Aryloxyesters. The Reactivity of the 
$\alpha$-Hydrogen and the Carbonyl Carbon towards 
Basic Reagents

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The two ways in which a base $B^-$ is able to react with a carbonyl compound, e.g. an aryloxyacetic ester, may be represented by the two equations:

\[
\text{ArO-CH}_2\text{C}^\text{O} + B^- \rightleftharpoons \text{ArO-CH-C}^\text{O} + \text{HB} \quad \text{(I)}
\]

\[
\text{ArO-CH}_2\text{C}^\text{O} + B^- \rightleftharpoons \text{ArO-CH}_2\text{C}^-\text{B} \quad \text{(II)}
\]

The reaction product of equation II may be stabilized by splitting off an alkoxide ion:

\[
\text{ArO-CH}_2\text{C}^-\text{B} \rightleftharpoons \text{ArO-CH}_2\text{C}^\text{O} + \text{OR} \quad \text{(III)}
\]

If the anion formed according to I acts as $B^-$ in II, condensation takes place, and the $\beta$-ketoester formed will be stabilized by donating a proton to the stronger base, the alkoxide ion:

\[
\text{ArO-CH}_2\text{C}^-\text{C}^\text{O} + \text{OR} \rightleftharpoons \text{ArO-CH}_2\text{C}^-\text{C}^\text{O} + \text{HOR} \quad \text{(IV)}
\]
In a previous paper the behaviour of alkoxy and aryloxy ketones and esters in acylation processes was discussed, and the view was expressed that the alkoxy group activates the carbonyl carbon relatively more than the $\alpha$-hydrogen towards basic reagents. The case of aryloxy esters, however, was not thoroughly studied, and, in view of the importance that many of the corresponding acids and some of the esters have recently acquired, a study was made of the acylation of certain of these esters.

The aryloxy group seems to activate the $\alpha$-hydrogen as well as the carbonyl carbon, but, as in the alkoxy esters, the carbonyl carbon is relatively more active than the $\alpha$-hydrogen when compared with the corresponding unsubstituted esters. All attempts to acylate ethyl phenoxyacetate (and ethyl 2,4-dichlorophenoxyacetate) with phenyl benzoate or phenyl propionate using sodium amide as a condensing agent, or with benzoyl chloride or acetyl chloride using potassium triphenylmethide failed completely, the self-condensation product exclusively being obtained. This was also the case when ethyl phenoxyacetate was added to the stirred and previously refluxed mixture of ethyl benzoate and sodium ethoxide and even when ethyl phenoxyacetate and sodium were added in small portions to heated ethyl benzoate over a period of three hours. Self-condensation also was the only result of an attempt to propionylate t-butyl phenoxyacetate, in which the carbonyl group should be less active than in the ethyl ester.

That the $\alpha$-hydrogen also is active was shown by an attempt to use ethyl phenoxyacetate as an acylating agent towards ethyl propionate and t-butyl acetate. Again mainly self-condensation of the phenoxy ester took place. Ketones, however, appear to be successfully acylated by phenoxy esters. Walther acylated acetophenone (and phenylacetonitrile) with ethyl phenoxyacetate using sodium ethoxide, but no yields are given. Henecka recently reported the acylation of acetone in 30% yield with methyl phenoxyacetate using pulverized sodium. In the present work acetophenone was acylated with ethyl phenoxyacetate using sodium amide in ether suspension the formation of the anion of acetophenone being indicated by the copious evolution

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* Phenyl esters are more active acylating agents than are ethyl esters; the reaction according to equation III is facilitated, since the phenoxy ion is a weaker base than the alkoxide ion.

** Apparently the more active esters ethyl formate or ethyl oxalate must be used in order to effect acylation by the usual procedures. A preliminary experiment was carried out condensing ethyl phenoxyacetate with benzaldehyde, the carbonyl group of which is much more active than those of the esters. Ethyl $\alpha$-phenoxyacinnamate, m. p. 47—48° and $\alpha$-phenoxyacinnamic acid, m. p. 181—182° (reported 184°) were obtained and identified. This reaction will be further studied.
of ammonia before adding the ester. A 60% yield was obtained. \(\omega\)-Methoxyacetophenone, however, was not acylated by ethyl phenoxyacetate under similar conditions, but this ketone was previously shown to be rather unreactive\(^1\).

Generally the self-condensations of phenoxy esters were satisfactory (Table 1). In most cases diisopropylaminomagnesium bromide\(^{1,11}\) was used as a condensing agent. Some of the acylation-attempts may be considered as self-condensations since they gave excellent yields as such, viz. those of ethyl phenoxyacetate, ethyl 2,4-dichlorophenoxyacetate and t-butyl phenoxyacetate, using sodium amide.

Ethyl 2,4,6-trichlorophenoxyacetate gives a notably low yield (28%) of self-condensation using diisopropylaminomagnesium bromide, and when sodium amide is used, no self-condensation occurs, the ester being almost completely converted into the amide (according to equations II and III). Similar results were obtained with ethyl 2-methyl-4-chlorophenoxyacetate. The t-butyl ester of 2,4,6-trichlorophenoxyacetic acid, however, gives a good yield (51%) of the corresponding acetoacetic ester, using diisopropylaminomagnesium bromide. These results may perhaps be explained by a steric effect of the large 2,4,6-trichlorophenoxy group. (This effect is also shown by the 2-methyl-4-chlorophenoxy group, but, apparently, not by the 2,4-dichlorophenoxy group.) In the case of the ethyl ester, the attack of the base on the \(\alpha\)-hydrogen should be hindered; the carbonyl group, therefore, will react first with the base, the yield of self-condensation product consequently being reduced. In the case of the t-butyl ester the steric effect of the trichlorophenoxy group should be counterbalanced by the t-butoxy group, which will delay the attack on the carbonyl carbon.

The t-butyl ester of phenoxyacetic acid also gave a good yield of self-condensation product. In the attempt to propionylate this ester, distillation \textit{in vacuo} of the condensation product was tried, but destruction took place. The yellow distillate, after standing for several days, crystallized and was identified as \(\alpha,\gamma\)-diphenoxyacetone, apparently the decarboxylation product of the self-condensation product.

The self-condensations of \(\alpha\)-aryloxypropionic esters were complicated by the fact that the resulting \(\beta\)-ketoesters have no \(\alpha\)-hydrogen and, accordingly, do not form any sodium derivative, so difficulties arose in separating them from the unchanged esters. Equation IV is not valid for \(\alpha\)-substituted propionic esters and, accordingly, the yields by the acylations of these esters are generally lower than by the corresponding acetic esters. In the case of both \(\alpha\)-phenoxypropionic and \(\alpha\)-(2,4-dichlorophenoxy)propionic ester\(^1\), however, probably self-condensation occurred and no carbonyl carbon attack by the
condensing base was observed (no nitrogen was found by the sodium fusion test). In order to obtain a crystalline product, ethyl α-(2,4,6-trichlorophenoxy)-propionate was prepared and self-condensed in the usual way. As in the case of the acetic ester, the yield was rather low, but the β-ketoester was obtained pure in a 22 % yield.

EXPERIMENTAL

All melting and boiling points are uncorrected. 

Ethyl 2,4-dichlorophenoxyacetate, b. p. 147° at 1 mm (reported 149—155° at 5 mm \(^{13}\)) was obtained in 66 % yield from 2,4-dichlorophenoxyacetic acid, m. p. 138.5—139.5° (reported 139—140° \(^{14}\) and 138° \(^{15}\)) by refluxing the ethanolic solution with a small amount of concentrated sulfuric acid.

Similarly ethyl 2-methyl-4-chlorophenoxyacetate, b. p. 158—160° at 10 mm was obtained in 82 % yield from the corresponding acid. This 2-methyl-4-chlorophenoxyacetic acid, m. p. 113—115° (reported 119—120° \(^{14}\)) was obtained by four recrystallizations from benzene of the technical product. Alkaline hydrolysis of the ester:

\[ C_{11}H_{12}O_3Cl \] (228.67)  Equiv. wt. found 228.5

The remaining ethyl esters were prepared according to the following general procedure: One equivalent of the corresponding phenol in ethanolic solution was added to a solution of one equivalent of sodium in ethanol. While this was gently refluxing, one equivalent of ethyl chloroacetate in ethanol was added from a dropping funnel. After refluxing on a water-bath (preferably with stirring to avoid bumping) for 3—4 hours, generally the equivalent amount of sodium chloride had separated. Most of the excess of ethanol was distilled on the water-bath, the residue cooled and poured into water. Ether was added, the water layer extracted with ether, the combined ether layers washed with ice-cold 2 \( N \) sodium hydroxide solution, and dried over anhydrous potassium carbonate. The ether was distilled and the residue distilled in vacuo.

Ethyl phenoxyacetate, b. p. 250—251° (reported 250° \(^{16}\)), yield 65 %. Alkaline hydrolysis:

\[ C_{15}H_{12}O_3 \] (180.20)  Equiv. wt. found 179.1

Ethyl 2,4,6-trichlorophenoxyacetate, m. p. 41.5—42.5° (reported 33—34° \(^{12}\)). On pouring the reaction mixture into water, the ester separated in solid form. After the above-mentioned treatment of the ether solution with sodium hydroxide and evaporation of the ether, the ester was recrystallized from ethanol into beautiful white crystals. Yield 80 %; alkaline hydrolysis:

\[ C_{16}H_{14}O_3Cl \] (283.54)  Equiv. wt. found 283.6

On acidification, 2,4,6-trichlorophenoxyacetic acid was isolated and recrystallized from benzene, m. p. 177—178° (reported 177—178° \(^{12}\) and 190° \(^{14}\)).

Ethyl β-naphthoxyacetate, b. p. 170—190° at 10 mm, recrystallized from ethanol, m. p. 49—51° (reported 48—49° \(^{17}\)), light bluish crystals, yield 70 %. Alkaline hydrolysis:

\[ C_{14}H_{14}O_3 \] (230.5)  Equiv. wt. found 229.0
**α-ARYLOXYESTERS**

*Ethyl α-(2,4,6-trichlorophenoxy)propionate*, b. p. 143° at 1 mm, 189° at 25 mm, m. p. 22°. 80 % yield from ethyl α-bromopropionate, only 30 % yield from ethyl α-chloropropionate.

\[
\text{C}_1\text{H}_1\text{O}_3\text{Cl}_3 \quad (297.57) \quad \text{Calc.} \quad \text{Cl} \quad 35.75
\]

\[
\text{Found} \quad 35.64
\]

Alkaline hydrolysis: Equiv. wt. found 299.0

On acidification after the alkaline hydrolysis α-(2,4,6-trichlorophenoxy)-propionic acid was isolated and recrystallized from benzene, m. p. 112–113° (reported 115–116° 14).

**t-Butyl phenoxyacetate.** The general procedure of treating the acid chloride with t-butyl alcohol in the presence of dimethylaniline was followed. Yield 55 %, b. p. 110–113° at 1 mm (attempted distillation at 15 mm resulted in destruction). Alkaline hydrolysis:

\[
\text{C}_{12}\text{H}_{16}\text{O}_3 \quad (208.25) \quad \text{Equiv. wt. found 207.1}
\]

**t-Butyl 2,4,6-trichlorophenoxyacetate.** Attempts to prepare this ester according to the above-mentioned general procedure for t-butyl esters failed: The acid was obtained by alkaline hydrolysis of the ethyl ester and was recrystallized from benzene, m. p. 177–178°. By treatment of the acid with excess thionyl chloride on a steam-bath, 2,4,6-trichlorophenoxyacetyl chloride was obtained in 83 % yield, b. p. 160–165° at 11 mm, m. p. 59° (reported 55–56° 12).

\[
\text{C}_8\text{H}_6\text{O}_2\text{Cl}_4 \quad (273.99) \quad \text{Calc.} \quad \text{Cl} \quad 51.78
\]

\[
\text{Found} \quad 51.99
\]

From the acid chloride, t-butyl alcohol and dimethylaniline, however, only the free acid could be obtained *. Instead the t-butyl ester was prepared from t-butyl chloroacetate 19 and potassium 2,4,6-trichlorophenolate (an attempt using the sodium phenolate failed) in t-butyl alcohol solution. The procedure was analogous to the above-described method for ethyl aryloxyacetates; only the final distillation was omitted. The residue, after evaporation of the ether, was heated in *vacuo* at 100° by which treatment a small amount of t-butyl chloroacetate was removed. On cooling in ice, the residue crystallized but melted again on standing at room temperature. The residue was mixed with methanol and this solution cooled in dry-ice. The crystals were filtered on a Buchner funnel, the funnel being cooled by surrounding it with dry-ice, and washed with cooled methanol. The white crystals melted on standing. To remove the methanol, the product was heated *in vacuo* on a boiling water bath, dry benzene added and again removed by distillation *in vacuo*. This benzene treatment was repeated, and the residue finally heated *in vacuo* at 100° for two hours. The yield of crude product on a 0.5 molar scale was 75 %. Alkaline hydrolysis:

\[
\text{C}_{12}\text{H}_{16}\text{O}_3\text{Cl}_3 \quad (311.59) \quad \text{Equiv. wt. found 307.1}
\]

* This was also the case in an attempt to prepare t-butyl 2,4-dichlorophenoxyacetate. 2,4-Dichlorophenoxyacetyl chloride was obtained in 89 % yield, b. p. 135° at 15 mm, m. p. 24°.

\[
\text{C}_8\text{H}_4\text{O}_2\text{Cl}_3 \quad (239.49) \quad \text{Calc.} \quad \text{Cl} \quad 44.41
\]

\[
\text{Found} \quad 44.32
\]

3
Attempted acylations of ethyl phenoxyacetate and ethyl 2,4-dichlorophenoxyacetate with phenyl benzoate or phenyl propionate using sodium amide. Several experiments were carried out. Although the relative quantities of sodium amide, ethyl phenoxyacetate and acylating ester were varied the general course remained the same. Generally 0.2 mol of sodium amide was employed. To the stirred suspension of sodium amide in ether was added ethyl phenoxyacetate. After a few minutes evolution of ammonia began, indicating the formation of the anion of the ester. The acylating ester was added and the reaction mixture refluxed for two to three hours then poured onto ice and concentrated hydrochloric acid added until acidic reaction. A white precipitate, insoluble in both water and ether, was filtered, washed with ether and water and recrystallized from ethanol; white crystals, m.p. 140°. This compound, apparently, is o,p'-diphenoxycetacetamide. The yield was 25—30%.

\[
\begin{array}{l}
\text{C}_{16}\text{H}_{25}\text{O}_{4}\text{N} (285.29) \\
\text{Calc.} \quad \text{C} \quad 67.35 \quad \text{H} \quad 5.30 \quad \text{N} \quad 4.91 \\
\text{Found} \quad \text{C} \quad 67.44 \quad \text{H} \quad 5.03 \quad \text{N} \quad 4.87
\end{array}
\]

The filtrate which consisted of a water and an ether layer was separated and the water layer extracted with ether. The combined ether extracts were shaken with 2 N sodium hydroxide solution, by which treatment in most cases a white solid precipitated. In some cases the ether layer, after shaking with sodium hydroxide, had to stand overnight in the ice-box, or it was necessary to evaporate the ether in order to effect crystallization. The yield of the sodium derivative of ethyl o,p'-diphenoxycetacetate was 40% of the theoretical, the overall yield of self-condensation products being 65—70%.

After filtration and washing, the sodium derivative was converted into the free \(\beta\)-ketoester by shaking with ether and 4 N hydrochloric acid. After washing the ether solution with saturated sodium bicarbonate solution and water and drying over anhydrous sodium sulfate, the solvent was evaporated and the free \(\beta\)-ketoester was obtained as an almost colorless oil, which, however, decomposed, when distillation in vacuo at 0.5 mm was attempted. With 2,4-dinitrophenylhydrazine a yellow hydrazine was obtained, m.p. 159—160°.

\[
\begin{array}{l}
\text{C}_{24}\text{H}_{25}\text{O}_{6}\text{N}_{4} (494.46) \\
\text{Calc.} \quad \text{C} \quad 58.29 \quad \text{H} \quad 4.48 \quad \text{N} \quad 11.33 \\
\text{Found} \quad \text{C} \quad 58.20 \quad \text{H} \quad 4.59 \quad \text{N} \quad 11.33
\end{array}
\]

With ethyl 2,4-dichlorophenoxyacetate an 87% yield of the sodium derivative of the \(\beta\)-ketoester was obtained directly from the reaction mixture by pouring onto ice. The sodium derivative was converted into the free ethyl o,p'-di(2,4-dichlorophenoxy)acetacetate which crystallized and was recrystallized from ethanol, white crystals, m.p. 96—98°, yield 60%.

\[
\begin{array}{l}
\text{C}_{18}\text{H}_{14}\text{O}_{2}\text{Cl}_{4} (452.12) \\
\text{Calc.} \quad \text{C} \quad 47.82 \quad \text{H} \quad 3.12 \quad \text{Cl} \quad 31.37 \\
\text{Found} \quad \text{C} \quad 47.64 \quad \text{H} \quad 3.19 \quad \text{Cl} \quad 31.35
\end{array}
\]

* In some experiments the acylating ester was added immediately after the phenoxy ester or the two esters were added in mixture; no difference in results was observed. During the addition of the acylating ester the ether refluxed, indicating that some reaction took place. The acylating phenyl esters were converted into the corresponding ethyl esters (see ref. 1, note 18).

In one experiment with ethyl phenoxyacetate the reaction time was reduced to thirty minutes. No acetoacetamide was formed, but 48% of the self-condensation product was obtained.
a-ARYLOXYESTERS

Attempted propionylation of t-butyl phenoxyacetate with phenyl propionate using sodium amide. The procedure was as described above; equivalent amounts (0.2 mole) of sodium amide, t-butyl phenoxyacetate (41.6 g) and phenyl propionate (30 g) were used except for a 10% excess of sodium amide. The reaction mixture was poured onto ice and filtered. The white precipitate of the sodium derivative, after washing and drying, weighed 28 g (77% yield of self-condensation). The free β-ketoester was obtained in the usual way (see above). Attempted distillation in vacuo resulted in decomposition. One fraction (7 g) of yellow distillate, after standing for six days, had crystallized and was recrystallized from ethanol, white needles, m.p. 59—60°. It was identified as a,γ-diphenoxyacetone:

\[
C_{15}H_{14}O_3 \ (242.26) \quad \text{Calc.} \quad \text{C} \quad 74.36 \quad \text{H} \quad 5.82
\]

\[
\text{Found} \quad \text{73.98} \quad \text{5.53}
\]

It formed a yellow 2,4-dinitrophenylhydrazone, m.p. 125-126°:

\[
C_{21}H_{18}O_6N_4 \ (422.39) \quad \text{Calc.} \quad \text{N} \quad 13.27
\]

\[
\text{Found} \quad \text{13.25}
\]

a,γ-Diphenoxyacetone, which apparently is not previously reported in the literature, was further identified in the following way: Glycerol-a,γ-diphenylether, m.p. 81—82° (reported 82° 28), which was obtained in 75% yield by refluxing one equivalent of glyceroaldi-chlorohydrin with an ethanolic solution of two equivalents of each of sodium and phenol, was oxidized with potassium dichromate in sulfuric acid for two hours on a steam-bath. The reaction mixture was extracted with ether and the ether distilled. From the residue, after fractional crystallization, by which most of the glyceroaldiphenylether was recovered, a small amount of a substance was isolated which was found to be identical with the decomposition product of the condensation product of t-butyl phenoxyacetate: m.p. 59—60°, mixed m.p. 59—60°, dinitrophenylhydrazone m.p. 125—126°.

Self-condensations (Table 1). Most of the esters were self-condensed by means of di-isopropylaminomagnesium bromide according to the general procedure previously described 1,11. The self-condensation of ethyl phenoxyacetate and of methyl 2,4-dichlorophenoxyacetate are previously described 1. Generally the β-ketoesters were obtained first as sodium derivatives when the ether extract of the reaction mixture was treated with sodium hydroxide solution (see above). These were converted into the free β-ketoesters which were obtained as almost colorless oils which could not be distilled.

### Table 1.

<table>
<thead>
<tr>
<th>Ester</th>
<th>Yield of a,γ-diaryloxy-acetoacetic ester %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl phenoxyacetate 1</td>
<td>63</td>
</tr>
<tr>
<td>Methyl 2,4-dichlorophenoxyacetate 1</td>
<td>65</td>
</tr>
<tr>
<td>Ethyl 2,4-dichlorophenoxyacetate</td>
<td>60</td>
</tr>
<tr>
<td>t-Butyl phenoxyacetate</td>
<td>55</td>
</tr>
<tr>
<td>Ethyl 2-methyl-4-chlorophenoxyacetate</td>
<td>21</td>
</tr>
<tr>
<td>Ethyl β-naphthoxyacetate</td>
<td>61</td>
</tr>
<tr>
<td>Ethyl 2,4,6-trichlorophenoxyacetate</td>
<td>28</td>
</tr>
<tr>
<td>t-Butyl 2,4,6-trichlorophenoxyacetate</td>
<td>51</td>
</tr>
<tr>
<td>Ethyl a-(2,4,6-trichlorophenoxy)propionate</td>
<td>22</td>
</tr>
</tbody>
</table>
1. *Ethyl phenoxyacetate* and *ethyl 2,4-dichlorophenoxyacetate*. Several acylation attempts using other bases (see above) resulted in self-condensation. By attempted benzylation of ethyl phenoxyacetate with ethyl benzoate using sodium ethoxide⁴ or sodium⁸ self-condensation was effected in 60 and 55 % respectively. The 2,4-dinitrophenylhydrazone is described above.

2. *t-Butyl phenoxyacetate*. The corresponding β-ketoester did crystallize and could be re-crystallized from ethanol, m. p. 57—58°.

\[
\text{C}_{20}\text{H}_{22}\text{O}_5 \ (342.38) \quad \text{Calc. C} \quad 70.15 \quad \text{H} \quad 6.48 \\
\text{Found} \quad 69.88 \quad 6.27
\]

The dinitrophenylhydrazone has the m. p. 143—144°.

3. *Ethyl 2-methyl-4-chlorophenoxyacetate* was self-condensed by diisopropylaminomagnesium bromide, the product being an oil, which was not purified. When sodium amide was used, the ester was converted into the amide, which was recrystallized from ethanol, m. p. 150—151°.

\[
\text{C}_{9}\text{H}_{10}\text{O}_2\text{NCl} \ (199.64) \quad \text{Calc. N} \quad 7.02 \quad \text{Cl} \quad 17.76 \\
\text{Found} \quad 6.98 \quad 17.78
\]

4. *Ethyl β-naphthoxyacetate*. The self-condensation product was an oil, which was not purified.

5. *Ethyl 2,4,6-trichlorophenoxyacetate*. The β-ketoester was obtained as white crystals (from ethanol). Rather surprisingly, the melting point was as low as 77—78°.

\[
\text{C}_{15}\text{H}_{12}\text{O}_5\text{Cl}_6 \ (521.02) \quad \text{Calc. C} \quad 41.49 \quad \text{H} \quad 2.32 \quad \text{Cl} \quad 40.83 \\
\text{Found} \quad 41.29 \quad 2.55 \quad 40.86
\]

When sodium amide was used as a condensing agent the ester was converted into the amide in 70 % yield, m. p. 195—196° (from ethanol) (reported 195—196°¹²).

\[
\text{C}_{8}\text{H}_6\text{O}_2\text{NCl}_3 \ (254.51) \quad \text{Calc. N} \quad 5.50 \quad \text{Cl} \quad 41.79 \\
\text{Found} \quad 5.38 \quad 41.56
\]

6. *t-Butyl 2,4,6-trichlorophenoxyacetate*. The β-ketoester was obtained as white crystals (from ethanol), m. p. 129—131°.

\[
\text{C}_{20}\text{H}_{18}\text{O}_5\text{Cl}_6 \ (549.07) \quad \text{Calc. Cl} \quad 38.75 \\
\text{Found} \quad 38.77
\]

7. *Ethyl α-(2,4,6-trichlorophenoxy)propionate*. The treatment with sodium hydroxide was not applied and the β-ketoester crystallized directly, after evaporation of the ether from the ether extract of the acidified reaction mixture¹. *Ethyl α,γ-dimethyl-α,γ-di-(2,4,6-trichlorophenoxy)acetoacetate*, white crystals (from ethanol), m. p. 116—117°. *A*
mixed melting point with α-(2,4,6-trichlorophenoxy)propionic acid, m. p. 112—113° (reported 115—116° 14) was found to be 84°.

C_{25}H_{16}O_5Cl_6 (549.07)  
Calc. Cl 38.75  
Found * 38.42

*Acylation of acetophenone with ethyl phenoxyacetate using sodium amide.* The general procedure given by Adams and Hauser 10 was followed except that equivalent amounts (0.2 mole) of each of sodium amide (10 % excess), the ketone (24 g) and the ester (36 g) were used. The reaction mixture was poured onto ice and the sodium derivative of the β-diketone was filtered and washed, and converted into the free β-diketone by shaking with ether and hydrochloric acid. The alkaline water layer from the filtrate, after washing with ether, was acidified and more β-diketone was obtained. After recrystallizations from ethanol and ligroin (b. p. 90—110°) in total 31 g (60 %) of α-phenoxy-γ-benzoylacetone was obtained, m. p. 81—82° (reported 79—80° 8).

C_{16}H_{14}O_3 (254.37)  
Calc. C 75.58 H 5.55  
Found * 75.63 * 5.52

**SUMMARY**

The behaviour of α-aryloxy esters in condensation processes brought about by basic reagents has been studied. These esters are shown to be extremely apt to self-condensation, and a number of such condensations have been effected, while mixed condensations between other esters and aryloxy esters for this reason have been unsuccessful. The influence of the aryloxy group is discussed.

The preparations of a number of aryloxy esters and certain other aryloxy compounds are given.

The acylation of acetophenone with ethyl phenoxyacetate to give phenoxybenzoylaceton is described.

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**REFERENCES**


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