K-band of the benzanils was generally at a shorter wavelength and of lower intensity than that of the azobenzenes. The reason no doubt lies in the smaller resonance energy of the —C=N— group and the heats of combustion of benzanil and azobenzene[17] show that the former has a considerably lower resonance energy.

A further difference between benzanils and azobenzenes is the formation of stable *cis*-isomers of the latter. Attempts to isolate *cis*-benzanils have not been successful.[18] Irradiation of solutions of benzanil produced no change in magnetic susceptibility[19] and as found in the present work (Table I) no appreciable change in the absorption spectra.

EXPERIMENTAL

Compounds. The benzanils were prepared by condensing centimolar quantities of the appropriate benzaldehyde and aniline, by dissolving them in the minimum volume of absolute ethanol, warming slightly on a steam bath and allowing to stand at room-temperature overnight. They were recrystallized from ethanol, or from benzene-hexane, in the case of the more soluble compounds. Their melting points, together with literature values, are given in Table III. The anilines used were Eastman-Kodak white label samples. Many of the substituted benzaldehydes were freshly prepared by the Étard oxidation of substituted toluenes.[20] The solid benzanils are stable and samples have been stored in tightly stoppered tubes for over 2 years without any change in melting point or spectrum.

Absorption spectra. The absorption spectra were determined in Merck reagent grade methanol, dried with magnesium methoxide, employing a Beckman D. U. spectrometer mounted in an air-conditioned room with relative humidity of 40–45% and temperature 22 ± 1°. The cells used were conventional silica cells with loose-fitting caps and no special precautions were taken to exclude atmospheric moisture. The spectra were determined immediately on making up the solution and again after 1 hr., when in no case were any differences noted.

Acknowledgment. The authors are greatful to Dr. M. J. Kamlet of the U. S. Naval Ordnance Laboratory, Silver Spring, Md., for communicating his own findings on the hydrolysis of benzanils in aqueous solution.

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[17] G. E. Coats and L. E. Sutton, *J. Chem. Soc.*, 1187 (1948).

[18] F. Kröhnke, *Ber.*, **71**, 2593 (1938); J. Van Alpen, *Rec. trav. chim.*, **61**, 875 (1942). The two crystalline forms of α-*o*-hydroxybenzanil have been shown to be allotropes. V. de Gaouch and R. J. W. Le Fèvre, *J. Chem. Soc.*, 741 (1938).

[19] S. S. Bhatnajer, P. L. Kapur and M. S. Hashmi, *J. Ind. Chem. Soc.*, **15**, 573 (1938).

[20] O. H. Wheeler, *Can. J. Chem.*, **36**, 667 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRANDEIS UNIVERSITY]

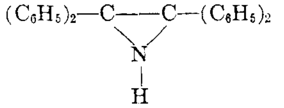
Some Reactions of Tetraarylethylenimines[1]

CHI-HUA WANG AND SAUL G. COHEN

Received December 30, 1960

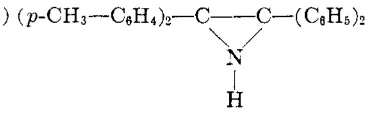
Reactions of 2,2,3,3-tetraphenylethylenimine I and 2,2-diphenyl-3,3-di-*p*-tolylethylenimine II have been studied. Compound I was converted (a) to tetraphenylethane by catalytic hydrogenation, (b) to benzophenone by periodic acid, and (c) to tetraphenylethylene, tetraphenylethylene oxide, and benzophenone by treatment with hydrochloric acid. Compound II was converted to *p,p'*-dimethylbenzophene and to a hydrocarbon by treatment with hydrochloric acid. The course of the reactions is discussed.

Study of the decomposition of azobisdiphenylmethane in the presence of thiophenol,[2] and then in the presence of benzophenone azine led to the conclusion that diphenylmethyl radical adds rapidly to benzophenone azine, leading to 2,2,3,3-tetraphenylethyleneimine

(I) 

$$\underset{\substack{\diagdown\ \diagup\\ \mathrm{N}\\ |\\ \mathrm{H}}}{(C_6H_5)_2\text{—C——C—}(C_6H_5)_2}$$

Subsequent experiments[3] indicated that I was also formed in decomposition of the azo compound in the presence of benzophenone hydrazone, ammonia being formed in this reaction. Also, diphenylmethyl radical from decomposition of the azo compound reacted rapidly with the azine from *p,p*-dimethylbenzophenone, leading to 2,2-diphenyl-3,3-di-*p*-tolylethylenimine[3]

(II) 

$$\underset{\substack{\diagdown\ \diagup\\ \mathrm{N}\\ |\\ \mathrm{H}}}{(p\text{-}CH_3\text{—}C_6H_4)_2\text{—C——C—}(C_6H_5)_2}$$

Although the oxide[4] and sulfide[5] of tetraphenylethylene have been known for some time, the

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[1] We are pleased to acknowledge generous support of this work by the National Science Foundation, Grant G.4244, and Fulbright and Guggenheim Fellowships to S.G.C.

[2] C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 1924 (1957).

[3] C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **82**, 4688 (1960).

[4] A. Behr, *Ber.*, **5**, 277 (1872).

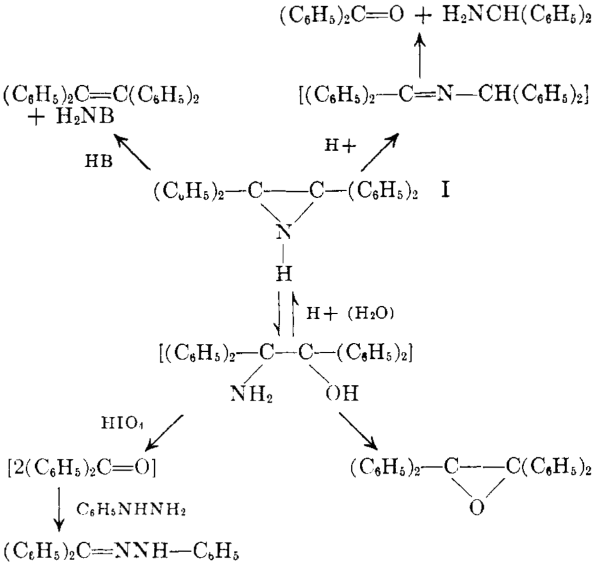
imine had not been reported, and it seemed of interest to confirm the structure of these tetraarylethylenimines and to study their reactions.

RESULTS AND DISCUSSION

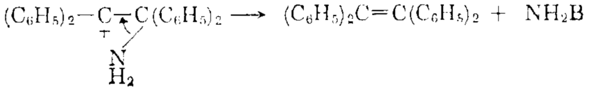
The imine I was obtained as yellow crystals from toluene or chloroform, m.p. 175–177°, but when crystallized from 1:1 benzene-ethanol it appeared as nearly white crystals which turned yellow in a melting point capillary at about 130° and then melted unsharply at 160–170°. Both forms were recovered unchanged from glacial acetic acid. Infrared spectra of the two forms in potassium bromide pellets were identical. Some chemical tests indicated that the two were not simply different crystal modifications but no definite conclusions in this respect can be reported at present.

The initial assignment[2] of structure to I was based on its composition and its catalytic hydrogenation to 1,1,2,2-tetraphenylethane; this hydrogenation has been repeated and the ethane has been isolated in 79% yield and ammonia detected in the reaction solution. An attempt to effect partial reduction to 1,1,2,2-tetraphenylethylamine by treatment with sodium borohydride failed, starting material being recovered. Similarly, treatment with dilute sodium hydroxide in dioxan led to no reaction and the imine was recovered.

On the other hand, the imine was very sensitive to mineral acid and underwent a variety of reactions. Treatment with periodic acid in acetic acid containing 0.05*N* hydrochloric acid led to benzophenone, isolated as its phenylhydrazone in 84% yield of two moles per mole of imine. Mild treatment of the imine I in dioxane solution with 3*N* hydrochloric acid led to isolation of tetraphenylethylene oxide in 72% yield, and, in another run, to tetraphenylethylene in 21% yield, both identified by mixed melting point. Photometric analysis of a portion of the solution indicated that ammonia was formed in 76% yield. Treatment with a lesser quantity of 1.2*N* hydrochloric acid in acetic acid led to the epoxide in 36% yield, identified by mixed melting point and infrared spectrum, and to some recovered unchanged imine. In addition a major product of this hydrolysis appeared to be benzophenone, isolated as its phenylhydrazone in 50% yield of one mole per mole of imine, and benzhydrylamine appears also to have been isolated as its hydrochloride. The reactions of I in the presence of mineral acid are indicated in the following chart, the reaction course in any one experiment depending upon the conditions.



It seems likely that the reaction with periodic acid proceeded by reversible hydrolysis to the unknown 1,1,2,2-tetraphenyl-2-aminoethanol, the equilibrium being displaced by rapid oxidative cleavage to benzophenone and its imine, both of which led to the phenylhydrazone. The presumed intermediate ethanolamine does not appear to persist in high concentration under these acidic conditions, and we were unable to isolate it from solutions from which both unchanged imine and newly formed epoxide were obtained. The formation and stability of the epoxide under these conditions is consistent with its formation from tetraphenylethylene dichloride in boiling water[6] and its dominant formation from tetraphenylethylene glycol in acetic acid in the course of the rearrangement of the pinacol to benzopinacolone[7] in the presence of perchloric acid. Benzopinacolone was not found in our work. The formation of tetraphenylethylene, while not anticipated, is analogous to the loss of chlorine from tetraphenylethylene dichloride,[8,9] and the failure of the ethylene to add bromine. The protonated imine is analogous to a chloronium or bromonium ion intermediate in halogenation and dehalogenation, and attack of a nucleophile on carbon leads to the substituted ethane, while attack on nitrogen (or halogen) leads to the ethylene.



$$(C_6H_5)_2-\underset{\substack{+\\N\\H_2}}{C-C}(C_6H_5)_2 \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + NH_2B$$

It may also be noted that tetraphenylethylene sulfide loses sulfur at elevated temperature and is converted to the ethylene.[5] Finally, the formation of benzophenone as a product of the hydrolysis is postulated to proceed by rearrangement of the ethylenimine to the benzophenone-benzhydrylketimine. This may imply that the protonated ethyl-

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(5) H. Staudinger, *Helv. Chim. Acta*, **3**, 838 (1920).

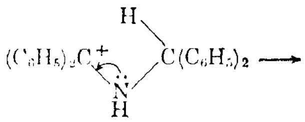
(6) J. Schmidlen and R. von Escher, *Ber.*, **43**, 1157 (1910).

(7) H. Gebhart and K. Adams, *J. Am. Chem. Soc.*, **76**, 3925 (1954).

(8) J. Norris, R. Thomas, and B. Brown, *Ber.*, **43**, 2952 (1910).

(9) R. M. McKinney, Ph.D. thesis, St. Louis University, 1958, p. 69.

enimine may undergo, in addition to heterolysis of a carbon-nitrogen bond with addition of the proton to nitrogen, heterolysis of the central carbon-carbon bond with addition of the proton to the anionic carbon. High resonance stabilization of both carbanion and carbonium ion in the present instance would favor this process:



Analogy for this rearrangement is found in the thermal conversion of 1,2-diphenylethylenimine to benzaldehyde-benzylimine.[10]

Two experiments were carried out on imine II, 2,2-diphenyl-3,3-di-*p*-tolylethylenimine with less clear results. Catalytic hydrogenation in ethanol led to absorption of slightly more than two moles of hydrogen, formation of one mole of ammonia, determined photometrically, and to only a trace of solid product. Treatment with aqueous hydrochloric acid in dioxan led to *p,p'*-dimethylbenzophenone in 56% yield, and in 35% yield to a hydrocarbon, m.p. 214–217° with analysis corresponding to $C_{28}H_{24}$. The epoxide was not found, loss of the NH group and rearrangement to the ketimine $(CH_3C_6H_4)_2—C{=}N—CH(C_6H_5)_2$ apparently being favored by the para-methyl substituents. Despite the satisfactory analysis, the hydrocarbon was not identical with a synthetic sample of 1,1-diphenyl-2,2-di-*p*-tolyl ethylene. It may be a dimethyl derivative of 9,10-diphenylphenanthrene, the formation of which from the imine may be formulated in a process analogous to the formation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride in the presence of aluminum chloride.[6]

EXPERIMENTAL

Hydrogenation of I. A solution of 0.20 g. (0.057 mmole) of I in 30 ml. of 95% ethanol was hydrogenated over platinum oxide, absorbing 2.8 ml. (0.11 mmole) of hydrogen. The solution showed a positive qualitative test for ammonia. It was filtered and concentrated, leading to 0.015 g. (0.045 mmole), 79% yield of tetraphenylethane, m.p. and mixed m.p. 208–210°.

Treatment of I *with basic reagents.* (i) A solution of I, 0.27 g., in 4 ml. of dioxane was treated with 0.5 ml. of 2% sodium hydroxide at 75° for 4 hr. There was no color change and I was recovered, 0.023 g., 87% yield, m.p. and mixed m.p. 174°. A trace of tetraphenylethane, m.p. 209–212° was also found.

(ii) A solution of 0.110 g. of I in 100 ml. of isopropyl alcohol and 1 ml. of water was treated with 0.015 g. of sodium borohydride at room temperature for several hours. The solution was concentrated and the residue chromatographed over florisyl leading to recovered I, 0.050 g., m.p. and mixed m.p. 172–175°.

Oxidation of I. (i) A solution of 0.088 g. of I in 50 ml. of glacial acetic acid was treated with 0.075 g. of iodine at room temperature for 2 hr. The solution was concentrated and the residue was crystallized from chloroform, leading to recovered I in essentially quantitative yield, m.p. and mixed m.p. 172–173°.

(ii) A solution of 0.050 g. (0.144 mmole) of I in 20 ml. of acetic acid and 6 ml. of 0.05*N* hydrochloric acid was treated with 0.150 g. of potassium periodate at room temperature for 2 hr., the color being discharged. The solution was concentrated and extracted with ether leading to a trace of tetraphenylethane, m.p. and mixed m.p. 206–207°. The ether solution was concentrated and the residue was taken up in alcohol, treated with phenylhydrazine, and boiled under reflux for 2 hr., leading to benzophenone phenylhydrazone, 0.066 g. (0.24 mmole, 84% yield). This was crystallized from ethanol, m.p. and mixed m.p. 134–136°.

Reactions of I *with acid.* (i) A solution of 0.065 g. (0.19 mmole) of I in 20 ml. of dioxane was treated with 3 ml. of 3*N* hydrochloric acid for 0.5 hr. at 60°, the yellow color being discharged rapidly. The solution was concentrated and the residue was dissolved in ether, dried and treated with hydrogen chloride, no precipitate forming. The solution was concentrated and the residue was crystallized from ethanol leading to tetraphenylethylene oxide, m.p. and mixed m.p. 204–205°, 0.047 g. 72% yield. A trace of hydrocarbon (C, 93.26; H, 6.67) was also found, melting unsharply, starting at 209°.

(ii) A solution of 0.245 g. (0.71 mmole) of I in 20 ml. of dioxane was treated with 4 ml. of 3*N* hydrochloric acid for 48 hr. at 6°. An aliquot, 0.02 ml. was treated with potassium carbonate solution and liberated ammonia was absorbed in 1 ml. of 2% boric acid, treated with Nessler's reagent, and analyzed photometrically, 0.47 and 0.43 μ mole being found in two runs, corresponding to 0.54 mmole in the reaction solution, 76% yield. From the reaction solution was isolated a hydrocarbon m.p. and mixed m.p. with tetraphenylethylene 218–220°, 0.050 g. 21% yield.

(iii) A solution of 0.070 g. (0.20 mmole) of I in 7 ml. of acetic acid and 0.5 ml. of 1.2*N* hydrochloric acid was stirred at room temperature for 1 hr., the yellow color being discharged. The solution was poured into water and the precipitate was crystallized from ethanol, tetraphenylethylene oxide, 0.025 g. (0.07 mmole) 36% yield, m.p. and mixed m.p. 204–205°, infrared spectrum in chloroform identical with that of an authentic sample. From the alcohol mother liquors was recovered 0.010 g., 14%, of compound I, m.p. and mixed m.p. 170–173°.

(iv) A solution of 0.200 g. (0.58 mmole) of I in 20 ml. of acetic acid and 2.5 ml. of 1.2*N* hydrochloric acid was stirred at room temperature for 18 hr. and worked up as in the preceding experiment, leading to tetraphenylethylene oxide, 0.065 g., 32% yield, m.p. 203–205°. The filtrate was boiled with 0.3 g. of phenylhydrazine in ethanol for 3 hr. leading to benzophenone phenylhydrazone, m.p. and mixed m.p. 134–136°, 0.079 g. (0.29 mmole) 50% yield. In another similar experiment, a solution of 0.050 g. (0.14 mmole) of I in 5 ml. of acetic acid and 0.5 ml. of 1.2*N* hydrochloric acid was stirred for 4 hr. The epoxide was removed and the remainder was concentrated, taken up in ether and treated with dry hydrogen chloride leading to a white precipitate, m.p. 240–244° from ethanol, possibly benzhydrylamine hydrochloride, 0.010 g. (0.046 mmole) 33% yield, reported,[11] m.p. 242°.

Hydrogenation of II. A solution of 0.022 g. (0.061 mmole) of II in 10 ml. of ethyl alcohol was hydrogenated over platinum oxide, absorbing about 3.5 ml. (0.14 mmole) of hydrogen. A trace of solid was isolated, m.p. 190–193°. An aliquot (0.02 ml.) of the hydrogenation solution was analyzed for ammonia, by isothermal distillation of the alkaline solution into boric acid, treatment with Nessler's reagent and colorimetric analysis, 0.02 ml. containing 0.12 μmole corresponding to 0.060 mmole in total.

Reaction of II *with acid.* A solution of 0.195 g. (0.52 mmole) of II in 15 ml. of dioxane and 3 ml. of 3*N* hydrochloric acid was kept at 6° for 2 hr. and at room temperature for 8 hr.

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[10] G. H. Coleman and C. S. Nicholopoulous, *Proc. Iowa Acad. Sci.*, **49**, 286 (1942).

[11] Valette, *Bull. Soc. Chim.*, **47**, 289 (1930).

The solution was concentrated under nitrogen, leading to a colorless compound, m.p. 214–217° from chloroform and from ethanol-acetone, m.p. depressed on mixture with tetraphenylethane and with tetraphenylethylene, 0.065 g., 35% yield.

Anal. Calcd. for $C_{28}H_{24}$: C, 93.3; H, 6.7; Found: C, 93.2; H, 6.8; N, 0.

The filtrates were concentrated and extracted with ether, leading to a solid which was crystallized from chloroform and ethanol, *p,p′*-dimethylbenzophenone, m.p. and mixed m.p. 90–92°, infrared spectrum in chloroform identical with that of an authentic sample, 0.060 g., (0.29 mmole) 56% yield. This product was also characterized as the oxime, m.p. 159–162°, reported[12] m.p. 161–162°.

Tetraphenylethylene was made by treatment of diphenylmethane with diphenyldichloromethane under reflux, m.p. 220–222°, reported[13] m.p. 223–224°.

Tetraphenylethylene oxide. Diphenyldichloromethane, 21 g. (0.09 mole) was treated with 28 g. (0.18 mole) of sodium iodide in 100 ml. of acetone for 2 days, leading to tetraphenylethylene dichloride, 12 g. (0.03 mole), 76% yield, m.p. 182°, reported[14] m.p. 182°. Treatment of the dichloride, 1.5 g. (3.7 mmoles) with 25 ml. of water under reflux for 18 hr. led to the epoxide, 0.8 g. (2.3 mmoles), 62% yield, m.p. 204–205°, reported[6] m.p. 203°.

1,1-Diphenyl-2,2-di-p-tolylethylene. Di-*p*-tolyl ketone (Eastman Kodak, m.p. 90–92°), 20 g. (0.095 mole) and phosphorus pentachloride, 15 g. (0.072 mole) were heated at 110° for 16 hr. Phosphorus oxychloride was removed in vacuum and the residue was treated with diphenylmethane (Matheson, b.p. 262–264°), 15 g. (0.09 mole) at 165° for 16 hr. The product was treated with 50 ml. of 1:1 benzene-ethanol and chromatographed over alumina, leading to 1,1-diphenyl-2,2-di-*p*-tolylethylene, 6.2 g. (0.017 mole), m.p. 161–163°, reported[15] m.p. 161°.

Acknowledgment. We are indebted to Alfred Stern for the preparation of tetraphenylethylene dichloride, tetraphenylethylene oxide, and tetraphenylethylene.

WALTHAM 54, MASS.

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[12] H. Goldschmidt, *Ber.*, **23**, 2747 (1890).

[13] O. Lohse, *Ber.*, **29**, 1789 (1896).

[14] H. Finkelstein, *Ber.*, **43**, 1533 (1910).

[15] E. Bergmann and D. Wagenberg, *Ber.*, **63B**, 2585 (1930).

[CONTRIBUTION FROM THE LION OIL CO., A DIVISION OF THE MONSANTO CHEMICAL CO.]

A New Urea Synthesis. I. The Reaction of Ammonia, Carbon Monoxide, and Sulfur[1]

RAYMOND A. FRANZ AND FRED APPLEGATH

Received December 28, 1960

Urea was prepared by a novel method based on two moles of ammonia to one each of carbon monoxide and sulfur. One mole of urea and one of hydrogen sulfide was produced. A mechanism, supported by experimental evidence, has been hypothesized for this reaction.

In spite of the fact that more than 125 years have passed since the synthesis of the first organic compound from inorganic materials, urea has again been made by a new method.[2] It was found that when a mixture of ammonia, carbon monoxide, and sulfur was heated at 120° for several hours in the presence of a suitable solvent, such as methanol, urea was formed in good yields. The stoichiometic equation is

$$CO + S + 2\,NH_3 \longrightarrow H_2NCONH_2 + H_2S$$

Although the mechanism of this reaction is still open to question, the one that is preferred by the authors is shown as follows:

$$\begin{tikzcd}
CO + S \arrow[r] & COS \arrow[r, "2\,NH_3"] & H_2NCOSNH_4 \arrow[dl] \\
H_2NCONH_2 & HNCO + NH_4HS \arrow[l, "NH_3"'] \arrow[r] & H_2S + NH_3
\end{tikzcd}$$

Experimental evidence for the proposed mechanism is as follows: The presence of as high as 30% carbonyl sulfide has been found by infrared in the product gases when the reaction was run at 150°. Ammonium thiocarbamate has been obtained in large quantities when the temperature of the reaction was held overnight at approximately 25–30° using carbon monoxide pressures of about 700 pounds per square inch gauge. Experimental evidence in support of isocyanic acid is based on the detection of the isocyanate group by infrared. An alcoholic solution of ammonium thiocarbamate was closely followed by infrared at room temperature for seven days. At the end of three days, a trace of a band at 4.63 μ showed up, which after five days had increased to a maximum. At the end of seven days this band had completely disappeared, while the urea band had grown progressively stronger, reaching its maximum in seven days. When a solution of known ammonium isocyanate in methanol was followed similarly by infrared, a very strong band was found at 4.65 μ, but after one day it almost disappeared with the simultaneous appearance of urea bands. Urea itself was identified by a mixed melting point with a known sample and quantitatively determined by the urease method.[3] The conversion of alcoholic

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[1] Presented at 16th Southwest Regional Meeting of the American Chemical Society, at Oklahoma City, December 1, 1960.

[2] U. S. Patent **2,857,430.**

[3] *Methods of Analysis AOAC*, 7th ed. (1950), p. 345.