.0 g. (0.3 mole, 27.5 ml.) of phosphorus oxychloride. The mixture was heated on a steam-bath with mechanical stirring for two hours. The reddish liquid was poured on crushed ice and 20% sodium hydroxide added to *p*H approximately 8. After heating until the crude nitrile had melted, the mixture was allowed to cool with continuous stirring. Crystallization of the resulting crude product from 95% alcohol, using Darco G-60, yielded 95.4 g. (90.4%) of diphenylacetonitrile melting at 72–73°.

Using an analogous procedure, 42.25 g. (0.2 mole) of diphenylacetamide and 28.8 g. (0.25 mole, 18.3 ml.) of thionyl chloride gave 32.8 g. (85%) of diphenylacetonitrile, m. p. 71.5–72.5°.

RESEARCH LABORATORY
THE UPJOHN COMPANY
KALAMAZOO, MICHIGAN

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[1] (a) Anschütz and Romig, *Ann.*, **223**, 349 (1886); (b) Neure, *ibid.*, **250**, 142 (1889); (c) Zinsser, *Ber.*, **24**, 3556 (1891); (d) Michael and Jeanpretre, *ibid.*, **25**, 1615 (1892); (e) Stalle and Schmidt, *ibid.*, **45**, 3144 (1912); (f) Lipp, *et al.*, *Ann.*, **449**, 15 (1926); (g) Wittig and Hopf, *Ber.*, **65B**, 760 (1932); (h) Hoch, *Compt. rend.*, **196**, 1619 (1933); (i) *ibid.*, **197**, 770 (1933); (j) Norris and Klemka, THIS JOURNAL, **62**, 1432 (1940).

[2] Rupe and Gisige, *Helv. Chim. Acta*, **8**, 338 (1925).

[3] Melting points are uncorrected.

[4] Klingemann, *Ann.*, **275**, 85 (1893).