Rearrangement of *p*-Chlorophenyl α-Phenethyl Ether.—This ether was rearranged according to a procedure described previously.[1] From 10 g. of ether prepared above, there was obtained 1.5 g. of *o*-α-phenethyl-*p*-chlorophenol, $\alpha^{25}\mathrm{D}$ +0.80°.

Reduction of *o*-α-Phenethyl-*p*-chlorophenol.—*o*-α-Phenethyl-*p*-chlorophenol (10.0 g., $\alpha^{25}\mathrm{D}$ −0.24°, *l* 1 dm., homogeneous) was reduced with nickel–aluminum alloy and aqueous alkali, according to the procedure of Papa and Schwenk.[22] The product was 6.9 g. (81%) of *o*-α-phenethylphenol, $\alpha^{25}\mathrm{D}$ +0.064 ± 0.005°, infrared spectrum identical with that of an authentic sample.

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[22] D. Papa, E. Schwenk and B. Whitman, *ibid.*, **7**, 587 (1942).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Phosphorus Acids in Organic Systems. I. Intermolecular Condensations Catalyzed by Polyphosphoric Acid

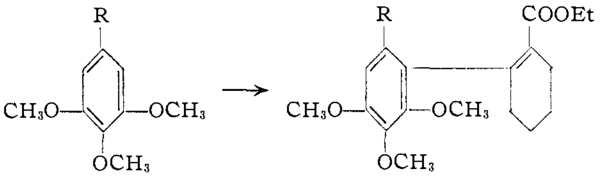
BY PETE D. GARDNER

RECEIVED MARCH 12, 1954

The reaction of anisole and trimethylpyrogallol with acetic acid, acetic anhydride, benzoic acid and β-carbomethoxypropionic acid is described. The product in all cases was the expected Friedel–Crafts adduct; but unlike the aluminum chloride catalyzed reaction, no ether cleavage was observed. Alkylation of anisole with 2-propanol and cyclohexanol and of phenol with cyclohexanol by means of this catalyst is also described.

The utility of polyphosphoric acid as a catalyst in the intramolecular acylation reaction with acids and anhydrides has been adequately demonstrated.[1-5] Further, the work of Horning and his associates[6] has shown it to be extremely effective in the Bougault type of cyclization. With the exception of one rather unsatisfying example,[7] nothing has been reported regarding the effectiveness of this Lewis acid in intermolecular acylations. This paper[7] also describes the only reported successful alkylation reaction using the catalyst.

The need for generalization of the reaction to intermolecular systems arose in connection with a projected synthesis of I in which the ester group may be considered a non-reactive function at moderate temperatures in the catalyst as a medium.[8] It should be recognized that this reaction would be the intermolecular equivalent of some of those effected by others.[6]



I, R = $CH_2CH_2COOCH_3$
II, R = H

When either anisole or trimethylpyrogallol was treated with acetic anhydride (or acetic acid), benzoic acid or β-carbomethoxypropionic acid the corresponding ketone or keto ester was obtained in excellent yield (75–100%). With these condensations, as with others, the catalyst itself proved to be the only suitable solvent found. This method appears to offer a serious limitation to the scope of the reaction by virtue of the insolubility of hydrocarbons in the system. Thus far, only phenols and phenyl esters and ethers appear to be useful as the aromatic component but the solvent might be expected to be equally useful with any substance possessing a center of electron density sufficiently high to serve as a solubilizing influence (subject, of course, to the usual activation restrictions characteristic of all aromatic electrophilic substitutions). Attempted condensations with benzene, toluene and cyclohexene failed completely and recovery of the hydrocarbon was above 90% in all cases. Solubility is not a problem in cyclization reactions because of the solubilizing effect of the carboxyl group.

The preparation of chloroacetomesitylene (16%) reported by Snyder and Roeske[7] used a 2:1 catalyst to hydrocarbon ratio and a reaction time of 5 hr. at reflux temperature. It was found in the present study that, due to the enhanced reactivity of the aromatic components used, long reaction times and, more particularly, high temperatures were not required. The substituted benzoylpropionic esters required temperatures of only 30–45° and in this range, prolonged reaction times did not appear to be particularly detrimental. Temperatures of 40–50° were optimum for the acetophenones and 70–80° most satisfactory for the two benzophenones studied. Higher temperatures (80–100°) gave slightly lower yields of the acetophenones but drastically lower yields in the case of the esters. The ratio of catalyst to aromatic did not determine the yield in any case until it was reduced to 6:1.

In addition to the simplicity of the method and the high yields obtained, the absence of ether cleavage products makes the reaction the one of choice for this type of compound. The usual Friedel–Crafts technique utilizing an acid chloride in conjunction with aluminum chloride as a catalyst invariably results in total or partial ether cleavage when the acyl function enters *ortho* to a methoxyl group.[9]

To further generalize the catalyst, the alkylation of anisole and phenol with 2-propanol and cyclohexanol was studied. Although these proceeded nor-

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[1] A. Koebner and R. Robinson, *J. Chem. Soc.*, 1994 (1938).

[2] W. E. Bachmann and W. J. Horton, THIS JOURNAL, **69**, 58 (1947).

[3] H. R. Snyder and F. X. Werber, *ibid.*, **72**, 2965 (1950).

[4] P. D. Gardner, W. J. Horton, G. Thompson and R. R. Twelves, *ibid.*, **74**, 5527 (1952).

[5] P. D. Gardner and W. J. Horton, *ibid.*, **75**, 4976 (1953).

[6] For leading references see J. Koo, *ibid.*, **75**, 2000 (1953).

[7] H. R. Snyder and R. W. Roeske, *ibid.*, **74**, 5820 (1952).

[8] Unpublished data obtained in this Laboratory.

[9] E. Berliner in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, Table VII, p. 271.

mally, the yields were very much lower due, presumably, to the formation of bis- and tris-condensation products. The effect of the catalyst in this type of condensation is not startling since concentrated phosphoric acid (d. 1.85) has been shown to operate effectively in the case of substituted β-naphthols.[10]

As a model of I, the preparation of II was attempted from trimethylpyrogallol and 2-carbethoxycyclohexanone. A variety of conditions of time and temperature all gave a mixture of products from which none of the expected one could be isolated. Similarly, methyl 3,4,5-trimethoxyhydrocinnamate under these conditions gave a mixture of products not yet completely resolved. No tar formation was observed in either case but both afforded small amounts of the starting ether. Saponification of both reaction products gave semi-solid acid fractions which have resisted separation. The study of this and related reactions is being continued. The reaction between acids and phenols or phenol esters gave normal acylation products accompanied by rearrangement (Fries) products. These will be the subject of another communication.

Acknowledgment.—The author is grateful to Victor Chemical Works for the gift of generous samples of polyphosphoric acid.

Expermental[11]

General.—Reactions were carried out simply by mixing the two organic components in an erlenmeyer flask, melting to ensure homogeneity and then adding the catalyst. The stoppered flask was placed in a bath maintained at the desired temperature for the chosen period of time with swirling as frequently as was convenient. Alternatively the mixture was agitated with an electrically driven ($^1/_{12}$ h.p.) paddle stirrer to give essentially the same results. When possible, the three-component system was manually mixed to homogeneity with a spatula prior to the heating period.

2,3,4-Trimethoxyacetophenone. (a) Acetic Anhydride.—A solution of the reactants was prepared by gently warming a mixture of 16.8 g. (0.100 mole) of trimethylpyrogallol[12] and 6.0 g. (0.059 mole) of acetic anhydride. To this was added 150 g. of polyphosphoric acid (PPA) and the mixture swirled in a bath at 45° to effect dissolution. During the reaction period of 3 hr. at that temperature, the stoppered flask was frequently swirled and a red color developed. The mixture was poured into 600 ml. of ice and water and the whole extracted with two portions of ether. The organic extracts were washed with dilute sodium bicarbonate and then with water. Following removal of solvent on a steam-bath, the product was obtained by distillation; 19.7 g. (93.5%), b.p. 179–180° (18 mm.) (lit.[13] 185° at 20 mm.).

(b) **Acetic Acid.**—When 7.2 g. (0.12 mole) of acetic acid was used in place of acetic anhydride in (a), there resulted 19.3 g. (92%) of ketone having the same boiling temperature.

The semicarbazone, prepared in absolute ethanol with pyridine, melted at 167–169° after purification from ethanol (lit.[14] 170° dec.).

2,3,4-Trimethoxybenzophenone.—A solution of 5.0 g. (0.030 mole) of trimethylpyrogallol, 4.1 g. (0.033 mole) of benzoic acid and 60 g. of PPA was prepared in the same manner as above. After 2 hr. at 80° the product was isolated as before as a pale yellow oil. All attempts to crystallize the substance failed. It was purified by distillation to give 7.5 g. (92%) of colorless liquid boiling at 161–162° (1 mm.) (lit.[15] m.p. 55°).

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.94; H, 6.15.

The semicarbazone was formed in pyridine and ethanol and recrystallized from ethanol; m.p. 195–196°.

Anal. Calcd. for $C_{17}H_{19}N_3O_4$: C, 61.99; H, 5.82. Found: C, 61.71; H, 5.89.

Methyl β-(2,3,4-Trimethoxybenzoyl)-propionate.—A solution of 16.8 g. (0.100 mole) of trimethylpyrogallol and 20.0 g. (0.151 mole) of β-carbomethoxypropionic acid[16] was treated with 230 g. of PPA for 2.5 hr. at 45°. The complex was decomposed in 700 ml. of ice and water to give a suspension. Cooling to 5° and filtering followed by washing with cold water gave the crude product. Recrystallization of the damp cake from methanol–water afforded 22.2 g. (78.8%) of pale yellow needles, m.p. 47–49°. The analytical sample melted at 48–49°. When higher temperatures and shorter reaction times or reduced amounts of the acid were used the yields were substantially reduced. In these cases, the product was isolated by distillation under reduced pressure.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.98; H, 6.47.

β-(2,3,4-Trimethoxybenzoyl)-propionic acid, formed by basic hydrolysis of the ester, melted at 89–90° after recrystallization from water (lit.[17] 89°).

4-Methoxyacetophenone.—A solution of 16.2 g. (0.150 mole) of anisole, 9.2 g. (0.090 mole) of acetic anhydride (or 10.8 g. of acetic acid) and 200 g. of PPA was heated for 3.75 hr. at 50°. Decomposition of the complex in the usual manner and suction filtration of the resulting solid afforded 18.8 g. (83.5%) of the ketone; m.p. 38–39°, unchanged by recrystallization from ethyl acetate–petroleum ether (30–40°) (lit.[18] 38–39°).

The semicarbazone, prepared and purified as above, melted at 194–195° dec. when placed in a bath at 170° (lit.[19] 181–182°).

4-Methoxybenzophenone.—From 16.2 g. (0.150 mole) of anisole, 24.4 g. (0.200 mole) of benzoic acid and 200 g. of PPA when heated at 75° for 2 hr. there was obtained a quantitative yield of crude product. Recrystallization from methanol–water afforded 29.0 g. (91.2%) of colorless prisms, m.p. 62–64° (lit.[20] 61–62°).

The oxime was formed in ethanolic pyridine and melted at 140–141° after extensive recrystallization from ethanol, corresponding to that reported[21] for the *syn* form (137–138°).

Methyl β-(4-Methoxybenzoyl)-propionate.—A mixture of 16.2 g. (0.15 mole) of anisole, 26.4 g. (0.200 mole) of β-carbomethoxypropionic acid and 200 g. of PPA was allowed to stand at 30° for 4.5 hr. and treated in the usual manner. There was obtained 25.0 g. (75%) of light yellow solid, m.p. 43–46°. Recrystallization from ethyl acetate–petroleum ether (30–40°) raised the m.p. to 48–49° (lit.[22] 47°).

The acid, obtained by saponification of the ester, melted at 144–146° (lit.[23] 147°).

2- and 4-Isopropylanisole.—A solution of 0.5 mole of anisole and 0.5 mole of 2-propanol was treated with 500 g. of PPA. The mixture was stirred briskly for 15 minutes, stoppered and heated at 85° for 1 hr. Dilution with ice and water, followed by isolation by extraction with ether, ultimately gave 73 g. of a pale yellow mixture of alkylation products. Distillation at 750 mm. through a 12 in. helices-packed column afforded 6.0 g. (11%) of recovered anisole (b.p. 150–155°) and 25.3 g. (33.7%) of 2-isopropylanisole (b.p. 198–201°, $n^{26}D$ 1.5070) (lit.[24] 198–200°).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.10; H, 9.42.

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(10) Ng. Ph. Buu-Hoi, H. Le Bihan and F. Binon, *J. Org. Chem.*, **16**, 185 (1951).

(11) Melting points are corrected.

(12) K. H. Slotta and H. Heller, *Ber.*, **63B**, 3029 (1930).

(13) Ng. Ph. Buu-Hoi and P. Cagniant, *Rec. trav. chim.*, **64**, 214 (1945).

(14) K. Okazaki, *J. Pharm. Soc. Japan*, **59**, 547 (1939); *C. A.*, **34**, 1004 (1940).

(15) J. Herzig and K. Klimosch, *Monatsh.*, **30**, 537 (1909).

(16) J. Cason, THIS JOURNAL, **64**, 1106 (1942).

(17) R. H. F. Manske and H. L. Holmes, *ibid.*, **67**, 95 (1945).

(18) L. Gattermann, E. Ehrhardt and H. Maisch, *Ber.*, **23**, 1199 (1890).

(19) E. Mameli, *Gazz. chim. ital.*, **39II**, 165 (1909).

(20) E. H. Rennie, *J. Chem. Soc.*, **41**, 220 (1882).

(21) A. Hantzsch, *Ber.*, **24**, 51 (1891).

(22) D. A. Hahn, THIS JOURNAL, **38**, 1517 (1916).

(23) L. F. Fieser and E. B. Hershberg, *ibid.*, **58**, 2314 (1936).

(24) I. Tzukervanik and Z. Nazarova, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 767 (1935); *C. A.*, **30**, 443 (1936).

Following an intermediate fraction, there was obtained 9.5 g. (12.7%) of 4-isopropylanisole boiling all at 204°, $n^{26}\text{D}$ 1.5000 (lit.[25] b.p. 208° at 728 mm., $n^{7}\text{D}$ 1.513).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.29; H, 9.64.

The remainder of the material had a boiling range up to 155°. Distillation fractions of 3 ml. were taken and combined into the above major fractions on the basis of their refractive indices.

2- and 4-Cyclohexylanisole.—A mixture of 0.5 mole of anisole, 0.52 mole of cyclohexanol and 400 g. of PPA was stirred at 85° for 35 min. Isolation in the usual fashion and distillation at 750 mm. yielded 68 g. (72%) of a mixture of the two isomers, b.p. 275–283°. These could not be separated by distillation, although a small amount of the pure 4-isomer (5.5% g., 5.8%) could be obtained by dissolving the mixture in 40 ml. of petroleum ether (50–60°) and cooling; m.p. 58–59° (lit.[25] 58–59°). The combined reaction products were distilled again to give 64 g., b.p. 146–150° (15 mm.). This was analyzed as a mixture of the two isomers.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.99; H, 9.53.

2- and 4-Cyclohexylphenol.—Half-mole quantities of phenol and cyclohexanol were treated with 400 g. of PPA at 85° for 40 min. The product was isolated as above as 50.3 g. (53.7%) of a mixture of the two isomers, b.p. 155–170° (15 mm.). Fractional crystallization from ethyl acetate–petroleum ether (30–40°) and then from petroleum ether afforded 16.1 g. (17.2%) of 4-cyclohexylphenol, m.p. 129–130° (lit.[25] 131°). Further crystallization from the latter solvent yielded 20.5 g. (21.9%) of 2-cyclohexylphenol, m.p. 53–54° (lit.[25] 56–57°).

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[25] H. Lefebvre and E. Levas, *Compt. rend.*, **220**, 782 (1945); *C. A.*, **40**, 1478 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH DAKOTA]

Substituted Phenylsilanes. I. The Autoxidation of *o*-, *m*- and *p*-Trimethylsilylethylbenzene[1]

BY ROLAND G. SEVERSON AND ROBERT J. ROSSCUP

RECEIVED MARCH 1, 1954

The trimethylsilylethylbenzenes have been prepared and the oxidation of these silanes with oxygen has been studied. This oxidation, carried out at 200–220° in the presence of chromic oxide and calcium carbonate, has given moderate yields of *o*-, *m*- and *p*-trimethylsilylacetophenone as well as the corresponding trimethylsilylbenzoic acids. The resulting new organosilanes have been characterized and derivatives have been prepared wherever possible.

It is well known that the methods which are available for the establishment of carbon–silicon linkages are not adapted readily to the preparation of organosilanes containing reactive functional groups. Furthermore, in the case of arylsilanes, the introduction of reactive functional groups into the aromatic ring by the usual electrophilic substitution reactions is complicated by the ease of cleavage of the aromatic carbon–silicon bond under the conditions employed in such reactions. The Friedel–Crafts acylation of phenylsilanes has been notably unsuccessful. Dolgov and Panina[2] have found that acyl halides in the presence of aluminum chloride react with triethylphenylsilane to form alkyl phenyl ketones and triethylchlorosilane rather than alkyl triethylsilylphenyl ketones.

This susceptibility of phenylsilanes to cleavage during reactions of this type has led us to an investigation of the preparation of the trimethylsilylacetophenones by methods which do not involve electrophilic reagents. This paper describes the results of an investigation of the action of oxygen on trimethylsilylethylbenzenes at elevated temperatures in the presence of chromic oxide and calcium carbonate. Apparently, only two studies of oxidation procedures as a means of introducing reactive functional groups into organosilanes have been made. Benkeser and Landesman[3] found that the mild oxidizing agent, selenium dioxide, will convert 2-acetyl-5-trimethylsilylthiophene and 2-acetyl-5-trimethylsilylfuran to the corresponding glyoxals while Lewis and Gainer[4] were able to oxidize 1,3-bis-(*p*-tolyl)-tetramethyldisiloxane to 1,3-bis-(*p*-carboxyphenyl)-tetramethyldisiloxane with chromic acid in acetic acid–acetic anhydride at low temperatures.

The trimethylsilylethylbenzenes used in this investigation were prepared by converting *o*-, *m*- and *p*-bromoethylbenzene into the corresponding organolithium reagents and treating these with trimethylethoxysilane. The yields in these preparations varied from 55% for *o*-trimethylsilylethylbenzene to 82% for the *para* isomer. When *p*-trimethylsilylethylbenzene was treated with dry oxygen at 200–214° for six hours in the presence of chromic oxide and calcium carbonate a 21% yield of *p*-trimethylsilylacetophenone and a 12% yield of *p*-trimethylsilylbenzoic acid were obtained. Increasing the reaction time to 12 hours at 209–225° gave no appreciable change in the yield. However, when the reaction mixture was illuminated with ultraviolet light, the yields of ketone and acid were increased to 25 and 15%, respectively. By means of this oxidation either with or without ultraviolet light it was possible to obtain comparable yields of *o*-trimethylsilylbenzoic acid and *o*-trimethylsilylacetophenone with the better yield of ketone (19%) being obtained when ultraviolet light was used. The oxidation of *m*-trimethylsilylethylbenzene was carried out with ultraviolet light and gave somewhat lower yields (10% of acid and 14% of ketone) than in similar reactions with the other two isomers. It would appear that temperatures of about 200° are essential in these reactions since no detectable amounts of ketone or acid were obtained when *o*-trimethylsilylethylben-

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[1] This work was supported in part by a grant from the National Science Foundation.

[2] B. N. Dolgov and O. K. Panina, *Zhur. Obshchei Khim.*, **18**, 1293 (1948); *C. A.*, **43**, 2177 (1949).

[3] R. A. Benkeser and H. Landesman, THIS JOURNAL, **71**, 2493 (1949).

[4] D. W. Lewis and G. C. Gainer, *ibid.*, **74**, 2931 (1952).