with 20–50 mesh Dowex 50-X10 ion exchange resin and eluted with water. The resulting solution was neutralized with phenolphthalein as indicator. The amount of 0.2 *N* sodium hydroxide solution required (14.5 ml.) corresponded to 0.133 g. of formic acid (1.77 moles of acid per mole of tertiary amine). The neutralized solution was concentrated to dryness using a rotary evaporator, and the residue was washed with acetone and dried at 0.1 mm., yielding 0.175 g. of white crystals, the infrared spectrum of which (in a potassium bromide pellet) was identical with that of an authentic sample of sodium formate. Formation of the amine formate was avoided by oxidizing the amine in the presence of three equivalents of sodium carbonate.

Quaternary ammonium hydroxides were prepared from the methiodides as previously described.[4]

Pyrolysis of Amine Oxides and Quaternary Ammonium Hydroxides.—An aqueous solution containing 0.03 to 0.05 mole of the N-oxide or methohydroxide was concentrated and decomposed as described previously.[3] The product was dissolved in 50 ml. of cold pentane and washed as rapidly as possible with cold 50-ml. portions of 10% hydrochloric acid, 5% sodium bicarbonate solution and water. The pentane solution containing the olefins was dried over magnesium sulfate, filtered and distilled without fractionation through a semi-micro column. Small samples obtained before extraction, before drying and after distillation served for the gas chromatographic analyses, which were averaged and are reported in Tables V and VI. The aqueous washings were extracted twice with pentane and made basic with sodium hydroxide. The liberated amines were taken up in pentane, dried with sodium sulfate and distilled. The recovered amine in each case had a refractive index agreeing closely with that of the original amine. Treatment with acid was avoided in the isolation of the eight-membered cyclic olefins; they were separated from recovered tertiary amine by distillation.

Olefins.—The olefins newly prepared in this study are listed in Table VII. *trans*-1-Methylcyclononene was obtained from the olefinic products of the pyrolysis of N,N-dimethyl-1-methylcyclononylamine N-oxide. The olefin mixture (2.5 g.) was dissolved in 50 ml. of pentane and extracted twice with 50 ml. of a 50% aqueous silver nitrate solution. The silver nitrate solutions containing most of the *trans*-olefin were added to 350 ml. of cold concentrated ammonium hydroxide and extracted with pentane. The product, *trans*-1-methylcyclononene of 67% purity, was further purified by preparative gas chromatography at 90° using 4-methyl-4-nitropimelonitrile[36] (30% on firebrick) as the stationary phase. The collected material was distilled through a micro-distillation apparatus. Methylenecyclodecane was obtained analytically pure by pyrolysis of N,N-dimethylcyclodecylmethylamine N-oxide (Table VI). *cis*- and *trans*-1-methylcyclodecene were isolated from the products of the pyrolysis of N,N-dimethyl-1-methylcyclodecylamine N-oxide (Table V) by preparative gas chromatography at 90° using a 52% solution of silver nitrate in tetraethylene glycol (30% on firebrick) as the stationary phase.

Methylcycloalkanes.—Samples (0.002 mole) of the olefins produced by several of the elimination reactions were hydrogenated in the presence of 50 mg. of prereduced platinum oxide in 3 ml. of glacial acetic acid; 0.002 mole of hydrogen was taken up in each case. The mixtures were filtered, made basic with 2.4 g. of sodium hydroxide in a small amount of water, and extracted with two portions of pentane. The products were dried with magnesium sulfate and distilled in a micro-distillation apparatus. The olefin mixtures obtained by pyrolysis of N,N-dimethyl-1-methylcyclononylamine N-oxide (Table V) and of N,N-dimethylcyclononylmethylamine methohydroxide (Table VI) gave 67 and 86%, respectively, of methylcyclononane. Methylcyclodecane (70–86% yield) was obtained by hydrogenation of the olefinic products of the pyrolyses of the N-oxide and methohydroxide of N,N-dimethyl-1-methylcyclodecylamine (Table V) and of N,N-dimethylcyclodecylmethylamine methohydroxide (Table VI). The physical properties of the two methylcycloalkanes are listed in Table VII.

Stability of Methylenecycloöctane under the Conditions of the Oxidation.—To a mixture of 0.50 g. of N,N-dimethylcycloöctylmethylamine, 0.20 g. of methylenecyclooctane and 1 ml. of methanol was added 1.0 g. of 30% hydrogen peroxide solution. After stirring at room temperature for 48 hr. the excess hydrogen peroxide was destroyed by stirring the mixture with platinum black for 12 hr. The olefin was separated from the solution containing the N-oxide of N,N-dimethylcycloöctylmethylamine (which is stable at room temperature) by extraction with pentane. Analysis of the dried pentane solution by gas chromatography showed that no isomerization of the methylenecycloöctane to its endocyclic isomer had occurred. This experiment was repeated with the exception that N,N-dimethyl-1-methylcycloöctylamine was oxidized instead of N,N-dimethylcycloöctylmethylamine. The resulting olefin mixture was composed of 51% of methylene cyclooctane and 49% of 1-methylcycloöctene. The calculated olefin composition, assuming that the N,N-dimethyl-1-methylcycloöctylamine on oxidation gave a 56% yield of 1-methylcycloöctene and that the added methylenecycloöctane did not rearrange during the oxidation, is 50% each of methylenecycloöctane and 1-methylcyclooctene.

CAMBRIDGE, MASS.

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[36] H. A. Bruson, U. S. Patent 2,361,251; *C.A.*, **39**, 2079 (1945).

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC., WILMINGTON 98, DEL.]

The Wittig Reaction as a Polymerization Method[1a]

BY RICHARD N. MCDONALD AND TOD W. CAMPBELL[1b]

RECEIVED FEBRUARY 22, 1960

p-Xylylene-bis-(triphenylphosphonium chloride) reacted with terephthalaldehyde in the presence of lithium ethylate to yield a decamer of poly-*p*-xylylidene (II, $n = 9$, X = CHO). Treatment of (2-methoxy-5-methylalbenzyl)-triphenylphosphonium chloride with base produced the methoxy derivative of poly-*m*-xylylidene (V). (*p*-Hydroxyphenyl)-triphenylphosphonium bromide on treatment with base failed to yield poly-*p*-phenylene.

In recent work employing the Wittig reaction for the preparation of distyrylbenzenes,[2] diarylbutadienes[3] and 1,4-bis-(arylbutadienyl)-benzenes,[3] it became evident from the excellent yields in many of these syntheses that the Wittig reaction might lend itself to the preparation of polymers if suitable intermediates could be prepared. The polymers would be poly-xylylidenes which have not been reported in the literature, though the saturated poly-

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[1] (a) Paper III in the series "Synthesis of Hydrocarbon Derivatives by Wittig Synthesis." (b) To whom requests for reprints should be sent.

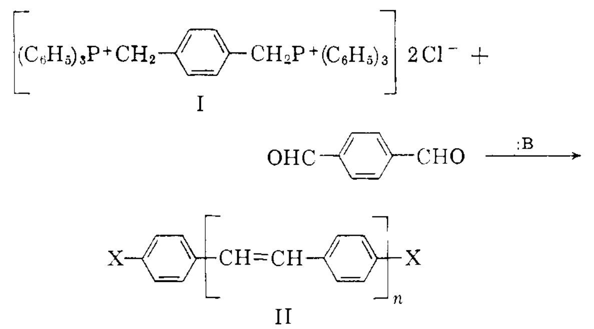
[2] T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

[3] R. N. McDonald and T. W. Campbell, *ibid.*, **24**, 1969 (1959).

mers, poly-xylylenes, have been well characterized.[4]

Two modes of synthesis of poly-xylylidenes by the Wittig reaction are apparent. These are (1) the reaction of an aryl bis-phosphorane and an aromatic bis-carbonyl compound, and (2) the preparation of a monomer containing both the phosphorane and carbonyl functions. This paper describes the use of method 1 for the preparation of a poly-*p*-xylylidene, and method 2 for the preparation of a poly-*m*-xylylidene and an attempt to prepare poly-*p*-phenylene.

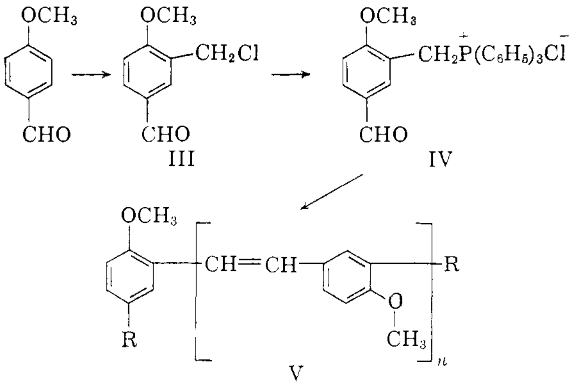
p-Xylylene-bis-(triphenylphosphonium chloride)[2] (I), a potential aryl bis-phosphorane, should react with terephthalaldehyde to produce poly-*p*-xylylidene (II).



From the highly conjugated nature of this polymer (II) it would be expected to be colored, whereas the unconjugated *m*-isomer should be colorless.

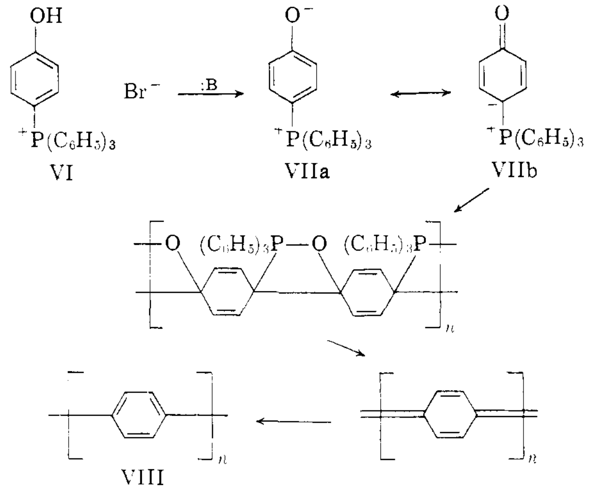
Treatment of an ethanolic solution of I and terephthalaldehyde with lithium ethylate in alcohol[5] gave a quantitative yield of an intensely yellow, insoluble polymer with a number average molecular weight of about 1200 calculated from elementary analyses (II, n = 9), terminated by carboxaldehyde groups (I, X = –CHO). This polymer readily added bromine to give a colorless solid, the saturated, brominated analog of II (X = –CHO).

The chloromethylation of anisaldehyde[6] to 2-methoxy-5-methylal-α-chlorotoluene (III) provided a convenient intermediate for the preparation of a poly-*m*-xylylidene by method 2. Compound III reacted with triphenylphosphine to give an excellent yield of the phosphonium salt, (2-methoxy-5-methylalbenzyl)-triphenylphosphonium chloride (IV). Treatment of an ethanolic solution of the phosphonium salt IV with a solution of lithium ethylate in ethanol gave an 81% yield of colorless, soluble polymeric *m*-xylylidene (V) with inherent viscosity of 0.31.[7] The infrared spectrum is in agreement with the structure of V and shows carboxaldehyde groups present as end groups. No bands attributable to the phosphonium salt grouping[8] were detected in



the polymer. Polymerization of IV in dimethyl sulfoxide with dry sodium methylate as base gave the same polymer, but of slightly lower molecular weight.

With the successful polymerizations given above utilizing the Wittig reaction, an extension of this chemistry to the preparation of poly-*p*-phenylene (VIII) seemed possible. This scheme is shown



The preparation of (*p*-hydroxyphenyl)-triphenylphosphonium bromide (VI) has been described by Horner and co-workers[9] by diazotizing the *p*-amino compound. However, this was a laborious method involving three low-yield steps. It was found that a phosphonium salt assigned structure VI could be prepared directly by heating *p*-bromophenol and triphenylphosphine at 200° under nitrogen for 4 hours. This gave a 44% yield of product, isolated as an anisole solvate, which on prolonged heating *in vacuo* gave the product solvent-free. Treatment of this salt in ethanol with lithium ethylate gave no evidence of reaction.

Experimental

Bis-phosphorane Polymerization.—Twenty grams (0.027 mole) of *p*-xylylene-bis-(triphenylphosphonium) chloride (*II*)[2] (recrystallized from ethanol–ether mixture) and 3.84 g. (0.029 mole) of terephthalaldehyde were stirred together in 200 ml. of absolute alcohol. A solution of 0.40 g. (0.058 g. atom) of lithium dissolved in ethanol (150 ml.) was added dropwise under nitrogen over a period of 1 hour. An intense orange-red color developed at the point of contact. On mix-

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[4] L. A. Auspos, L. A. R. Hall, J. K. Hubbard, W. Kirk, Jr., J. R. Schaefgen and S. B. Speck, *J. Polymer Sci.*, **15**, 9(1955); L. A. Auspos, C. W. Burnam, L. A. R. Hall, J. K. Hubbard, W. Kirk, Jr., J. R. Schaefgen and S. B. Speck, *ibid.*, **15**, 19 (1955); L. A. Errede and M. Szwarc, *Quart. Revs.*, **12**, 301 (1958).

[5] This base–solvent system had proved very useful in previous work.[2,3] If the desired product is insoluble in alcohol, it may be separated readily from the soluble by-product, triphenylphosphine oxide.

[6] R. Quelet and J. Allard, *Compt. rend.*, **205**, 238 (1937).

[7] Inherent viscosity = ln η_{rel}/concn., where concentration is 0.5% in *m*-cresol at 25°.

[8] J. C. Sheldon and S. Y. Tyree, This Journal, **80**, 2117 (1958).

[9] L. Horner, H. Hoffman, H. G. Wippe and G. Hassel, *Chem. Ber.*, **91**, 52 (1958).

ing, a bright lemon-yellow precipitate formed which was filtered, washed with alcohol and dried to give 6.4 g. (quantitative) of the poly-*p*-xylylidene (II), m.p. > 400°. The alcohol filtrate gave 13.4 g. (77%) of triphenylphosphine oxide, m.p. 158–159°.

Compound II was extracted with benzene to remove lower molecular weight material. Infrared and oxygen analyses indicated that II had an average value of $n = 9$, with aldehyde end groups.

Anal. Calcd. for $(C_8H_6)_n$: C, 94.1; H, 5.9. Calcd. for $C_{80}H_{60}O_2$: C, 91.2; H, 5.7; O, 3.0. Found: C, 91.0; H, 5.8; O, 3.2.[10]

Reaction of II with bromine in carbon tetrachloride gave a colorless solid, primarily the saturated, brominated analog of II, $C_{80}H_{60}Br_{18}O_2$.

Anal. Calcd. for $(C_8H_6Br_2)_n$: C, 36.6; H, 2.4; Br, 61.0. Calcd. for $C_{80}H_{60}Br_{18}O_2$: C, 38.5; H, 2.4; Br, 57.8. Found: C, 34.3; H, 2.2; Br, 55.9.

2-Methoxy-5-methylal-α-chlorotoluene (III).—Anisaldehyde was chloromethylated according to the procedure of Quelet and Allard.[6] The yield of III was 65%.

(2-Methoxy-5-methylalbenzyl)-triphenylphosphonium Chloride (IV).—A mixture of 74.7 g. (0.40 mole) of 2-methoxy-5-methylal-α-chlorotoluene (III) and 131 g. (0.50 mole) of triphenylphosphine in 600 ml. of xylene was heated under reflux for 20 hours. The off-white crystalline product was isolated by filtration, washed with xylene and dried *in vacuo* at 60°; yield 173.7 g. (97%), m.p. 207–209°. An analytical sample was recrystallized from dimethylformamide to give colorless needles, m.p. 208–210°.

Anal. Calcd. for $C_{27}H_{24}Cl_2O_2P$: C, 72.6; H, 5.4; Cl, 7.9. Found: C, 72.2; H, 5.7; Cl (total), 7.6.

Polymerization of IV.—To a solution of 10.0 g. (0.021 mole) of IV in 100 ml. of ethanol was added a solution of 0.16 g. (0.023 g. atom) of lithium dissolved in ethanol (100 ml.). The colorless poly-*m*-xylylidene (V) which precipitated from solution was isolated by filtration, washing with methanol and dried *in vacuo* at 60°. The yield of V was 2.4 g. (81%), with the polymer melt temperature of about 180° and inherent viscosity of 0.31.[7] The infrared spectrum showed the presence of unsaturation and carboxyaldehyde, presumably as end groups. No band attributable to the phosphonium salt group[8] was observed.

Anal. Calcd. for $(C_9H_9O)_n$: C, 81.2; H, 6.81; O, 12.02. Found: C, 80.9, 80.7; H, 6.34, 6.44; O, 12.15, 12.07.

The preparation of V also was carried out by the action of anhydrous sodium methylate on IV in dimethyl sulfoxide solution. The polymer obtained had an inherent viscosity of 0.21.[7]

(4-Hydroxyphenyl)-triphenylphosphonium Bromide (VI).—A mixture of 84 g. (0.33 mole) of triphenylphosphine and 56 g. (0.32 mole) of *p*-bromophenol was melted and stirred together under nitrogen. The mixture was heated for 4 hours at 200°, cooled to room temperature then mixed with 50 ml. of anisole and 50 ml. of cyclohexane. The top layer was separated and rejected, and the bottom layer was diluted with an additional 25 ml. of anisole and set aside in the refrigerator for 48 hours. In this manner 77 g. (44% based on a solvate with one mole of anisole) of a coarse, crystalline product was obtained essentially free of gummy by-products. The product was purified by recrystallization from anisole. Analysis of a freshly crystallized sample showed 14.6% ionic bromide *vs.* the calculated 18.4%. A direct oxygen analysis gave 5.82 and 5.88%. This and the bromide analysis corresponded to a solvate containing one mole of anisole. Prolonged heating *in vacuo* removed the solvent. The infrared spectrum showed no carbonyl and two types of benzene rings, both mono- and disubstituted. No band attributable to the phenolic hydroxyl could be detected.

Anal. Calcd. for $C_{24}H_{20}OPBr$: C, 66.2; H, 4.60. Found: C, 66.5, 66.2; H, 4.69, 4.81.

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[10] The method of J. Unterzaucher, *Analyst*, **77**, 584 (1952), was employed for direct oxygen determination.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

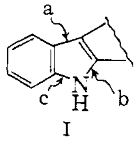
Dehydration of α-Phenylcyclohexanone Oxime

BY ERNEST WENKERT AND BUFORD F. BARNETT

RECEIVED NOVEMBER 9, 1959

The pyrolysis of α-phenylcyclohexanone oxime in a closed system and the characterization of the resulting products are described. The oxidation of tetrahydrocarbazole to carbazole by cyclohexanone oxime and the significance of this novel dehydrogenation in relation to the oxime pyrolysis is discussed. Both the thermal and acid-catalyzed conversions of 2-hydroxylaminobiphenyl to azo, azoxy and amino systems are portrayed. A variant of the Neber reaction on an ester of 2-phenylcyclohexanone oxime is described.

The most common methods of synthesis of indolic compounds (I) involve the formation of bonds a or b of the heterocyclic ring (*cf.* I) at the end of a reaction sequence, *e.g.*, the Fischer or Reissert syntheses. However, an occasion may arise which would demand the creation of bond c (*cf.* I) as the final step of a series of conversions of aromatic precursors. Such procedure is illustrated by three recently reported, different syntheses of carbazole derivatives. The pyrolysis of *o*-nitrobiphenyl with ferrous oxalate[1] as well as the pyrolysis or ultraviolet irradiation of *o*-axidobiphenyl[2] have been shown to yield carbazole, while the pyrolysis of α-phenylcycloalkanone oximes has led to 2,3-cycloalkindoles.[3] The last of these processes appears to be of potentially widest utility. For this reason a study of the pyrolysis of α-phenylcyclohexanone oxime was undertaken. While, as will be seen, this pyrolysis in a closed system was of greatly inferior synthetic value to that already explored in an open system,[3b] it led to valuable tangential information



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Heating of a benzene solution of α-phenylcyclohexanone oxime (IIa) in a sealed tube at 270° for twenty-four hours yielded a complex mixture of products from which the following substances could be isolated and characterized: carbazole (III), tetrahydrocarbazole (IV), α-phenylcyclohexanone (IIb), *trans*-2-phenylcyclohexanol (Va), *o*-hydroxybiphenyl (VIa), *trans*-2-phenylcyclohexylamine (Vb), *o*-aminobiphenyl (VIb), ε-phenyl-ε-caprolac-

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[1] H. C. Waterman, *J. Org. Chem.*, **14**, 289 (1949).

[2] P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2435 (1951).

[3] (a) D. Ginsburg and R. Pappo, *ibid.*, **75**, 1094 (1953); (b) D. Ginsburg and A. Loffler, *Nature*, **172**, 820 (1953).