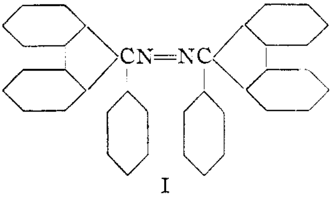
[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS UNIT OF THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Some Reactions of Hydrazophenylfluorene

BY LOUIS A. PINCK

As part of a program of research on the organic chemistry of nitrogen it was desired to determine more fully the properties of a few symmetrical azotriarylmethanes. It has been shown by Wieland[1] that azotriphenylmethane, $(C_6H_5)_3CN{=}NC(C_6H_5)_3$, is extremely unstable, decomposing into triphenylmethyl and nitrogen. On that basis it might be assumed that similar symmetrical azotriarylmethanes would likewise be unstable. The present investigation was undertaken with the object of attempting the preparation of azophenylfluorene, I, by the oxidation of the corresponding hydrazo compound. This paper will deal principally with the preparation and reactions of hydrazophenylfluorene.



I

A series of preliminary oxidation experiments, first carried out with hydrazotriphenylmethane, consisted largely of a repetition of the work reported by Wieland. His observation concerning the probable transitory existence of azotriphenylmethane was confirmed. It was found, for example, that the halogens, bromine and iodine, reacted with hydrazotriphenylmethane even at −40°. The ultimate products identified were nitrogen, triphenylmethyl peroxide, triphenylmethyl halide, triphenylcarbinol and hydrazine hydrohalide.[2] In this study no greater success was achieved from attempts to oxidize hydrazotriphenylmethane with freshly prepared oxides of silver, lead,[3] mercury and manganese. The action of benzoyl peroxide and benzoyl hydroperoxide upon the hydrazo compound yielded nitrogen and triphenylmethyl peroxide. Hydrazotriphenylmethane was decomposed by iodine pentoxide with the evolution of nitrogen and the simultaneous liberation of iodine.

It was considered that the extreme instability of azotriphenylmethane was intimately related to the weak affinity of the substituent triphenylmethyl group, which is manifested by the ability of the latter to exist as a free radical. In making another choice for the synthesis of a compound of

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[1] Wieland, *Ber.*, **42**, 3020 (1909). See also Stieglitz and Brown, THIS JOURNAL, **44**, 1270 (1922).

[2] Wieland reported the formation of hydrazotriphenylmethane hydrochloride from the hydrazo compound and hydrogen chloride. Upon repeating this experiment it was found that the reaction yielded triphenylchloromethane and hydrazine hydrochloride.

$$(C_6H_5)_3CNHNHC(C_6H_5)_3 + 3HCl \longrightarrow 2(C_6H_5)_3CCl + N_2H_4{\cdot}HCl$$

This reaction was found to be useful in the identification of a mixture of hydrazotriphenylmethane and triphenylmethyl peroxide.

[3] The use of silver and lead oxides was a repetition of Wieland's work and his results were confirmed.

the azotriarylmethane type, azophenylfluorene was selected. This compound seemed to be somewhat more promising because the related hydrocarbon, dibiphenylenediphenylethane, is reported to be dissociated to a less extent than hexaphenylethane.[4] Furthermore, the derivatives of phenylfluorene are much more stable and in general react more sluggishly than the corresponding derivatives of triphenylmethane. For example, Kliegl[5] pointed out that halogen derivatives of phenylfluorene appeared to be unusually stable when digested with water. He also reported his inability to secure condensations between the carbinol with aniline, hydroxylamine and phenylhydrazine similar to the well-known condensations of triphenylcarbinol that were first carried out by Baeyer and Villiger.[6] It is of interest, in this connection, that the chloride and carbinol derived from triphenylmethane are much more easily and smoothly reduced by various reagents to the parent hydrocarbon than the corresponding derivatives of phenylfluorene.[7]

Hydrazophenylfluorene was synthesized by the reaction of hydrazine hydrate with phenylbromofluorene in xylene solution. In various attempts to convert the product to the corresponding azo compound the following reagents were tried: "active" silver oxide,[8] potassium permanganate, benzoyl peroxide, bromine and palladium black. In the experiment with silver oxide practically all of the hydrazo compound was recovered. With potassium permanganate in anhydrous acetone and with benzoyl peroxide hydrazophenylfluorene was oxidized to phenylfluoryl peroxide. Better control of the oxidation did not result when bromine was employed.

Wieland's work[9] on the use of palladium black as catalyst for oxidation and reduction suggested the possibility that this reagent might cause the dehydrogenation of hydrazophenylfluorene, with the formation of the corresponding azo compound as one of the products. The results of the present investigation indicated that palladium black did promote the dehydrogenation of hydrazophenylfluorene. The principal products were nitrogen, phenylfluroene and a relatively small amount of dibiphenylenediphenylethane. It is not improbable that azophenylfluorene was an intermediate product. Its formation might be followed by its thermal decomposition and the subsequent hydrogenation of some of the resulting phenylfluoryl to phenylfluorene in the presence of palladium.

The action of oxygen upon hydrazophenylfluorene in the presence of palladium was studied. The hydrazo compound was oxidized, yielding a mixture of phenylfluoryl peroxide and phenylfluorenol. No other product could be isolated. The action of hydrogen in the presence of palladium

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(4) Schlenk, Herzenstein and Weickel, *Ber.*, **43**, 1754 (1910).

(5) Kliegl, *ibid.*, **38**, 284 (1905).

(6) Baeyer and Villiger, *ibid.*, **35**, 3015 (1902).

(7) Unpublished work.

(8) Willstätter and Müller, *Ber.*, **41**, 2580 (1908).

(9) Wieland, *ibid.*, **45**, 484, 2606, 2615 (1912); **46**, 2085, 3327 (1913).

black upon phenylfluoryl peroxide yielded phenylfluorene. A similar result has been noted for triphenylmethyl peroxide.[10]

Experimental

Preparation of Hydrazotriphenylmethane.—The following procedure is similar to the methods previously reported by Wieland and Stieglitz and Brown but is more convenient and results in higher yields. To a solution of 30 g. of 90% hydrazine hydrate in about 100 cc. of dry pyridine, 114 g. of triphenylchloromethane was added in small portions so that the temperature of the reaction mixture did not rise above 45–50°. The solution was agitated during the addition of the halide and for an hour thereafter. The solid organic matter was precipitated by the dilution of the reaction mixture with a large volume of water, collected and then extracted with alcohol, which dissolved triphenylcarbinol and left the hydrazotriphenylmethane. The latter was then crystallized and recrystallized from a mixture of benzene and alcohol as recommended by Wieland; yield 66.5 g., m. p. 212° with decomposition.

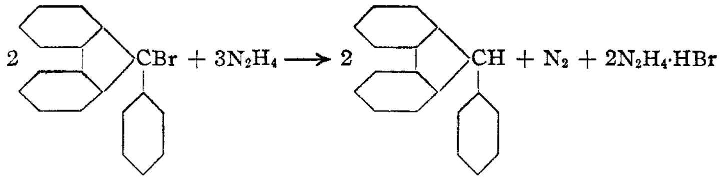
Preparation of Hydrazophenylfluorene.[11]—A mixture of 15 g. of phenylbromofluorene and 7.5 cc. of hydrazine hydrate (90%) in 50 cc. of xylene was heated at 100° for about two hours. The excess hydrazine was separated from the supernatant xylene solution and the latter diluted with petroleum ether and cooled in an ice-bath. A white solid (4.1 g.) precipitated; m. p. 181–182° with decomposition. This product was identified as a mixture of hydrazophenylfluorene and phenylfluoryl peroxide. The mixture was treated with warm ether, in which the hydrazo compound is considerably more soluble than the peroxide. Separation was thus effected. The hydrazo compound was recovered from the ether solution and upon recrystallization from the same solvent a yield of but 2 g. was obtained; m. p. 195–196°, with decomposition. The identification of the residual phenylfluoryl peroxide is detailed below.

Anal. Calcd. for $C_{38}H_{28}N_2$: C, 89.02; H, 5.51; N, 5.47. Found: C, 88.69, 88.77; H, 5.25, 5.34; N, 5.47, 5.55.

Hydrazophenylfluorene is very soluble in chloroform, xylene, acetone and benzene, somewhat soluble in alcohol and ether, and less soluble in petroleum ether, and acetic acid. This compound is much more susceptible to oxidation by air than hydrazotriphenylmethane, and, unlike the latter, does not react readily with ethereal or aqueous hydrogen chloride.

The ether insoluble fraction after two recrystallizations from benzene melted at 194°, and its melting point was not depressed after mixing with phenylfluoryl peroxide. Upon concentration of the mother liquor (xylene and petroleum ether solution) a crop of 3.5 g. of phenylfluorene, m. p. 146°, was obtained; mixed m. p. with phenylfluorene, 147°.

When the reaction was carried out at room temperature, the chief product was phenylfluorene.



A solution of 2 g. of phenylbromofluorene, 1 cc. of hydrazine hydrate (90%) in 20 cc. of xylene was allowed to stand at room temperature for about a week. Gas was slowly

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[10] Wieland and Müller, *Ann.*, **401**, 233 (1913).

[11] This compound can also be advantageously prepared by the use of acetonitrile as the solvent (unpublished work).

evolved and a small deposit of needle-like crystals was formed. The xylene solution was pipetted from the hydrazine hydrate and concentrated to a small volume; alcohol was added and crystallization induced, whereupon 0.70 g. of white solid separated; m. p. 144–145°. This was recrystallized from alcohol and ether; m. p. 147°; mixed m. p. with phenylfluorene, 147°.

Action of Sodium upon Hydrazophenylfluorene.—It had been observed that hydrazotriphenylmethane dissolved in liquid ammonia reacts at 0° with sodium; the product after treatment of the reaction mixture with water is triphenylmethane in 90% yield.[12]

A similar reaction was observed with hydrazophenylfluorene. A solution of 0.162 g. of hydrazophenylfluorene with an excess of sodium (0.029 g.) in dry liquid ammonia reacted vigorously at 0°, forming an orange colored solid (sodium phenylfluorene?). This was treated with water, and 0.150 g. of a white hydrolysis product was obtained; m. p., 143°. After one recrystallization from alcohol its melting point was 147° and was not depressed when the substance was mixed with phenylfluorene.

Attempts to Prepare Azophenylfluorene by the Oxidation of Hydrazophenylfluorene.—Four-tenths gram of hydrazophenylfluorene, 0.05 g. potassium permanganate and several grams of preheated sodium sulfate were added to acetone which had been purified by four distillations in the presence of potassium permanganate and dried over potassium hydroxide. The reaction mixture was shaken for four hours until all of the permanganate had been brought into reaction. The solution was filtered and concentrated in a vacuum desiccator. The first crop of crystals were white in the presence of the solvent and turned pink when dry, a property characteristic of phenylfluoryl peroxide; m. p. 189°, and m. p. of a mixture with phenylfluoryl peroxide, 192°. The residual material was found to consist of a mixture of hydrazophenylfluorene and phenylfluoryl peroxide.

A solution of 0.100 g. of benzoyl peroxide and 0.212 g. of hydrazophenylfluorene in 15 cc. of benzene was allowed to stand in a glass-stoppered Erlenmeyer flask in the dark for several weeks. Crystals were formed which upon filtration turned pink and melted at 192–193°. The melting point of a mixture with phenylfluoryl peroxide was also 192–193°.

When a gas-evolution tube containing 0.1 g. of hydrazophenylfluorene in about 10 cc. of xylene was heated in a water-bath to 80°, a slow evolution of a gas resulted. Another tube (Pyrex glass) containing a similar solution was placed in direct sunlight (temperature, 8°). Within two hours the solution turned yellow and gas was slowly given off. From a third tube kept in the dark for two weeks, less than 0.1 cc. of gas was obtained. After a specimen of the pure, solid hydrazo compound had been stored in a stoppered bottle in the dark for three to four months, it was re-analyzed; the nitrogen content (Dumas) was found to be 4.0%, representing a loss of 1.5%.

Behavior of Hydrazophenylfluorene in the Presence of Palladium Black.—Palladium black was prepared according to the directions given by Wieland.[13] In order to remove occluded oxygen from the palladium, the latter was treated with a stream of hydrogen for half an hour at room temperature and then for an hour at 100°. It was found that such treatment did not reduce the activity of the catalyst. One-tenth gram samples of hydrazophenylfluorene in 10 cc. of benzene (sodium-dried) and quantities varying from 0.2 g. to 0.8 g. of palladium black were used in each experiment. The air over the benzene solution was displaced by nitrogen in the presence of which the palladium was added. The tubes containing the reaction mixture were cooled in a liquid ammonia bath, evacuated, sealed and removed from the bath. A fairly vigorous gas evolution was observed for a period ranging from one to two hours. In a "blank run"

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(12) Unpublished work.

(13) Wieland, *Ber.*, **45**, 484 (1912).

with palladium black and benzene there was no perceptible gas evolution. In order to decrease the rate of decomposition, ether was substituted for benzene in one experiment and the observation was made at −48°. Here, too, gas was evolved. It was observed that the reactions did not go to completion, even when they were carried out at a higher temperature for several days or when a second addition of fresh palladium was made.

The contents of a tube which had been shaken at room temperature for three to four hours were filtered in an atmosphere of nitrogen. The solvent was evaporated in a stream of nitrogen, leaving a residue which melted and decomposed over the range 130 to 185°. It was extracted with petroleum ether (b. p. 35 to 55°) and the material (0.070 g.) recovered by evaporation of the petroleum ether was recrystallized from ligroin (b. p. 90 to 120°); m. p. 142°; mixed m. p. with phenylfluorene, 144–145°. The portion insoluble in petroleum ether melted and decomposed over the range 185 to 212°. This behavior is similar to that of a mixture of hydrazophenylfluorene and dibiphenylenediphenylethane. Since dibiphenylenediphenylethane is rather rapidly converted to the corresponding peroxide upon exposure to air, the petroleum ether insoluble portion was allowed to stand exposed to air for twenty-four hours. It was then found to melt with decomposition at 185°; mixed m. p. with known phenylfluoryl peroxide 189°, mixed m. p. with known hydrazophenylfluorene, 188–189°. A known mixture of hydrazophenylfluorene and phenylfluoryl peroxide (1:1) melted with decomposition at 189°. The gas evolved in the reaction of hydrazophenylfluorene with palladium black was freed from benzene vapor in a special gas analysis apparatus and was found to consist of nitrogen.

Action of Oxygen upon Hydrazophenylfluorene in the Presence of Palladium Black.—To a solution of 0.1 g. of hydrazophenylfluorene in 10 cc. of benzene, 0.5 g. of palladium black was added, and air was bubbled through the solution for three hours at room temperature. The solution was filtered and the solvent evaporated. The residue was washed with petroleum ether; m. p. 189–190°, with the characteristic orange-red coloration given by phenylfluoryl peroxide; mixed m. p. with the peroxide, 193°. The petroleum ether washings were evaporated and a substance was obtained which melted at 109°; mixed m. p. with phenylfluorenol, 109°.

Action of Hydrogen and Palladium Black upon Dibiphenylenediphenylethane.—Some of the ethane derivative, dissolved in benzene, was treated with hydrogen in the presence of palladium black for six hours at room temperature. The solution was filtered and the benzene evaporated in a stream of nitrogen. The residue melted at 142–143°; mixed m. p. with phenylfluorene, 145–146°.

Action of Hydrogen upon Phenylfluoryl Peroxide in the Presence of Palladium Black.—To a solution of 0.1 g. of phenylfluoryl peroxide in benzene was added some palladium black and the solution was treated with hydrogen at room temperature for three hours. The solvent was evaporated and the residue was found to melt at 180–182°. It was extracted with petroleum ether. The insoluble portion melted at 194–195° (unchanged phenylfluoryl peroxide) and the fraction recovered by evaporation of the petroleum ether melted at 145°; mixed m. p. with phenylfluorene, 145°.

The author is indebted to a number of his colleagues for helpful suggestions and especially to Dr. Leslie Hellerman of the Johns Hopkins University for advice and encouragement.

Summary

1. Wieland's observation concerning the momentary existence of azotriphenylmethane was confirmed.

2. Hydrazophenylfluorene was synthesized by the action of hydrazine

hydrate upon phenylbromofluorene. With sodium in liquid ammonia solution, the hydrazo compound reacted to form a product, which, when hydrolyzed, yielded phenylfluorene. With various oxidizing agents, hydrazophenylfluorene yielded mainly phenylfluoryl peroxide.

3. In experiments with palladium black, evidence was obtained for the possible momentary existence of azophenylfluorene; the compound, if formed, decomposed under the experimental conditions yielding nitrogen, phenylfluorene and dibiphenylenediphenylethane. The action of oxygen upon hydrazophenylfluorene in the presence of palladium black led to the formation of phenylfluoryl peroxide and phenylfluorenol.

4. The action of hydrogen upon dibiphenylenediphenylethane and upon phenylfluoryl peroxide in the presence of palladium black yielded phenylfluorene.

WASHINGTON, D. C.

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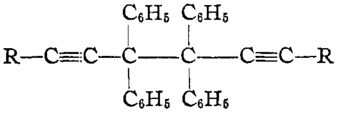
Rearrangements of Polyines. IV. Tetraphenyl-di-(3-methyl-3-ethylpentinyl-1)-ethane

BY J. HARMON AND C. S. MARVEL

Acetylenic hydrocarbons of the type represented in formula I have been found to be quite unstable and to undergo a characteristic rearrangement to produce more stable isomeric hydrocarbons.[1] The nature of this rearrangement is still unknown and as yet it is impossible to assign definite structures to the stable hydrocarbons. The present communication describes another unstable hydrocarbon of type I and its rearrangement products.



$$R-C\equiv C-\underset{C_6H_5}{\overset{C_6H_5}{C}}-\underset{C_6H_5}{\overset{C_6H_5}{C}}-C\equiv C-R$$

I

The reduction of diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol (II) with titanium trichloride to give the hydrocarbon $C_{42}H_{46}$ (III) has already been described.[2] The evidence indicated that this hydrocarbon was not the ethane (IV) but its stable rearrangement product. This fact has now been definitely established by the synthesis of the ethane derivative. The following chart indicates the method used in this synthesis and summarizes the reactions of the two isomeric hydrocarbons which have been studied in the hope of furnishing evidence which will eventually make it possible to understand the rearrangement of this class of polyines.

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(1) For references to earlier work, see Halley and Marvel, THIS JOURNAL, **54**, 4450 (1932).

(2) Sweet and Marvel, *ibid.*, **54**, 1184 (1932).