[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF OSAKA PREFECTURE]

The Reaction of Olefins with Aromatic Substances in the Presence of Mercury Salts and Catalyst. II. Synthesis of β-Arylethyl Alcohols and *sym*-Diarylethanes

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The reaction of ethylene and benzene in the presence of a mercury salt and sulfuric acid to form *sym*-diphenylethane has been further investigated. Three of the common alkylation catalysts were found to be effective. Good yields of β-arylethyl alcohols or their acetates also can be obtained by this reaction, their relative abundance in the reaction product depending on the catalyst and reaction conditions. β-(*p*-Methoxyphenyl)-ethylmercuric salt was isolated as an intermediate in the reaction of ethylene and anisole and, with this new evidence, a previously proposed mechanism has been corrected.

The synthesis of *sym*-diphenylethane by the reaction of ethylene with benzene in the presence of sulfuric acid and a mercury salt[1] has been reinvestigated and this reaction extended to other aromatic compounds. A reaction mechanism is proposed which is based on the isolation of a mercuric salt intermediate.

Two experimental methods were used: In method A, ethylene was introduced into a mixture of aromatic compound, mercury salt and catalyst. In method B, the aromatic compound was added to a previously prepared ethylene–mercury salt addition compound in acetic acid, and then the catalyst was introduced. In both methods the reaction mixture was kept at the reaction temperature until the mercury salt was reduced quantitatively to free mercury.

In contrast to previous results in which the only product was 1,2-diarylethane, β-arylethyl alcohol or acetate frequently was formed in addition to the ethane derivative. Whether the alcohol or acetate is formed depends on the mercury salt used and is independent of the catalyst when acetic acid is not used as the solvent. Mercuric acetate gives the acetate, while the alcohol is obtained from mercuric sulfate; apparently, the β-arylethyl sulfate hydrolyzes to the alcohol.

The reaction, therefore, can be expressed by the equations

$$\mathrm{ArH} + \mathrm{CH_2CH_2} + \mathrm{HgZ_2} \longrightarrow \mathrm{ArCH_2CH_2Z} + \mathrm{Hg} + \mathrm{HZ} \text{ and/or}$$

$$2\mathrm{ArH} + \mathrm{CH_2CH_2} + \mathrm{HgZ_2} \longrightarrow \mathrm{ArCH_2CH_2Ar} + \mathrm{Hg} + 2\mathrm{HZ}$$

In order to compare the catalytic activities of the various acids, a series of experiments was run with anisole. The results are given in Table I, the molar ratio anisole to mercury salt was 10:1. Yields were calculated on the basis of the mercury salt used according to the above equations.

TABLE I

REACTION OF ETHYLENE WITH ANISOLE IN THE PRESENCE OF MERCURY SALT AND CATALYST

		Product g./g. anisole		
Method A	G. acid/g. anisole	II or III	I	Total yield, %
$HgSO_4$, H_3PO_4(98.6%)		II		
1	0.28		0.10	46
2	.92		.13	56
3	.92		.14	60
4	1.85		.10	46
H_3PO_4 (88%)				
5	0.92	0.03	0.11	72
H_3PO_4 (69%)				
6	0.92	0.01	Trace	9[a]
$Hg(OAc)_2$, H_3PO_4 (98.6%)		III		
7	0.185		0.01	4[a]
8	.16	0.01	.007	9[a]
9	.46	.065	.06	64
10	.46	.026	.017	21[a]
H_3PO_4 (88%)				
11	0.92	0.06	0.02	40
H_3PO_4 (69%)				
12	0.92	0.02	Trace	12[a]
Hg_2SO_4, H_3PO_4 (98.6%)		II		
13	0.46		0.13	57
$HgSO_4$, H_2SO_4 (96%)				
14[b]	0.6		0.18	37
15	.3		.09	39
16	.3		.10	41
$HgSO_4$, H_2SO_4 (80%)		II		
17[b]	1.5	0.04	0.02	17
$Hg(OAc)_2$, $HClO_4$ (60%)		III		
18	1.0	0.065	0.03	46
19	0.17	.065	.025	44
20[b,e]	.34	.15	.08	55
$Hg_2(OAc)_2$				
21	1.0	0.022	0.024	42
Method B	50 g. acetic acid/0.15 mole mercury salt			
$Hg(OAc)_2$, H_3PO_4 (98.6%)				
22	0.68	0.11	0.06	60
23[d]	.20	.015	.003	9
H_2SO_4 (96%)				
24	0.10	0.057	0.025	40
$HClO_4$ (60%)				
25	0.17	0.13	0.04	87
26	.085	.13	.03	82
$(HgNO_3)_2 \cdot 2H_2O$, $HClO_4$ (60%)				
27[e]	0.78	0.14		59
$Hg(OAc)_2$, BF_3[e], HOAc				
28[e]	1.3	0.15		31[f]

[a] The mercuric salt was reduced to mercurous salt; no free mercury formed. [b] Mole anisole:mole mercury salt, 5:1. [c] After 2.3 hours at 29–38°, the reaction mixture was allowed to stand overnight at 30–33°. [d] 150 g. of acetic acid/0.15 mole of mercuric acetate. [e] 100 g. of acetic acid/0.15 mole of mercury salt. [f] A small amount of free mercury was obtained.

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[1] K. Ichikawa, H. Tozaki, I. Ueki and H. Shingu, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 267 (1951).

TABLE II

REACTION OF ANISOLE (1 MOLE) WITH ETHYLENE IN THE PRESENCE OF MERCURIC SULFATE (0.1 MOLE), 60% PERCHLORIC ACID (0.2 MOLE) AND ORGANIC ACIDS (0.5 MOLE) BY METHOD A

		β-(p-Methoxyphenyl)-ethyl ester								
			B.p.,				Analyses, %			
							Calcd.		Found	
Acid[a]	Anisil, % yield	Yield, %	°C.	Mm.	$n^{20}D$	Formula	C	H	C	H
Formic	17	46	103.5–104	3	1.5178	$C_{10}H_{12}O_3$	66.65	6.71	66.87	6.82
Propionic	13	42	129–132	3.5	1.5063	$C_{12}H_{16}O_3$	69.21	7.74	69.49	8.07
n-Caproic	23	27	146–148	2	1.4992	$C_{15}H_{22}O_3$	71.97	8.86	72.10	8.67

[a] Acetic acid gave anisil in 19% yield and the ester in 39% yield.

The following results were obtained with method A. The catalytic agent had a marked effect on the temperature at which the reaction occurred. With 96% sulfuric acid the temperature range was −5 to 15°. With 98.6% phosphoric acid, the optimum temperature was 130° (yield 46–60%), very low yields were obtained at 120° and 150–155°. With perchloric acid, the usual temperature range was 50–70°.

With mercuric sulfate, both concentrated sulfuric and phosphoric acids gave only anisil (I), a mixture of 1,2-di-(*p*-methoxyphenyl)-ethane and 1-(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)-ethane in a molar ratio of roughly 1:1. The dilute acids (expts. 5, 17) yielded a mixture of I and II, β-(*p*-methoxyphenyl)-ethyl alcohol, presumably formed by hydrolysis of the sulfate.

With mercuric acetate, concentrated as well as dilute phosphoric acid always gave β-(*p*-methoxyphenyl)-ethyl acetate (III) in addition to I; however, with the dilute acid the proportion of acetate in the product was larger (*cf.* expts. 11 and 9). With dilute phosphoric acid and mercuric sulfate (expt. 5), the predominant product is anisil, whereas in a comparable experiment with mercuric acetate (expt. 11) the chief product is the acetate.

Method A gave the best results with 88% phosphoric acid and mercuric sulfate. Complete reduction of the mercuric salt is not necessary for the reaction; in expt. 12 a 12% yield of the acetate was obtained although the reduction of mercuric acetate proceeded only to the mercurous stage. Other mercury salts (mercuric oxide, phenylmercuric acetate and *p*-methoxyphenylmercuric acetate) were used successfully with concentrated phosphoric acid (total yields 28–52%).

Like dilute phosphoric acid, perchloric acid (60%, 40%) gave the acetate as the main product; no reaction occurred with 20% perchloric acid. Other alkylation catalysts were found to be effective, *viz.*, boron trifluoride–acetic acid complex and benzene- and toluenesulfonic acid, which gave total yields of 70, 44 and 18%, respectively.

The total yield is not affected by the choice of method (A or B) except in the case of perchloric acid where B gives better results. The most important side reaction is the formation of mercury from the ethylene–mercury salt addition compound before its reaction with anisole. This side reaction seems to be catalyzed by perchloric acid; *e.g.*, when ethylene was introduced into a perchloric acid solution of mercuric acetate at 55–60° for an hour in the absence of anisole, 18% of the mercury salt was reduced. On the other hand, an acetic acid solution of the addition compound does not form free mercury under similar conditions even in the presence of perchloric acid. This accounts for the lower yields obtained in method A in which the perchloric acid is not diluted with acetic acid.

Method B, in which acetic acid serves as the solvent for the addition compound, favors the formation of acetate; the ratio acetate:anisil in the product tends to be higher than in the comparable experiments with method A. Even with concentrated sulfuric acid (expt. 24) acetate was formed.

Mercurous compounds also can be used as the source of mercury; see expts. 13, 21 and 27. As the formation of addition compounds between mercurous salts and olefins has not been reported, the absorption of ethylene by mercurous nitrate was investigated. A suspension of $(HgNO_3)_2 \cdot 2H_2O$ (1 mole) in 70 ml. of acetic acid absorbed 600 ml. of ethylene in 2 hours at room temperature; the addition of perchloric acid increased the absorption rate, the total amount of ethylene absorbed corresponding to a 1:1 addition compound with mercurous nitrate, which presumably can react with the aromatic compound.

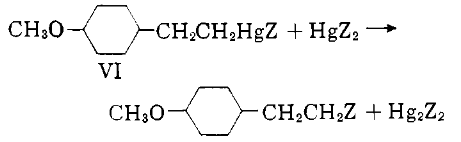
β-Arylethyl acetates were prepared by method A from benzene, toluene, *o*-xylene, chlorobenzene and naphthalene (see Experimental); with benzene and naphthalene, the diaryl-substituted ethanes also were detected. The usual order of reactivity of aromatic compounds in cationic substitution was observed.

The reaction of anisole with ethylene (method A) in the presence of various organic acids yielded the corresponding esters of β-(*p*-methoxyphenyl)-ethyl alcohol; see Table II.

An intermediate compound in this reaction was isolated under the following conditions. The reaction of anisole with the addition compound was stopped by adding water. The resulting heavy oil, treated with potassium iodide, yielded IV which was identified as β-(*p*-methoxyphenyl)-ethylmercuric iodide. This was shown by converting the latter to β-(*p*-methoxyphenyl)-ethyl iodide (V) and subsequent hydrolysis to alcohol. This indicates that $p\text{-}CH_3OC_6H_4CH_2CH_2HgZ$ (VI) (Z = acid radical) is an intermediate. Further evidence was obtained by the conversion of IV to β-(*p*-methoxyphenyl)-ethylmercuric acetate (VII).

In the beginning of the reaction, two types of white crystals (the type depending upon the method used) were observed which both gave a positive test for mercurous ion. In the case of method A (phosphoric acid and mercuric acetate), a large amount of crystals was formed; they disappeared slowly with the simultaneous formation of free mercury and were identified as Hg_2HPO_4 (VIII) which was stable to phosphoric acid at 130° for 3 hours. The small amount of white crystals formed in method B (phosphoric acid) disappeared rapidly with the formation of free mercury. This unstable mercurous intermediate IX is, therefore, different for VIII, apparently it reacts to form the final products, II or III and free mercury.

Hg_2HPO_4 (VIII) probably is formed from the intermediate VI as



(1)

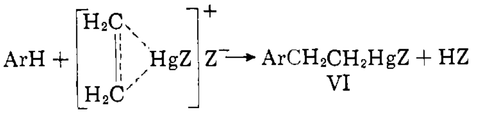
This mechanism is based upon the finding that in the absence of anisole, the ethylene–mercuric acetate addition product, when treated with phosphoric acid (98.6%), decomposed slowly without the appearance of white crystals to give free mercury. Furthermore, the addition of phosphoric acid to a mixture of β-(*p*-methoxyphenyl)-ethylmercuric acetate (VII) and mercuric acetate resulted in the formation of VIII in an almost quantitative yield.

The reaction of VII with phosphoric acid (98.6%) is interesting; it decomposed to give grayish-black mercury in a few minutes at room temperature. This decomposition was much slower in a mixture of acetic and phosphoric acids. When mercuric acetate or the product of the mercuration of anisole was added to phosphoric acid, no decomposition was observed even at 60°. Apparently these compounds react with VII to form a substance which is rather stable to phosphoric acid.

Discussion

It seems, from a consideration of the catalysts and reaction conditions, that this is an ionic reaction. The mercury compounds isolated as intermediates indicate that the reaction proceeds not by aromatic mercuration, but by condensation of the aromatic compound with the ethylene–mercury salt addition compound.

There has been much discussion concerning the structure of this addition compound. Although considerable data show that it is β-acetoxyethylmercuric acetate in acetic acid, there are indications that a complex is formed.[2,3] Moreover, the isolation of β-(*p*-methoxyphenyl)-ethylmercuric salt as an intermediate is not consistent with the assumption of β-acetoxyethylmercuric acetate as the reacting species. Moreover, ethyl acetate does not react with aromatic compounds under these conditions, and the reaction of β-acetoxyethylmercuric acetate should be even more difficult because of the effect of the acetoxymercury group on this carbonium ion reaction. A complex, perhaps a π-bonded one, is thus a more plausible reaction intermediate, and the equation given is the most probable first step of the reaction



This complex will be formed easily in the presence of acid and should be a good alkylating agent. The aromatic compound either may react with the carbonium ion from the complex form or it may participate directly in a substitution reaction with the complex. A choice between these possibilities is not possible at this time. A low concentration of the complex will be sufficient for the reaction, if the velocity of the equilibrium shift between complex and β-acetoxyethylmercuric acetate is large enough.

The next step is the further reaction of the β-(*p*-methoxyphenyl)-ethylmercuric salt (VI). The literature contains few reports of the formation of mercury by the reaction of alkyl or aralkyl mercurials with acids.[4,5] We found that benzylmercuric acetate decomposes to give mercury and benzyl acetate in the presence of phosphoric acid at room temperature.

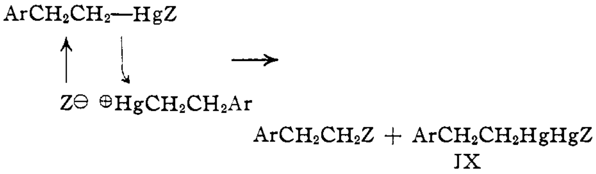
By method A, reaction 1 gives β-(*p*-methoxyphenyl)-ethyl acetate and Hg_2HPO_4. The latter reacts further, while the formation of free mercury appears to proceed through the unstable mercurous compound IX. Although its structure was not determined, an analogy to equation 1 suggests the reactions

$$\underset{\text{VI}}{2ArCH_2CH_2HgZ} \longrightarrow ArCH_2CH_2Z + \underset{\text{IX}}{ArCH_2CH_2HgHgZ} \quad (2)$$

IX then decomposes to form the product and free mercury

$$\underset{\text{IX}}{ArCH_2CH_2HgHgZ} \longrightarrow ArCH_2CH_2Z + 2Hg \quad (3)$$

Reaction 2 cannot be explained by the acid cleavage mechanism proposed for RHgR by Winstein and Traylor[5] because this should yield hydrocarbon and no RZ. The most probablemech anism for 2 appears to be the formation of $ArCH_2CH_2Hg^{\oplus}$ by acid with subsequent electrophilic attack on the mercury of $ArCH_2CH_2HgZ$.



$$\begin{matrix} ArCH_2CH_2\text{—}HgZ \\ \uparrow \quad \downarrow \\ Z^{\ominus} \quad {}^{\oplus}HgCH_2CH_2Ar \end{matrix} \longrightarrow ArCH_2CH_2Z + \underset{\text{IX}}{ArCH_2CH_2HgHgZ}$$

$ArCH_2CH_2^{\oplus}$ then combines with an acid radical (anion) and forms the organic ester in the presence of organic acid, or reacts with aromatics to form 1,2-diarylethane. Nucleophilic substitution of $Z^{\ominus}$ on carbon is ruled out by the fact that reaction 2 did not occur when sodium perchlorate was added to the acetic acid solution of β-(*p*-methoxyphenyl)-ethylmercuric acetate.

Acetate is the predominant product formed in the presence of acetic acid; apparently it is more difficult for β-arylethyl acetate to undergo further alkylation than it is for the corresponding alcohol or inorganic ester.

The problem of orientation in this reaction requires explanation. In the case of anisole, the β-

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[2] H. J. Lucas, F. R. Hepner and S. Winstein, This Journal, **61**, 3102 (1939).

[3] J. Chatt, *Chem. Revs.*, **48**, 7 (1950).

[4] L. W. Jones, This Journal, **40**, 1269 (1918).

[5] S. Winstein and T. G. Traylor, *ibid.*, **77**, 3747 (1955).

arylethyl acetate formed was almost exclusively the *p*-isomer, while the anisil contained almost equal amounts of the *o,p'*- and *p,p'*-isomers. This seems to show a difference in the reactivities of the species reacting in the first and second steps of the alkylation. If the first stage involves a reaction between the carbonium ion and the aromatic compound, the results cannot be explained by an inductive effect, since both reactions occur on the β-carbon. Since stabilized reactant species tend to be highly selective, it seems likely that the *para* selectivity noted is a property of the ethylene–mercury salt complex which is assumed to be the reactant species in the first stage of the alkylation.

Experimental

Experimental procedures are indicated by the examples.

Method A.—A mixture of phosphoric acid (98.6%, 100 g.), anisole (108 g., 1 mole) and mercuric sulfate (30 g., 0.1 mole) was gradually heated with vigorous stirring; at 70° the mercury salt dissolved completely in the acid layer. Then ethylene gas was introduced at the rate of about 3 l./hr. After the reaction temperature (130°) had been maintained for 30–60 minutes, a large amount of white or pale pink crystals of Hg_2HPO_4 (VIII) was formed; positive test for mercurous ion with sodium hydroxide. *Anal.* Calcd. for Hg, 80.70. Found: Hg, 80.72. The crystals disappeared gradually with the simultaneous formation of mercury. The introduction of ethylene into the reaction mixture was continued until the reduction of mercury salt to free mercury was complete (0.11–0.13 mole of ethylene was absorbed). After cooling, the oily layer was separated from the acid layer. The latter was poured into water (300 ml.) and extracted three times with benzene (60 ml.). The oily layer and the benzene extract of the acid layer were combined and washed first with 5% sodium carbonate solution and then with water, and finally dried over anhydrous sodium sulfate. After removal of solvent by distillation on a steam-bath, the residue was distilled under reduced pressure and the fraction (I) boiling between 179° and 190° at 7–9 mm. was collected. This fraction was cooled to 0° and filtered. The precipitate was washed with cold ether (yield 6.8 g.) and recrystallized from ethanol as white needles of *p*-anisil (Ia), m.p. 127.2–127.8° (reported[6] 125.5–127°).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.05; H, 7.75.

The residual oil (6.8 g.), which was separated from the crystals, became semi-solid on long standing. Recrystallization from methanol gave white needles of 1-(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)-ethane (Ib), m.p. 40–40.5° (reported 40–42°).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.32; H, 7.52.

The anisils (Ia, Ib) were demethylated and identified as the corresponding hydroxy compounds. Compound Ia (0.5 g.), mixed with acetic acid (10 ml.) and 48% hydrobromic acid (10 ml.), was heated under reflux for 13 hours. The reaction mixture was poured into ice-water (50 ml.). The precipitate, recrystallized from 30% methanol (yield 0.3 g.), melted at 196–196.5°; m.p. reported for 1,2-bis-(*p*-hydroxyphenyl)-ethane, 197–199°[7] and 198–199°.[6]

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.16; H, 6.73.

1-(*o*-Hydroxyphenyl)-2-(*p*-hydroxyphenyl)-ethane (1.5 g.) was prepared in a similar manner from Ib (4 g.), m.p. 132–132.5°, reported[7] 131–133°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.28; H, 6.64.

Method B.—The apparatus described in method A was used. Ethylene was introduced into a mixture of mercuric acetate (48 g., 0.15 mole) and acetic acid (50 ml.) with stirring at room temperature, until a mercuric ion test with sodium hydroxide solution became negative. Anisole (150 g.) and 60% perchloric acid (26 g., 0.15 mole) were added and the mixture was heated at 53° for 3 hours with stirring. The reaction mixture became brownish-pink and then free mercury was observed. When water (70 ml.) was added to the cooled mixture, an oily layer separated. The acid layer was extracted with benzene three times. The combined oily layer and benzene extract was treated as in method A. Distillation gave the two main products, 20 g. of III boiling at 114–115° (2.5 mm.) and 6.5 g. of I boiling at 173–175° (5 mm.). The latter was identical with the mixture (Ia and Ib) mentioned above. Compound III, a liquid ($n^{20}D$ 1.5082), was identified as β-(*p*-methoxyphenyl)-ethyl acetate. It (24 g.) was hydrolyzed by boiling with 20% alcoholic potassium hydroxide solution for 3 hours. The alcohol was removed and the residue extracted with ether. The ether extract was washed with water, neutralized with dilute sulfuric acid, washed again with water and dried over anhydrous sodium sulfate. Distillation gave a liquid (15 g.) boiling at 114–115° (4 mm.), which was identified as β-(*p*-methoxyphenyl)-ethyl alcohol (II) by means of the phenylurethan, m.p. 127–127.5°, reported,[8] m.p. 128°. The same alcohol, which was also identified as the phenylurethan, was obtained when mercuric sulfate was used.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.63; H, 8.15. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 70.60; H, 6.37. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.20; H, 7.44.

The acetate III (2.8 g.) was boiled with 5% sodium hydroxide solution (50 ml.) and 4% potassium permanganate solution (140 ml.). As the color of the permanganate disappeared, potassium permanganate (9 g.) was added in five portions and ethanol was added to decolorize the excess permanganate. Manganese dioxide was removed, the solution evaporated to 70 ml. and the residue acidified with dilute hydrochloric acid. The white crystals obtained (m.p. 177–179°) were recrystallized from ethanol to give *p*-anisic acid (1 g., m.p. 182–183°), reported[9] m.p. 183–184°. A mixed melting point with an authentic sample showed no depression. The combined mother liquor was evaporated. An alcoholic extract of the residue gave only *p*-anisic acid; no *o*-anisic acid could be obtained.

The β-(*p*-methoxyphenyl)-ethyl acetate and alcohol fractions obtained with the other catalysts were identified as III and II, respectively, in the same manner.

Reaction of Other Aromatic Compounds (Method A).—The reaction was carried out with various aromatic substances (60% perchloric acid or 98.6% phosphoric acid with mercuric acetate). The resulting β-arylethyl acetates were hydrolyzed to yield the alcohols which were identified as the phenylurethans. The results are summarized in Table III.

In addition to the β-arylethyl acetates, benzene (with phosphoric acid) and naphthalene (with perchloric acid) yielded the corresponding diarylethanes: bibenzyl (m.p. 52°, reported[10] 51°) and di-(α-naphthyl)-ethane (m.p. 160°, reported[11] 161–162°).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.22; H, 6.98.

Oxidation of β-Arylethyl Acetates with Permanganate.—The procedure is essentially that described under method B. After removal of the manganese dioxide, the reaction mixture was acidified. In the case of the tolyl derivative (2.7 g.), the resulting precipitate (2.7 g.) upon esterification yielded the dimethyl ester of terephthalic acid; yield 2 g., m.p. 138–139° (reported[12] 139–140°). A mixed melting point with an authentic sample showed no depression. The mother liquor, evaporated to dryness and extracted with ethanol, yielded phthalic acid; yield 0.1 g., m.p. 195–197° dec. These results show that the ratio of β-(*p*-tolyl)-ethyl acetate to β-(*o*-tolyl)-ethyl acetate is approximately 95:5.

In the case of the β-chlorophenylethyl acetate (2 g.), acidification of the filtered reaction mixture gave *p*-chlorobenzoic

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[6] E. M. Richardson and E. F. Reid, This Journal, **62**, 413 (1940).

[7] A. T. Carpenter and R. F. Hunter, *J. Applied Chem. (London)*, 1, 217 (1951).

[8] K. Kindler and L. Blaas, *Ber.*, **77B**, 585 (1944).

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[10] T. Reichstein and R. Oppenauer, *Helv. Chim. Acta.*, **16**, 1377 (1933).

[11] Ng. Ph. Buu-Hoï and Nguyen Hoán, *J. Org. Chem.*, **14**, 1023 (1949).

[12] N. M. Cullinane and D. M. Leyshon, *J. Chem. Soc.*, 2942 (1954).

TABLE III

REACTION OF VARIOUS AROMATIC COMPOUNDS WITH ETHYLENE IN THE PRESENCE OF MERCURY SALT AND CATALYST BY METHOD A

Aromatic compound	β-Arylethyl derivative	B.p. °C.	B.p. Mm.	n^tD	, °C.	Formula	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
Benzene	Acetate	85–86	7.5									
	Urethan	78–78.5[a,b]				$C_{15}H_{15}NO_2$	74.66	6.27	5.81	74.46	6.36	5.37
Toluene	Acetate	114.5–115	8[c]	1.5030	20	$C_{11}H_{14}O_2$	74.13	7.92		74.47	8.05	
	Alcohol	105–106	2.5[d]	1.5288	26	$C_9H_{12}O$						
	Urethan	115–115.2[a,e]				$C_{16}H_{17}NO_2$	75.27	6.71	5.49	75.72	6.90	5.69
o-Xylene	Acetate	126–127	6.5	1.5071	20	$C_{12}H_{16}O_2$	74.97	8.39		74.42	8.39	
	Alcohol	113–114	4[f]	1.5329	25	$C_{16}H_{14}O$	79.95	9.39		79.18	9.47	
	Urethan	111.5–112.3[a,g]				$C_{17}H_{19}NO_2$	75.81	7.11	5.20	75.99	7.19	5.62
Naphthalene	Acetate	181–184	12	1.5852	20	$C_{14}H_{14}O_2$	78.48	6.59		78.47	6.56	
	Alcohol[h]	60.5[a,i]				$C_{12}H_{12}O$	83.69	7.02		83.23	7.32	
	Urethan	116[a,j]				$C_{19}H_{17}NO_2$	78.33	5.88	4.81	78.43	6.36	5.05
Chlorobenzene	Acetate	117–120	5	1.5122	20	$C_{10}H_{11}ClO_2$	60.46	5.58		60.51	5.74	

[a] Melting points. [b] M.p. 80°; H. Hopff and K. Koulen, *Ber.*, **85**, 899 (1952). [c] B.p. 120–121° (12 mm.); ref. 8. [d] β-(*p*-Tolyl)-ethyl alcohol, b.p. 100–106° (1 mm.), n^{26}D 1.5282; N. L. Drake and W. C. McVey, *J. Org. Chem.*, 4, 464 (1939). [e] β-(*p*-Tolyl)-ethylurethan, m.p. 115°; ref. 8. [f] β-(3,4-Dimethylphenyl)-ethyl alcohol, b.p. 109–110° (3 mm.), n^{25}D 1.530; G. M. Pope and M. T. Bogert, *J. Org. Chem.*, 2, 276 (1937). [g] β-(3,4-Dimethylphenyl)-ethylurethan, m.p. 108–108.5°; ref. footnote *f*. [h] The acetate was refluxed with 20% alcoholic potassium hydroxide for 5 hours. After evaporation of the ethanol, the residue was extracted with ether. Removal of the ether gave a solid (b.p. 182–184° at 14.5 mm.) from which the alcohol was obtained by recrystallization from ethanol. [i] β-(α-Naphthyl)-ethyl alcohol, m.p. 60.5–61.5°; H. Adkins, THIS JOURNAL, 71, 3528 (1949). [j] M.p. 116–116.5°; ref. footnote *i*.

acid which was recrystallized from 75% ethanol; yield 0.9 g., m.p. 235–236° (reported[13] 234–236°). The mixed melting point showed no depression. Esterification of the acid with methanol and dry hydrogen chloride gave the methyl ester of *p*-chlorobenzoic acid; yield 0.6 g., m.p. 34.5–35° (reported[14] 34°).

Anal. Calcd. for $C_8H_7ClO_2$: C, 56.32; H, 4.14. Found: C, 56.60; H, 4.38.

Addition of water to the recrystallization filtrate gave *o*-chlorobenzoic acid; yield 0.8 g., m.p. 139.3–139.8° (reported[15] 140°). A mixed melting point showed no depression. These results indicate that β-chlorophenylethyl acetate is a mixture containing the *o*-chlorophenyl and *p*-chlorophenyl derivatives in a ratio of approximately 1:1.

Isolation of Mercury Containing Intermediate: β-(*p*-Methoxyphenyl)-ethylmercuric Iodide (IV) and Acetate VII.—An acetic acid solution and the addition compound (made from mercuric acetate (64 g.), acetic acid (60 ml.) and ethylene) was added to a mixture of anisole (100 g.) and 98.6% phosphoric acid (100 g.) with stirring at 22–23°. After 1.5 hours, water (400 ml.) was added to the acid layer. The resulting heavy gray oil was mixed with a little water and 700 ml. of a 5% potassium iodide solution was added with stirring. The white precipitate (IV), 46 g., which separated was recrystallized five times from ethanol, m.p. 146–148°. This material, after treatment with zinc dust and aqueous sodium hydroxide, yielded mercury which was separated from the aqueous layer as an amalgam, dissolved in nitric acid and then analyzed.[16] The aqueous layer was analyzed for iodine by the silver nitrate method.

Anal. Calcd. for $C_9H_{11}HgIO$: Hg, 43.36; I, 27.43. Found: Hg, 43.22; I, 27.25.

The reaction mixture, prepared as described above with 34 g. of 60% perchloric acid, was stirred at 33–35° for 2.5 hours. A small amount of free mercury was filtered, and the filtrate was poured into ice-water (600 ml.). The resulting heavy oily layer (122 g.), dissolved in acetic acid (200 ml.), was treated with 30% potassium iodide solution (62 g.). The white precipitate (42 g.) thus obtained melted at 127–150° dec. after one recrystallization from ethanol. Another recrystallization did not alter the wide melting point range. However, the mercury and halogen analyses corresponded approximately to IV.

Anal. Calcd. for $C_9H_{11}HgIO$: Hg, 43.36; I, 27.43. Found: Hg, 41.90; I, 26.43.

Silver acetate (3.3 g.) was added slowly at 60° to the precipitate (9 g.) suspended in methanol (100 ml.). After 20 minutes of stirring, the hot reaction mixture was filtered. Distillation of the methanol and recrystallization of the residue from ethanol gave white crystals (VII), m.p. 104.5–105.2°. Titration of VII (0.423 g.) in aqueous acetic acid solution with 0.1 *N* ammonium thiocyanate showed that VII is β-(*p*-methoxyphenyl)-ethylmercuric acetate; calcd. 10.71 ml., found 10.60 ml.

Conversion of IV to V.—An iodine solution containing 6 g. of iodine and 12 g. of potassium iodide in 120 ml. of water, was added to IV (9.2 g.) and the mixture was heated on a water-bath for 20 minutes. The excess iodine was decolorized with a solution of sodium thiosulfate and the resulting oily brown layer was extracted with benzene. The benzene extract was washed with water, dried over anhydrous sodium sulfate and evaporated. Distillation of the residue under reduced pressure gave white crystals (2.9 g.) of β-(*p*-methoxyphenyl)-ethyl iodide (V) which were recrystallized from ethanol; m.p. 30.4–30.6°.

Anal. Calcd. for $C_9H_{11}IO$: C, 41.24; H, 4.23; I, 48.42. Found: C, 41.40; H, 4.28; I, 48.91.

Conversion of V to II.—Compound V was hydrolyzed with sodium hydroxide solution to give the alcohol I, the phenylurethan of which (m.p. 127–127.5°) showed no depression of m.p. when mixed with an authentic sample.

Reaction of VII with Mercuric Acetate in the Presence of Phosphoric Acid.—To a mixture of VII (1.2 g.) and mercuric acetate (1 g.) was added 98.6% phosphoric acid (10 g.), and the mixture was shaken vigorously over a steam-bath for 20 minutes. Mercuric acetate disappeared in a few minutes, and white mercurous phosphate precipitated. The precipitate was washed with warm 98.6% phosphoric acid, then with water and finally with acetone; yield 1.4 g. Mercury analysis by iodometry showed the precipitate to be Hg_2HPO_4.

Anal. Calcd. for Hg_2HPO_4: Hg, 80.70. Found: Hg, 80.64.

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