

now prepared 4-nitro-3-picoline which we required.³ The position of the nitro group in the latter was established by reduction to the known 4-amino-3-picoline.⁴ Since 4-nitro-3-picoline-oxide can also be hydrogenated directly to 4-amino-3-picoline in good yield, the method proves to be very convenient for the preparation of this amine.

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Experimental

3-Picoline 1-Oxide.—3-Picoline 1-oxide, which was extremely hygroscopic and was not isolated in pure form, melted at 33–36° (evacuated capillary) and was characterized by its picrate which after three recrystallizations from methanol furnished a sample of m.p. 141–143° (lit.⁵ 138–139°).

Anal. Calcd. for $C_{12}H_{10}O_3N_4$: C, 42.61; H, 2.98; N, 16.57. Found: C, 42.80; H, 2.99; N, 16.2.

4-Nitro-3-picoline 1-Oxide.—Fifty grams of 3-picoline was mixed with 150 cc. of 40% peracetic acid and 9 g. of anhydrous sodium acetate. The mixture was allowed to stand for 20 hours at room temperature. Dilute hydrochloric acid (100 ml.) was added and the solvent was distilled under reduced pressure below 50°. The residue was dissolved in 505 g. of concentrated sulfuric acid and 84 g. of potassium nitrate was added slowly. The mixture was heated on a steam-bath for 14 hours, basified with concentrated potassium hydroxide solution and extracted several times with chloroform. The chloroform solution was dried over anhydrous sodium sulfate and evaporated to a small volume. Two crops of the nitro compound were collected as yellow crystals, m.p. 129–133°, total yield 29 g. (35% based on 3-picoline). Two recrystallizations from acetone followed by two more from methanol furnished pale yellow prisms, m.p. 136–138°.

Anal. Calcd. for $C_8H_6O_3N_2$: C, 46.75; H, 3.92; N, 18.18. Found: C, 47.24; H, 4.13; N, 18.1.

4-Amino-3-picoline.—One gram of 4-nitro-3-picoline 1-oxide was hydrogenated over 0.5 g. of palladium-black catalyst in 20 cc. of acetic acid and 1 cc. of acetic anhydride for 36 hours under a pressure of 54 pounds per sq. in. After filtering off the catalyst the solution was concentrated *in vacuo*, diluted with 20 ml. of water, made basic with 20% NaOH solution and extracted with five 25-ml. portions of ether. The combined ether extracts were dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The light brown solid residue was crystallized from benzene and gave colorless needles, m.p. 103–105°, yield 0.55 g. (78.5%). Two further recrystallizations from benzene-petroleum ether (b.p. 60–110°) afforded a sample with m.p. 107.4–108.6° (lit.⁴ 108–109°).

The picrate melted at 219–220° (lit.⁴ 224–225°).

The N-acetyl derivative prepared according to Clemo and Swan's procedure⁴ had a m.p. of 151–152° (lit.⁴ 152–154°).

4-Nitro-3-picoline.—A solution of 5 g. of 4-nitro-3-picoline 1-oxide in 100 ml. of dry chloroform was cooled in an ice-bath to 3°. Twenty ml. of phosphorus trichloride was added dropwise under stirring. The rate of addition was regulated so as to keep the temperature of the reacting mixture below 10°. After the addition was completed, the mixture was stirred for 40 minutes below 10°, poured into about 100 g. of ice and basified cautiously with 20% sodium hydroxide solution. The aqueous and organic layers were separated and the aqueous solution was extracted with three 20-ml. portions of chloroform. The extracts were combined with the chloroform layer and dried over anhydrous sodium sulfate and the solvent was removed by distillation under reduced pressure. The yellow oil obtained

was distilled *in vacuo* and 2.9 g. (65%) of 4-nitro-3-picoline was collected at 57–59° (0.4 mm.). Upon cooling in ice the liquid solidified into colorless crystals. An analytical sample was obtained by redistillation of the liquid, b.p. 67–69° (1.5 mm.), m.p. 27–29°.

Anal. Calcd. for $C_8H_6O_2N_2$: C, 52.17; H, 4.37; N, 20.28. Found: C, 51.49; H, 4.89; N, 20.0.

The picrate crystallized in bright yellow plates, m.p. 128–129°.

Anal. Calcd. for $C_{12}H_9O_3N_5$: C, 39.24; H, 2.47; N, 19.07. Found: C, 39.52; H, 2.97; N, 19.1.

Hydrogenation of 4-Nitro-3-picoline.—Four hundred and ninety milligrams of the nitro compound was hydrogenated over 100 mg. of palladium catalyst in ethanol. Three hundred milligrams (77%) of 4-amino-3-picoline (m.p. 107–109°) was isolated in the manner described previously.

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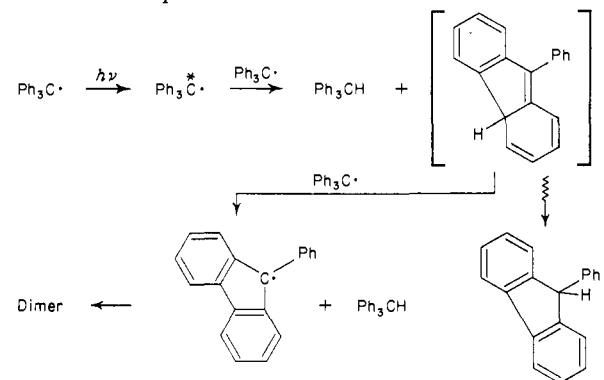
The Formation of 9-Phenylfluorene and Triphenylmethane by Disproportionation of Triphenylmethyl

By R. L. LETSINGER, R. COLLAT AND M. MAGNUSSON

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Triphenylmethyl undergoes a disproportionation when irradiated in benzene or a variety of other organic solvents¹ to yield 9-phenylfluorenyl (isolated as the dimer or peroxide) and triphenylmethane. We have observed that the reaction takes a somewhat different course when the solvent is dioxane which contains potassium hydroxide. In this case the products are 9-phenylfluorene and triphenylmethane, isolated in about equimolar amounts. As in benzene, however, the triphenylmethyl does not undergo disproportionation in the alkaline dioxane solution in the absence of light.

Apparently this is the first time that 9-phenylfluorene has been isolated from a reaction of the triphenylmethyl radical. The data for both the reaction in alkaline dioxane and in benzene are compatible with the paths indicated.



By this scheme the initial step would be the abstraction of a hydrogen atom from one triphenylmethyl radical by another radical which has been activated by the absorption of light. This reaction would give triphenylmethane and a diradical which could cyclize to give the reactive intermediate II. In the presence of alkaline dioxane, II could undergo aromatization by an allylic shift of a hydrogen ion to give 9-phenylfluorene (III). On

(3) We wish to thank the referee for pointing out that E. V. Brown, Abstracts of Papers, Los Angeles, Calif., Meeting of the A. C. S., March 15–19, 1953, p. 11M, has apparently prepared this compound by the persulfuric acid oxidation of 4-amino-3-picoline.

(4) G. R. Clemo and G. A. Swan, *J. Chem. Soc.*, 198 (1948).

(5) V. Boekelheide and W. J. Linn, *THIS JOURNAL*, **76**, 1290 (1954).

(1) M. Gomberg and L. H. Cone, *Ber.*, **37**, 3545 (1904); J. Schmidlin and A. Garcia-Banus, *ibid.*, 1344 (1912); S. T. Bowden and W. Jones, *J. Chem. Soc.*, 1149 (1928); M. Gomberg, *Chem. Revs.*, **1**, 91 (1924).

the other hand, in the absence of isomerizing conditions, II could react with another triphenylmethyl radical to give a second molecule of triphenylmethane and IV.

Experimental Part

Hexaphenylethane was prepared by reduction of triphenylchloromethane (10 g.) with vanadous chloride by the method of Conant and Scherp.² It was collected as a white powder on a Büchner funnel in an atmosphere of carbon dioxide, washed with boiled water, drained by suction and a rubber dam, and then dissolved in 250 ml. of purified dioxane which contained 5.6 g. of potassium hydroxide in solution. A nitrogen atmosphere was used. When air was passed through a 25-ml. aliquot of this solution, 0.75 g. of triphenylmethyl peroxide (m.p. 182–184°) precipitated.

A 100-ml. portion of the solution of hexaphenylethane was exposed to sunlight. At the end of three hours the reaction appeared complete, by the change in color from deep yellow to pale greenish yellow and the flask was opened. No precipitate of peroxide formed when air was passed into the flask. The solution was concentrated to 30 ml., then made up to a volume of about 100 ml. with ether, and washed with dilute hydrochloric acid. On evaporation of the ether solution a white crystalline solid separated, which after recrystallization from ethanol weighed 1.254 g. and melted at 142–146°. Further recrystallization raised the melting point to 146–147°. This material was identified as 9-phenylfluorene by a mixed melting point determination with a sample of 9-phenylfluorene prepared by the method of Kliegl.³ Triphenylmethane (0.898 g., m.p. 85–90°) was isolated from the mother liquors.

Another 100-ml. aliquot was allowed to stand in the dark for four days. At the end of this time air was passed into the solution, and 2.445 g. of triphenylmethyl peroxide (m.p. 185–186°) was obtained. No 9-phenylfluorene or triphenylmethane was found in the filtrate, which was treated as in the previous case. The only crystalline product isolated was a trace (0.012 g.) of triphenylcarbinol, m.p. 160–162°.

For comparison purposes, a sample of the hexaphenylethane (2 g.) was dissolved in 75 ml. of benzene and kept in the dark for 11 days. After aeration the reaction products were worked up as in the dioxane reaction. Only triphenylmethyl peroxide and a trace of ether soluble material were found. From a similar solution which had been exposed to sunlight a few hours, triphenylmethane and 9-phenylfluorene were obtained, m.p. 194.5–195.5, were obtained. There was no evidence for the presence of 9-phenylfluorene in either case.

(2) J. B. Conant and H. W. Scherp, *THIS JOURNAL*, **53**, 1941 (1931).

(3) A. Kliegl, *Ber.*, **38**, 284 (1905).

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Dialkyl α -Hydroxyphosphonates Derived from Chloral¹

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RECEIVED MARCH 20, 1954

As a part of a program on the preparation of candidate insecticides, we made a series of O,O-dialkyl 2,2,2-trichloro-1-hydroxyethylphosphonates, $(RO)_2P(O)CHOHCCl_3$, by condensing chloral with a dialkyl hydrogen phosphite.

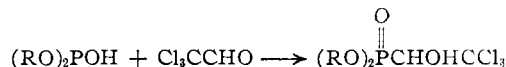
Abramov² described this condensation reaction, in which he used lithium or sodium methylate as a catalyst for condensing a series of aldehydes or ketones with a dialkyl hydrogen phosphite.

(1) This work was conducted under funds allotted by the Department of the Army to the Department of Agriculture.

(2) V. S. Abramov, *Doklady Akad. Nauk (S.S.S.R.)*, **73**, 487 (1950); *J. Gen. Chem. (U.S.S.R.)*, **22**, 647 (1952).

Fields³ obtained a process patent on the reaction of an aldehyde or ketone with diethyl hydrogen phosphite, using triethylamine as a catalyst to obtain a series of O,O-diethyl α -hydroxyphosphonates.

Craig and Hester⁴ condensed chloral and butyl chloral with some phosphite esters, particularly thiocyanalkyl phosphites, to obtain compounds claimed useful as toxic agents in insecticidal compositions. We found that no catalyst was necessary when the aldehyde used was chloral.



When equimolar quantities of chloral and dialkyl phosphite were mixed, an immediate exothermic reaction took place, which required moderate cooling. Since a catalyst was not added the purification of the final product was simplified. The lower members of the series (below butyl) are solids which were readily purified by recrystallization from appropriate solvents. The liquid dibutyl ester could not be purified by vacuum distillation since appreciable decomposition occurred on heating. The diethyl ester is described in the Fields' patent³ as a liquid which "decomposes over 100°." We found that the pure diethyl ester is a solid melting at 55–56°. The dimethyl ester⁵ has recently attracted interest as an insecticide effective against DDT-resistant house flies.

Dialkylhydrogen Phosphites.—These were prepared from phosphorus trichloride and the appropriate alcohol by the method of McCombie, *et al.*⁶ Their physical properties and yields are shown in Table I.

TABLE I
DIALKYL HYDROGEN PHOSPHITES

Phosphite	Yield, %	B.p.		n_D^{20}	Previously reported ⁷		n_D^{20}
		°C.	Mm.		B.p. °C.	Mm.	
Dimethyl	36	63–66	16	1.4005	55–55.5	10	1.4036
Diethyl	80	93	35	1.4057	75	15	1.4080
Dipropyl	65	97	23	1.4150	91.5	11	1.4172
Diisopropyl	55	97	40	1.4057	69.5	9	1.4008
Dibutyl	*	122–126	15	1.4220	115	10	1.4240

O,O-Dimethyl 2,2,2-Trichloro-1-hydroxyethylphosphonate.—To 15 g. of chloral (obtained by distilling chloral hydrate over sulfuric acid) was added 11 g. of freshly distilled dimethyl hydrogen phosphite. An immediate vigorous condensation reaction began, as evidenced by a sharp rise in temperature. The reaction mixture was kept below 80° by occasional cooling of the flask under the tap until the main reaction had subsided. The flask was stoppered and held overnight at room temperature. It was chilled in the refrigerator, but taken out from time to time and scratched with a stirring rod until crystallization was in-

(3) E. K. Fields, U. S. Patent 2,579,810 (1951).

(4) W. E. Craig and W. F. Hester, U. S. Patent 2,485,573 (1949).

(5) Technical grade O,O-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate has been designated as "L 13/59" and supplied by R. J. Geary, Bluepoint, N. Y., for entomological tests.

(6) I. H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

(7) B. A. Arbuzov and V. S. Vinogradova, *Izvestiya Akad. Nauk*, **55**, 620 (1947).

(8) Obtained from Virginia-Carolina Chemical Corporation, Richmond, Va.