trifluoroethanol was stirred at room temperature while 0.9 g. (0.005 mole) of cyanuric chloride was added gradually; the reaction temperature was held at 30–35°. After all the cyanuric chloride was added, the mixture was refluxed for 5 hr. A solid (potassium chloride) was separated by filtration. The filtrate was washed with water and the excess trifluoroethanol removed by distillation. The residue was washed with water and then dried. Recrystallizations from petroleum ether (b.p. 30–60°) gave colorless crystals; m.p. 45–46°; yield 1.2 g. (64%).

Anal. Calcd. for $C_9H_6F_9N_3O_3$: C, 28.80; H, 1.60; F, 45.60; N, 11.20. Found: C, 28.96; H, 1.54; F, 45.67; N, 11.60.

2,4,6-Tris(tribromoethoxy)-s-triazine (Ib). A solution of 0.9 g. (0.005 mole) of cyanuric chloride in 15 ml. of acetone was mixed with 4.4 g. (0.015 mole) of tribromoethanol in 15 ml. of acetone. A solution of 0.85 g. (0.015 mole) of potassium hydroxide in 10 ml. water was then added slowly in order to keep the reaction temperature around 45°. After all the solution was added, the mixture was continuously stirred for 20 min. The solid was separated by filtration and washed with water, alcohol, and then acetone. Repeated recrystallizations from methylene chloride and *n*-hexane yielded the product weighing 4.0 g. (86%); m.p. 280–281° dec.

Anal. Calcd. for $C_9H_6Br_9N_3O_3$: C, 11.70; H, 0.65; N, 4.56; Br, 77.89. Found: C, 11.57; H, 0.57; N, 4.64; Br, 78.38.

2,4,6-Tris[2,2,2-tris(nitroxymethyl)ethoxy]-s-triazine (Ic) was prepared in a manner similar to compound Ib by the reaction of cyanuric chloride with 2,2-bis(nitroxymethyl)-3-nitroxy-1-propanol; m.p. 131–132°; yield, 88%.

Anal. Calcd. for $C_{18}H_{24}N_{12}O_{30}$: C, 24.32; H, 2.71; N, 18.91. Found: C, 24.30; H, 2.89; N, 18.79.

2-Chloro-4,6-bis(2-methyl-2-nitropropoxy)-s-triazine was prepared in a manner similar to compound Ib by the reaction of cyanuric chloride with 2-methyl-2-nitro-1-propanol; m.p. 103–104°; yield, 17%.

Anal. Calcd. for $C_{11}H_{16}N_5O_6Cl$: C, 37.76; H, 4.57; N, 20.28; Cl, 10.15. Found: C, 38.16; H, 5.27; N, 20.33; Cl, 10.52.

2,4,6-Tris(2-methyl-2-nitropropoxy)-s-triazine (Id). A solution of 1.8 g. (0.01 mole) of cyanuric chloride and 3.7 g. (0.03 mole) of 2-methyl-2-nitro-1-propanol in 30 ml. of acetone was added to a solution of 1.7 g. of potassium hydroxide in 15 ml. of water. The temperature rose immediately to 55° and then the mixture was allowed to reflux for 1.5 hr. Evaporization of the acetone gave a white solid which was recrystallized from a nitromethane–methanol mixture; m.p. 248–249°. Analyses indicated the formation of the triester; yield, 0.7 g. (16%).

Anal. Calcd. for $C_{15}H_{24}N_6O_9$: C, 41.64; H, 5.55; N, 19.44. Found: C, 41.98; H, 5.65; N, 19.85.

Acknowledgment. We are indebted to Dr. J. H. Boyer and Professor M. L. Wolfrom for helpful discussions. We are also grateful to Mrs. P. Wheeler for the elemental analyses.

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An Intramolecular Wittig Olefin Synthesis[1,2]

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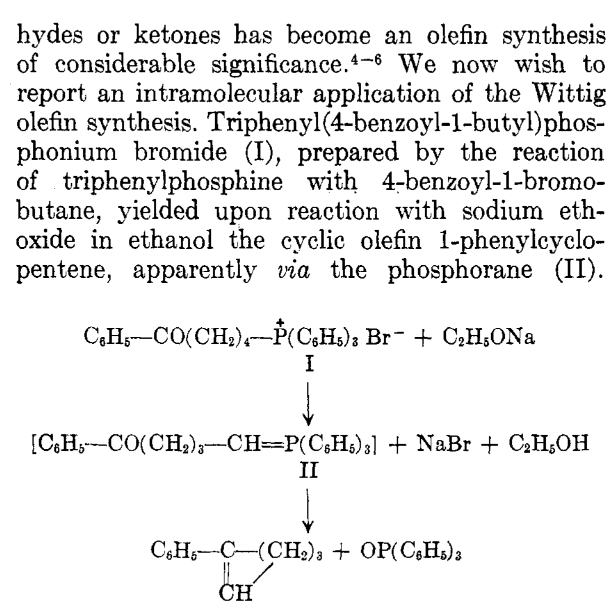
Received August 24, 1961

The Wittig reaction between phosphoranes (from phosphonium salts plus base) and aldehydes or ketones has become an olefin synthesis of considerable significance.[4–6] We now wish to report an intramolecular application of the Wittig olefin synthesis. Triphenyl(4-benzoyl-1-butyl)phosphonium bromide (I), prepared by the reaction of triphenylphosphine with 4-benzoyl-1-bromobutane, yielded upon reaction with sodium ethoxide in ethanol the cyclic olefin 1-phenylcyclopentene, apparently *via* the phosphorane (II).



$$C_6H_5—CO(CH_2)_4—\overset{+}{P}(C_6H_5)_3\,Br^- + C_2H_5ONa$$

I

$$[C_6H_5—CO(CH_2)_3—CH{=}P(C_6H_5)_3] + NaBr + C_2H_5OH$$

II

The olefin thus obtained was identical with 1-phenylcyclopentene synthesized according to Bauer[7] by addition of phenyl Grignard reagent to cyclopentanone and dehydration of the resulting 1-phenylcyclopentanol with formic acid. The yield of this internal Wittig olefin synthesis was 24%. With lithium ethoxide in ethanol a comparable yield was obtained, but with phenyllithium in ether only about 1% of the cyclic olefin resulted.

Even if the intramolecular Wittig olefin synthesis inherently gives low yields of cyclic olefins, the method may prove useful in those cases where the olefinic double bond is to be located in a given position and other methods involving an elimination reaction as the final step would yield mixtures of isomers or the wrong isomer. It is to be expected that the intramolecular Wittig olefin synthesis, like the well established intermolecular kind,[6] permits specific placement of the double bond and is not complicated by subsequent isomerization.

As to the mechanism of the intramolecular Wittig olefin synthesis, there is no reason to believe that it is basically different from that suggested[4–6] for the intermolecular kind.

Reaction of I with aqueous sodium hydroxide proceeded with the normal elimination of a phenyl

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(1) Supported in part by the Faculty Research Fund of the University of Mississippi.

(2) Some of this work was presented before the Southeastern Regional Meeting of the American Chemical Society in Birmingham, Ala., November 3, 1960, Abstracts p. 10.

(3) Taken from the M.S. dissertation submitted by Eugene H. Eisman to The University of Mississippi in June 1961.

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(5) G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

(6) S. Trippett, "The Wittig Reaction," in *Advances in Organic Chemistry: Methods and Results*, Vol. 1, R. Raphael, E. Taylor, and H. Wynberg, eds., Interscience, New York, 1960, pp. 83–102.

(7) E. Bauer, *Ann. chim. et phys.*, [9] **1**, 367 (1914).

group,[8] to give diphenyl(4-benzoyl-1-butyl)phosphine oxide (III), identified by elemental and infrared analysis.

$$\begin{array}{l} I + NaOH \longrightarrow \\ \qquad [C_6H_5—CO(CH_2)_4—P(OH)(C_6H_5)_3] + NaBr \\ \qquad\qquad \downarrow \\ C_6H_5—CO—(CH_2)_4—P(O)(C_6H_5)_2 + C_6H_6 \\ \qquad\qquad III \end{array}$$

EXPERIMENTAL[9]

4-Benzoyl-1-bromobutane. This was prepared by a method based upon that of Perkin[10] but greatly simplified.

To an ethanolic sodium ethoxide solution, prepared from 5.0 g. (0.22 mole) of sodium and 75 ml. of dry ethanol, was added with stirring a mixture of 40 g. (0.21 mole) of ethyl benzoylacetate and 42 g. (0.18 mole) of 1,3-dibromopropane. After a refluxing period of 4 hr. there was added a second portion of ethanolic sodium ethoxide solution, prepared with the same quantities of reagents as the initial portion, and refluxing was continued for 16 hr. The reaction mixture was filtered to free it from precipitated sodium bromide, and most of the alcohol was distilled. More sodium bromide precipitated during the removal of the alcohol. Addition of water to the residual mixture resulted in the formation of two liquid layers. The lower layer consisted of crude 3,4-dihydro-5-carbethoxy-6-phenyl-2*H*-pyran. This was treated without resort to purification with 83 ml. of 48% hydrogen bromide (d_4^{24} 1.49). The reaction mixture, which consisted of two layers, began to bubble vigorously (carbon dioxide) after standing a few minutes at room temperature. There were still two layers after one hour's refluxing. On cooling the upper layer solidified and could be separated by suction filtration. This solid (23.8 g.) consisted of crude 4-benzoyl-1-bromobutane. Another 3.1 g. could be recovered from the filtrate by extraction with petroleum ether and evaporation of the latter. The combined crude product was recrystallized from ethanol. The recrystallized product (14.8 g., 36%) had m.p. 52–54°, a lower m.p. than that (61°) reported by Perkin, but was of satisfactory quality for use in the subsequent step.

Triphenyl(4-benzoyl-1-butyl)phosphonium bromide. A mixture of 19.0 g. (0.079 mole) of 4-benzoyl-1-bromobutane and 22.8 g. (0.087 mole) of triphenylphosphine[11] was maintained at 100° for 88 hr., care being taken to screen the reaction mixture from light in view of the light sensitivity of alkyl bromides. The reaction mixture liquefied at first and then gradually resolidified. The crude product was ground under ether, filtered, and washed repeatedly with ether. There was thus obtained 28.2 g. (71%) of white product, m.p. 167° with softening at 163°. The purity of this product is adequate for the intramolecular Wittig olefin synthesis. To obtain a sample for analysis some of the product was recrystallized from ethanol–ether. The m.p. was then 167°.

Anal. Calcd. for $C_{29}H_{28}BrOP$: C, 69.23; H, 5.61; Br, 15.89; P, 6.16. Found: C, 68.97; H, 5.67; Br, 16.2; P, 5.98.

1-Phenylcyclopentene by intramolecular Wittig olefin synthesis. To a hot ethanolic sodium ethoxide solution prepared from 0.50 g. (0.022 mole) of sodium and 60 ml. of dry ethanol was added 10 g. (0.020 mole) of finely powdered triphenyl(4-benzoyl-1-butyl)phosphonium bromide. The solution turned bright orange and then a rust color. Subsequent refluxing for 0.5 hr. caused much sodium bromide to precipitate. This was removed by filtration. The alcohol was stripped from the filtrate by distillation and then the olefinic product was distilled at 121–122°/20 mm., the yield being 0.68 g. (24%). Infrared examination of the residue showed it to contain triphenylphosphine oxide. A redistilled sample of the olefin had m.p. 21–22° and n_D^{27} 1.5720. Bauer reports similar b.p., m.p., and n_D^{25} for 1-phenylcyclopentene prepared by addition of phenyl Grignard reagent to cyclopentanone and dehydration of the resulting 1-phenylcyclopentanol with formic acid.[7] We repeated Bauer's preparation and showed that the products of the two methods had identical infrared spectra.

Diphenyl(4-benzoyl-1-butyl)phosphine oxide. A solution of 10 g. of sodium hydroxide in 50 ml. of water was added to a solution of 1.00 g. (0.00199 mole) of triphenyl(4-benzoyl-1-butyl)phosphonium bromide in 100 ml. of water. A cloudiness resulted upon mixing, and on boiling a light yellow precipitate formed. The odor of benzene was evident during boiling. The precipitate was filtered, washed with water, and dried. It weighed 0.48 g. (65%) and had m.p. 148–149°. It was recrystallized from ethanol-water. The white crystals had m.p. 150–150.5°.

Anal. Calcd. for $C_{23}H_{23}O_2P$: C, 76.20; H, 6.40; O, 8.84; P, 8.55. Found: C, 76.27; H, 6.55; O, 8.83 (by direct analysis); P, 8.35.

The infrared spectrum of the substance corroborated its structure.

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[9] Temperatures are not corrected.

[10] W. H. Perkin, *J. Chem. Soc.*, **51**, 726 (1887).

[11] Donated by Metal and Thermit Corp., Rahway, N. J.

Electron Exchange Polymers. XVI. The Oxidation Behavior of Dimethyl Ethers of Hydroquinone and Methyl-Substituted Hydroquinones

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Received August 25, 1961

In the preparation of monomers derived from vinyl hydroquinone and their subsequent polymerization to poly(vinylhydroquinone)-based electron-exchange polymers[3] the ether link is useful for covering the sensitive hydroquinone hydroxyl group. However, it is then difficult to uncover these groups after the polymer has been prepared. A study of oxidative cleavage of the hydroquinone methyl ethers produced the results reported here.

It has been reported[4] that oxidations of 1,4-dimethoxy-2-substituted benzenes with chromic oxide yield diquinones, and that diquinones are also produced in the oxidation of 2-methoxy-6-[1-propyl]quinone in the presence of hydrochloric

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[3] H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 402 (1949). I. H. Updegraff and H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 407 (1949). R. Stern, J. English, Jr., and H. G. Cassidy, *J. Am. Chem. Soc.*, **79**, 5792 (1957).

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