hr. The methanol was removed under reduced pressure and the solid remaining was washed with water. Recrystallization from methanol afforded 1.2 g. (50%) of XV, m.p. and mixed m.p. with authentic sample, 101–102°.

2,9-Dichloro-6H,13H-*p*-dithiino[2,3-*c*:5,6-*c*′]bis[1]benzopyrane-6,13-dione (XVI).—A solution of 2.50 g. of Ib and 2.28 g. of thiourea in 125 ml. of absolute methanol was refluxed for 5 hr. A yellow precipitate formed after about 20 min. and became progressively heavier. The yellow solid was filtered from the hot methanol, washed with hot methanol (*ca.* 100 ml.), washed with water (*ca.* 100 ml.), and dried to yield 1.98 g. (94%) of XVI, m.p. > 450° (5.88 μ, 1770 cm.$^{-1}$). The material could not be satisfactorily recrystallized from any of the solvents tried nor could it be sublimed under vacuum. The analytical sample was obtained by extracting 0.5 g. with 200 ml. of boiling methanol and sending the residue for analysis.

Anal. Calcd. for $C_{18}H_6Cl_2O_4S_2$: C, 51.3; H, 1.4; Cl, 16.8; S, 15.2. Found: C, 51.0, 51.1; H, 2.0, 1.8; Cl, 16.7; S, 15.3.

4-(β-Hydroxyethylamino)coumarin (XVII).—A solution of 1.80 g. of 4-chlorocoumarin[25] and 1.22 g. of ethanolamine in 40 ml. of absolute methanol was refluxed for 45 min. The methanol was removed under reduced pressure and the resulting solid was washed with 30 ml. of water and recrystallized from methanol (*ca.* 15 ml.) to yield 1.50 g. (74%) of XVII, m.p. 171–173° (6.00 μ, 1643 cm.$^{-1}$). Several recrystallizations from methanol gave the analytical sample, m.p. 172.5–174.0°.

Anal. Calcd. for $C_{11}H_{11}NO_3$: C, 64.5; H, 5.4; N, 6.8. Found: C, 64.8; H, 5.7; N, 7.0.

A solution of 1.02 g. of XVII and 0.05 g. of fused sodium acetate in 5 ml. of acetic anhydride was refluxed for 2 hr., cooled, and poured into 40 ml. of cold water. The pH was adjusted to about 7.3 by the addition of potassium carbonate and the resulting white solid was filtered, washed with 75 ml. of water, and recrystallized from methanol (*ca.* 10 ml.) to yield 1.12 g. (90%) of 4-(β-acetoxyethylamino)coumarin, m.p. 161–163° (5.84 μ, 1716 cm.$^{-1}$). Several recrystallizations from methanol gave the analytical sample, m.p. 162–163°.

Anal. Calcd. for $C_{13}H_{13}NO_4$: C, 63.3; H, 5.3; N, 5.7. Found: C, 63.5; H, 5.5; N, 6.0.

N-(2-Acetoxyethyl)-N-acetyl-*o*-toluidine (XXII).—A solution of 100 g. of β-*o*-toluidinoethanol[26] (XVIII) and 0.1 g. of fused sodium acetate in 100 ml. of acetic anhydride was refluxed for 1 hr., cooled, and poured into 500 ml. of cold water. The pH was adjusted to about 7.5 by the addition of potassium carbonate. The mixture was extracted twice with 100 ml. of benzene. The combined benzene extract was washed twice with 50 ml. of water and once with 50 ml. of a saturated aqueous sodium chloride solution. The benzene was removed under reduced pressure. Two distillations of the residual oil gave 10.5 g. (68%) of XXII, b.p. 150–153° (4 mm.), n^{24}D 1.5138 (5.78 μ, 1730 cm.$^{-}$) (6.02 μ, 1661 cm.$^{-1}$).

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.4; H, 7.3; N, 6.0. Found: C, 66.4; H, 7.4; N, 6.0.

3,6-Dichloro-4-(*n*-propylamino)coumarin (XIX).—A stirred slurry of 2.50 g. of Ib in 25 ml. of absolute methanol was cooled to 2° and to it was added 1.18 g. of *n*-propylamine. The stirring was continued and the temperature was maintained at 2–3° for 1 hr. at which point solution was complete, at 24–26° for 2 hr., and at 40–50° for 3 hr. The methanol was removed under reduced pressure and the resulting white solid was washed with 25 ml. of water and recrystallized from absolute methanol (*ca.* 25 ml.) to yield 2.63 g. (97%) of XIX, m.p. 189–190° (6.01 μ, 1664 cm.$^{-1}$). Several recrystallizations from methanol gave the analytical sample, m.p. 189.6–190.2°.

Anal. Calcd. for $C_{12}H_{11}Cl_2NO_2$; C, 53.0; H, 4.1; Cl, 26.0; N, 5.1. Found: C, 53.3; H, 4.3; Cl, 25.8; N, 5.1.

All attempts to prepare the bis-*n*-propylamino compound failed. When XIX was treated with two equivalents of *n*-propylamine in methanol or NMP it was recovered unchanged. Then XIX was added to excess *n*-propylamine at 2° only tars were isolated. When XIX was treated with refluxing acetic anhydride (sodium acetate catalyst), it was recovered unchanged.

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[25] Prepared from 4-hydroxycoumarin (Aldrich Chemical Co., Milwaukee, Wis.) by the procedure of D. P. Spalding, H. S. Mosher, and F. C. Whitmore, *J. Am. Chem. Soc.*, **72**, 5338 (1950).

[26] Purchased from Distillation Products Industries, Rochester 3, N. Y.

Isolation, Identification, and Synthesis of Components of a "Styrene Dimer Fraction"

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The following components were isolated and identified in a "styrene dimer fraction" obtained by refluxing styrene with a small amount of sulfur: 1,3-diphenylpropane (I), *cis*-1,3-diphenyl-2-butene (IV), 2,4-diphenyl-1-butene (III), and *trans*-1,3-diphenyl-2-butene (V). This paper illustrates the utility of the combination of mass, infrared, n.m.r., and ultraviolet spectrometry in the identification of small amounts of organic compounds isolated by gas chromatography.

A "styrene dimer fraction" was obtained by refluxing 104 g. (1.00 mole) of freshly distilled styrene and 0.32 g. (0.010 mole) of sulfur for three hours at 143–150° (pot temperature) under nitrogen. Distillation at 0.2 mm. through a Vigreux column (8 in. × 1 in.) at 0.2 mm. gave 3.9 g. of a "dimer fraction" (head temperature 80–135°). We are concerned here with the isolation, identification, and synthesis of the components of this mixture. Results of a continuing study[1] of styrene dimerization will be presented elsewhere.

Four pure components were isolated by gas chromatography. The initial separation was made on a DC-710 silicone substrate; each of the three initial cuts was subjected to further separation on a QF1-0065 fluorosilicone substrate. Heart cuts on the latter substrate were taken until each of the four components isolated appeared to be chromatographically homogeneous on both substrates. Tentative identification was made by mass, infrared, nuclear magnetic resonance, and ultraviolet spectrometry, and by derivatization when indicated. Comparison of spectral characteristics and gas chromatographic behavior with those of authentic samples afforded conclusive identification. The components are numbered in order of elution from the DC-710 silicone column.

Identification

Component No. 1.—Components no. 1 and no. 2 were eluted together from the DC710 silicone column and were separated by repeated passes on the QF1-0065 fluorosilicone column. On the latter column, component no. 2 preceded component no. 1.

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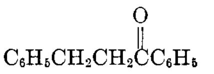
[1] F. R. Mayo, Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

A mass spectrum of component no. 1 showed a mass 208 peak (styrene dimer molecular weight is 208) whose intensity was 4% of the base peak, mass 92, which is a common benzyl rearrangement peak. The benzyl ion peak (91) was 57%; an unexpected peak at mass 196 (intensity 49%) was also present. The infrared spectrum showed more methylene absorption at 3.42 μ compared with the other components, and the n.m.r. spectrum effectively ruled out any styrene dimer structure we could write, including olefins, cyclobutanes, tetralins, or indanes. The n.m.r. spectrum showed 10 protons at τ 2.91, 4 protons as a slightly distorted triplet at τ 7.41, and 2 protons as a quintet (with some second-order perturbation) at τ 8.1. The answer quickly became apparent, once we assumed the mass 208 peak to be an impurity and took mass 196 as the parent peak. The parent +1 peak was 16.3% of the parent peak and the parent +2 peak was 1.26% of the parent peak. These values give an excellent fit for the calculated values[2,3] for empirical formula $C_{15}H_{16}$. With this information available, the n.m.r. spectrum spells out 1,3-diphenylpropane (I). Comparison with an authentic sample confirmed this identification.

$C_6H_5CH_2CH_2CH_2C_6H_5$

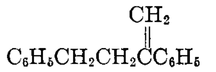
I

Though in retrospect the picture seems clear, considerable confusion ensued when chromic acid oxidation of component no. 1 yielded the same product obtained on oxidation of component no. 3; the product was β-phenylpropiophenone (II). Marion[4] pointed out that chromic acid oxidation of 1,3-diphenylpropane (I) gave a good yield of β-phenylpropiophenone (II). Marion also noted that Staudinger[5] obtained β-phenylpropiophenone (II) on oxidation of a "styrene dimer fraction" from pyrolysis of polystyrene. On this basis, Staudinger assumed the presence of 2,4-diphenyl-1-butene (III) in his "styrene dimer fraction." Marion suggested that Staudinger's precursor was, in fact, 1,3-diphenylpropane (I) rather than 2,4-diphenyl-1-butene (III).



$C_6H_5CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5$

II

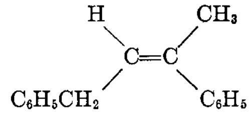


$C_6H_5CH_2CH_2\overset{\overset{\displaystyle CH_2}{\|}}{C}C_6H_5$

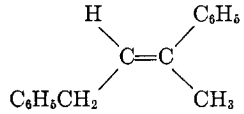
III

The presence of 1,3-diphenylpropane (I) in our "styrene dimer fraction" can be attributed to pyrolysis, during distillation, of the considerable amount of polystyrene present.

Component No. 2 and Component No. 4.—Component no. 2, a minor component, was separated, as noted above, from component no. 1 on the fluorosilicone column. The infrared spectrum showed two strong bands in the 13–14.5-μ region, characteristic of the C—H bending vibrations of monosubstituted benzene rings. The aliphatic C—H stretching band at 3.45 μ was weaker than the aromatic and olefin C—H stretching band at 3.32 μ. There was no sign of a C=C absorption in the 6.0–6.2-μ region nor could any band be definitely assigned to an olefinic C—H bending vibration. The n.m.r. spectrum was more informative. It showed ten aromatic protons at τ 2.85 and 2.93, one olefinic proton (triplet) at τ 4.42, two aliphatic protons (doublet) at τ 6.74, and three aliphatic protons (singlet) at τ 7.93. Under the circumstances, it is difficult to write any structure other than 1,3-diphenyl-2-butene (IV). The ultraviolet spectrum showed benzenoid absorption in the 265–275-mμ region and a shoulder at 230 mμ (ε 7350). Comparison of the n.m.r. and ultraviolet spectra with those of component no. 4 permitted assignment of the *cis* structure to component no. 2, and the *trans* structure to component no. 4 (V).



IV



V

Component no. 4 gave infrared and n.m.r. spectra very similar to those of component no. 2. The n.m.r. spectrum of component no. 4 showed ten aromatic protons at τ 2.85, one olefinic proton (triplet) at τ 4.08, two aliphatic protons (doublet) at τ 6.50, and three aliphatic protons (singlet) at τ 7.88. The significant downfield shift to τ 4.08 of the olefinic proton in component no. 4, compared with its position (τ 4.42) in component no. 2, permitted tentative assignment of structures; the phenyl ring of the *trans* configuration (V) accounts for the extra deshielding of the olefinic proton. The assignments were confirmed by the longer wave length absorption band in the ultraviolet spectrum of component no. 4 ($\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 245 mμ, ε 8250); this, presumably, is a consequence of less steric interference with coplanarity in the *trans* form.

The spectra of components 2 and 4 were identical with those of synthesized samples of IV and V.

Component No. 3.—The infrared spectrum of component no. 3, the major component, showed a C=C stretching absorption at 6.14 μ of medium intensity, and a fairly strong C—H bending absorption at 11.16 μ, characteristic of 2,2-disubstituted olefins ($R_2C=CH_2$). The n.m.r. spectrum showed 10 aromatic protons at τ 2.85 and 2.93, one olefinic proton (doublet with *J* of about 2 c.p.s.) at τ 4.84, one olefinic proton (poorly resolved doublet) at τ 5.05, and 4 aliphatic protons (sharp singlet) at τ 7.31.

The n.m.r. spectrum presented an impasse. As mentioned above, component no. 3 gave β-phenylpropiophenone (II) on oxidation. The mass spectrum supported the empirical formula $C_{16}H_{16}$: parent 208, 24% of base, parent + 1, 17.5% of parent (Calcd. 17.5%), impurity at parent + 2, base 91. The structure we were forced to write, 2,4-diphenyl-1-butene (III), would be expected to show two triplets for the

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[2] J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960.

[3] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," J. Wiley and Sons, Inc, New York, N. Y., in press. Table of Isotope Abundance Values reproduced with the kind permission of Dr. Beynon.

[4] L. Marion, *Can. J. Res.*, **16B**, 213 (1938).

[5] H. Staudinger and A. Steinhofer, *Ann.*, **517**, 35 (1935).

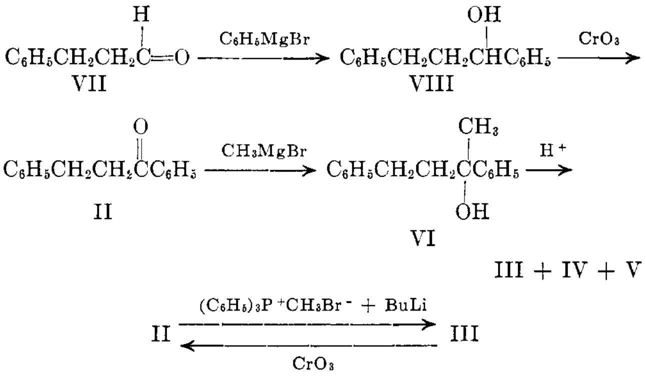
—CH_2CH_2— moiety or at least a broad partially split peak if the chemical shifts were similar. The singlet at τ 7.31 remained sharp with no sign of splitting on the 100-Mc. n.m.r. instrument. Apparently the chemical shifts of the two methylene groups are identical within present-day limits of resolution. An authentic sample of 2,4-diphenyl-1-butene (III) gave identical n.m.r. and infrared spectra.

To our knowledge, 2,4-diphenyl-1-butene (III) has not been previously identified in a styrene dimer fraction. Its significance as a major component in the present fraction will be described as part of the broad study of styrene dimerization.

Synthesis

An authentic sample of 1,3-diphenylpropane (I) was prepared by Clemmensen reduction of 1,3-diphenyl-2-propanone. The infrared and n.m.r. spectra and the gas chromatographic behavior of the synthetic product were identical with those properties of component no. 1.

The following sequence was carried out to furnish samples for comparison with components no. 2, 3, and 4.



Dehydration of 2,4-diphenyl-2-hydroxybutane (VI) gave a crude mixture of olefins which gave three peaks on gas chromatography on QF1–0065 fluorosilicone substrate. These peaks coincided precisely with the peaks of components no. 2, 3, and 4 of the "styrene dimer fraction." Infrared and n.m.r. spectra of the fractions isolated by gas chromatography of the dehydration mixture were identical with the spectra of the corresponding components isolated from the styrene dimer mixture.

Chromic acid oxidation of 2,4-diphenyl-1-butene (III) gave β-phenylpropiophenone (II). An unequivocal synthesis of 2,4-diphenyl-1-butene (III) was effected by reaction of β-phenylpropiophenone (II) with triphenylmethylphosphonium bromide (Wittig synthesis). The susceptibility to air oxidation of 2,4-diphenyl-1-butene (III), noted by Marion,[4] was confirmed; the infrared spectrum of a month-old sample showed diminution of the bands at 6.14 and 11.16 μ and appearance of an aromatic C=O band at 5.93 μ.

Experimental

Gas chromatography was carried out on a Wilkens Aerograph instrument. Infrared spectra were obtained on a Perkin–Elmer 221 instrument; n.m.r. spectra on a Varian HR-60; ultraviolet spectra on a Cary Model 14M; and mass spectra on a Consolidated Electrodynamics Corp. Model 21-103C.

Components no. 1 and 2 were eluted in 15 min., component no. 3 in 20 min., and component no. 4 in 30 min. under the following conditions: 30 λ sample, 30% DC710 silicone oil (Dow Corning) on firebrick, 6 ft. × 1/4 in. copper tubing, temperature 210°, helium flowrate 30 ml./min. The area ratios were 1:8:2.5 for components no. 1 and 2, component no. 3, and component no. 4, respectively.

Component no. 1 (elution time 17 min.) was separated from component no. 2 (elution time 15.5 min.) under the following conditions: 20 λ sample, 30% QFI-0065 fluorosilicone oil (Dow Corning) on Chromosorb W, 5 ft. × 1/4 in. copper tubing, temperature 155°, helium flow rate 40 ml./min. The ratio was 10 (component no. 1):1 (component no. 2). The elution times on the fluorosilicone column under the same conditions for components no. 3 and 4 were 22 and 32 min., respectively.

1,3-Diphenylpropane (I).—Clemmensen reduction[6] of 1,3-diphenyl-2-propanone (Eastman) gave 1,3-diphenylpropane (I) in 80% yield; b.p. 92°/0.15 mm. (lit.,[4] 124°/2 mm.); infrared (film); μ 3.33 (m), 3.43 (m), 3.51 (w), 6.25 (m), 6.67 (m), 9.24 (w), 9.70 (w), 11.06 (w), 13.45 (s), 14.35 (s); n.m.r. (CCl_4): τ 2.91 (singlet, 10), 7.41 (triplet, 4), 8.1 (perturbed quintet, 2).

1,3-Diphenyl-1-propanol (VIII).—The Grignard reagent, prepared from 2.43 g. of sublimed magnesium turnings and 15.7 g. of bromobenzene (0.1 mole) in dry ether, was added slowly to 13.4 g. (0.1 moles) of hydrocinnamaldehyde (Eastman), and the mixture was refluxed for 3 hr. Water was added, and the separated ether layer was washed with dilute hydrochloric acid and with water, then dried. The dried ether solution was evaporated on the steam bath. The residue was used directly in the next step.

β-Phenylpropiophenone (II).—The crude carbinol (VIII) was added portionwise over a period of 1 hr. to a warm (40°) chromic acid solution (50 g. of sodium dichromate dihydrate, 20 ml. of concentrated sulfuric acid, 400 ml. of water). The solution was allowed to stand at room temperature for 1 hr., cooled in an ice bath and extracted with ether. The ether solution was dried, and the ether was removed by distillation. The light tan solid residue (17 g.) was recrystallized from petroleum ether (b.p. 30–65°); the off-white product melted at 69–71° (lit.,[7] m.p. 73°); 2,4-dinitrophenylhydrazone (recrystallized from ethanol–water) 166–168° (lit., m.p. 142–144°,[8] 166°,[9] 186.6–187.2° [10]).

2,4-Diphenyl-2-hydroxybutane (VI).—A solution of 2.1 g. (0.01 mole) of β-phenylpropiophenone in 50 ml. of ether was added over a period of 20 min. to a refluxing solution of 0.015 mole of methylmagnesium iodide in 100 ml. of ether. Refluxing was continued for another 20 min. The mixture was cooled; water was added dropwise; the mixture was acidified with dilute hydrochloric acid and extracted with ether. The ether solution was dried and evaporated. The crude residue was used directly in the next step.

Dehydration of 2,4-Diphenyl-2-hydroxybutane (VI).—A mixture of 1.16 g. (0.00515 mole) of the crude carbinol (VI) and 25 ml. of 50% sulfuric acid was heated on the steam bath for 15 min. The reaction mixture was cooled, diluted with 50 ml. of water, and extracted with ether. Drying and evaporation of the ether solution gave 0.88 g. (82% yield) of a crude mixture of olefins. An infrared spectrum showed no hydroxyl band. The crude olefin mixture was chromatographed on a fluorosilicone column as described above. The three peaks obtained coincided with the peaks of components no. 2, 3, and 4 of the "styrene dimer fraction"; the area ratios were 1.7:1:7.3, respectively.

Olefin Mixture. A. *cis*-1,3-Diphenyl-2-butene (IV).—The compound that was eluted in 15.5 min. on the fluorosilicone column gave the following spectra. Infrared (film): μ 3.29 (shoulder), 3.32 (w), 3.45 (w), 3.51 (shoulder), 6.25 (w), 6.68 (m), 6.87 (w), 6.96 (w), 7.30 (w), 9.15 (w), 9.32 (w), 9.73 (w), 10.95 (w), 13.12 (m), 14.35 (s); n.m.r. (CCl_4): τ 2.85 and 2.93 (10), 4.42 (triplet, 1), 6.74 (doublet, 2), 7.93 (singlet, 3); ultraviolet (95% ethanol): 230 mμ (ϵ 7350), 266 mμ (ϵ 2600), 273 mμ (ϵ 1838).

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(6) E. Clemmensen, *Ber.*, **47**, 681 (1914).

(7) R. Adams, J. W. Keon, and R. L. Shriner, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 101.

(8) L. F. Chelpanova, and Z. V. Printseva, *Zh. Obsch. Khim.*, **23**, 1135 (1953); *Chem. Abstr.*, **47**, 12211a (1953).

(9) J. Frederick, J. Dippy, and R. L. Lewis, *Rec. trav. chim.*, **56**, 1000 (1937); *Chem. Abstr.*, **32**, 5215 (1938).

(10) M. Romero and J. Romo, *Bol. inst. quim. univ. nal. auton. Mex.*, **4**, 3 (1952); *Chem. Abstr.*, **47**, 10498a (1953).

B. 2,4-Diphenyl-1-butene (III).—The compound that was eluted in 22 min. on the fluorosilicone column gave the following spectra. Infrared (film): μ 3.28 (shoulder), 3.32 (w), 3.42 (w), 3.50 (shoulder), 6.14 (m), 6.24 (w), 6.67 (w), 6.86 (m), 9.30 (w), 9.70 (w), 11.16 (m), 12.87 (m), 13.40 (m), 14.35 (s); n.m.r. (CCl_4): τ 2.85 and 2.93 (10), 4.84 (doublet, 1, J = 2 c.p.s.), 5.05 (partially resolved doublet, 1), 7.31 (singlet, 4).

C. *trans*-1,3-Diphenyl-2-butene (V).—The compound that was eluted in 32 min. on the fluorosilicone column gave the following spectra. Infrared (film) μ 3.28 (shoulder), 3.30 (w), 3.43 (w), 6.25 (w), 6.68 (m), 6.87 (m), 7.25 (w), 9.32 (w), 9.47 (w), 9.71 (w), 13.25 (s), 13.50 (shoulder), 14.40 (s); n.m.r. (CCl_4): τ 2.85 (multiplet, 10), 4.08 (triplet, 1), 6.50 (doublet, 2), 7.88 (singlet, 3); ultraviolet (95% ethanol): 245 mμ (ϵ 8250), 273 mμ (ϵ 3750 sh).

2,4-Diphenyl-1-butene (III) (Wittig Synthesis[11]).—A suspension of triphenylmethylphosphonium bromide (Beacon Chemical Industries) (1.43 g., 0.004 mole) in a solution of 0.320 g. (0.005 mole) of *n*-butyllithium in 25 ml. of ether was stirred at 25° under nitrogen for 2 hr. To the solution which was effected during this period, was added 0.84 g. (0.004 mole) of β-phenylpropiophenone (II); stirring was continued at 25° for another 0.5 hr. Dry tetrahydrofuran (50 ml.) was added, the ether removed by distillation, and the solution was refluxed for 4 hr. The tetrahydrofuran was distilled at 20 mm., and the residue was triturated with six 40-ml. portions of pentane. Removal of the pentane left 0.68 g. of a colorless oil. Chromatography on the fluorosilicone column at 190° and 40 ml. min. gave a major peak at 9 min. and a small peak (starting ketone, 5% of the major peak) at 21 min. The infrared and n.m.r. spectra of the compound represented by the major peak were identical with those obtained from component no. 3 of the "styrene dimer fraction," and from the second fraction of the chromatographed olefinic dehydration mixture.

Anal. Calcd. for $C_{16}H_{16}$ (208.29): C, 92.26; H, 7.74. Found: C, 92.38; H, 8.03.

Oxidation of Component No. 1.—To a solution of 10 mg. of component no. 1 in 0.5 ml. of glacial acetic acid held at 70°, was added, portionwise, 50 mg. of chromic anhydride over a period of 45 min. The mixture was cooled and extracted with ether which then was washed with 10% sodium hydroxide solution, dried, and evaporated. The residue in 0.2 ml. of hexane was placed on an alumina column (Merck, acid-washed, 0.5 g. in a 4-mm. tube) and eluted with hexane. The hexane solution was concentrated to 0.2 ml., cooled to −30°, and filtered. A 4-mg. crop of crystals was obtained, m.p. 70–73° (lit.,[7] m.p. for β-phenylpropiophenone 73°). Admixture with an authentic sample (II) did not depress the melting point; infrared (melt): 5.92 μ (C=O).

Oxidation of Component No. 3.—A 2% aqueous solution of potassium permanganate was added dropwise over a period of 2 hr. to 10 mg. of component 3 on a steam bath until the permanganate color persisted. The mixture was extracted with ether, and the ether solution was dried and evaporated. The residue was treated with 2,4-dinitrophenylhydrazine. Three recrystallizations of the product from ethanol-water gave the 2,4-dinitrophenylhydrazine, m.p. 162–164.5°, whose identity was proved by mixed melting point with an authentic sample of β-phenylpropiophenone 2,4-dinitrophenylhydrazone and by comparison of the infrared spectra.

Acknowledgment.—The work described is part of a broad study of styrene dimerization by Dr. F. R. Mayo who furnished the fraction described. The authors are indebted to Mr. Norman Bhacca of Varian Associates for the 100-Mc. n.m.r. spectrum, and to Dr. S. A. Fuqua of Stanford Research Institute for many helpful discussions of n.m.r. spectra. The n.m.r. and mass spectra were run at Stanford Research Institute by Mr. W. R. Anderson, Jr., and Mrs. L. Peters, respectively.

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[11] S. Trippett, "Advances in Organic Chemistry," Vol. I, Interscience Publishers, New York, N. Y., 1960, p. 83.

The Metalation of Methyl(disubstituted)phosphine Oxides and Their Subsequent Reactions

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A series of phosphine oxides containing an additional carboxy, hydroxy, carbonyl, or phosphinyl group was prepared by reaction of the lithium metalated methyl(disubstituted)phosphine oxide with the appropriate reagent. The physical data and the infrared frequencies of the main functional groups are reported.

Bis(disubstituted phosphinyl)methanes, $R_2P(O)CH_2P(O)R_2$, appear to be more effective extractants for various metal ions than the monophosphine oxides.[1] It was found desirable to study the effect of substitution of other functional groups for one of the phosphinyl groups on the extractability of metal ions.

Use was made of the acidic nature of the hydrogen atom of a methylene group adjacent to the P—O group of a phosphine oxide to introduce functional groups such as carboxy, hydroxy, and carbonyl into the molecule.[2-6] Di-*n*-hexylmethylphosphine oxide and methyldiphenylphosphine oxide were first metalated with *n*-butyllithium and the resulting intermediate was treated with the various types of compounds listed below to give the indicated product. The method also can be used to prepare bis(disubstituted phosphinyl)methanes (equation 5).

$$R_2P(O)CH_2Li + CO_2 \longrightarrow \xrightarrow{H^+} R_2P(O)CH_2CO_2H \quad (1)$$

$$R_2P(O)CH_2Li + R'CHO \longrightarrow \xrightarrow{H^+} R_2P(O)CH_2C(OH)HR' \quad (2)$$

$$R_2P(O)CH_2Li + R_2'CO \longrightarrow \xrightarrow{H^+} R_2P(O)CH_2C(OH)R_2' \quad (3)$$

$$R_2P(O)CH_2Li + R'CO_2Et \longrightarrow R_2P(O)CH_2C(O)R' \quad (4)$$

$$R_2P(O)CH_2Li + R_2'P(O)Cl \longrightarrow R_2P(O)CH_2P(O)R_2' \quad (5)$$

Although the lithium salts of the methyl(disubstituted)phosphine oxides were not isolated, they were formed in at least 60–70% yield as indicated by the recovery of the carboxymethyl(disubstituted)phosphine oxides.

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[1] K. E. Burke, J. J. Richard, H. Sakurai, J. W. O'Laughlin, and C. V. Banks, 138th National Meeting of the American Chemical Society, Abstracts, p. 13-B; *Chem. Eng. News*, p. 57, (September 19, 1960).

[2] L. Horner, H. Hoffmann, and H. G. Wippel, *Ber.*, **91**, 61 (1958).

[3] L. Horner, H. Hoffmann, H. Wippel, and G. Klahre, *ibid.*, **92**, 2499 (1959).

[4] F. Hein and H. Hecker, *ibid.*, **93**, 1339 (1960).

[5] L. Horner, H. Hoffmann, and V. G. Toscano, *ibid.*, **95**, 536 (1962).

[6] L. Horner, H. Hoffmann, W. Klink, H. Ertel, and V. G. Toscano, *ibid.*, **95**, 581 (1962).