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# ORGANOCADMIUM REAGENTS
# VII*. COMPETITION BETWEEN DISPLACEMENT OF ALKOXY AND ACYLOXY IN 3-SUBSTITUTED PHTHALIDES

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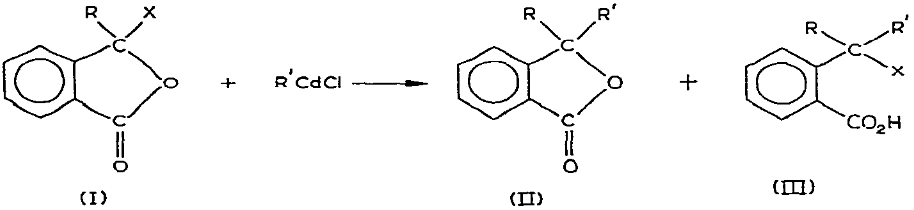
## SUMMARY

The reaction of organocadmium reagents with 3-alkoxyphthalides to give *o*-substituted benzoic acids by an acyloxy displacement is found to be general and highly favored over the displacement of an alkoxy substituent. In the case of 3-acyloxyphthalides, the "exocyclic" group is displaced preferentially. Two concerted reaction pathways, consistent with the stereochemical results, could account for this behavior.

## INTRODUCTION

The distinctively diminished reactivity of organocadmium reagents, by comparison with the Grignard or lithium analogs, makes it possible to effect unusual reactions of $R_2Cd$ or RCdX with substrates containing carbonyl groups, which are not attacked themselves[2].

Among this group of fascinating reactions is the attack of organocadmium reagents on 3-substituted phthalides (I), the overall result being an effective displacement of one of the substituents at the 3-position. In 1967 we first noted[2] two instances where the displaceable group was acyloxy, as opposed to halogen, hydroxy, or alkoxy. Thus, the reaction of (I) in its most general form [eqn. (1)] is a competition between displacement of "X" to give new phthalide (II) and displacement of acyloxy with ring opening to afford an *o*-substituted benzoic acid (III).



(1)

In an effort to learn whether the lactone ring-opening reaction [(I) → (III)] was widely applicable, we have prepared several diverse phthalides [(I), X = alkoxy or acyloxy] and studied their behavior toward organocadmium reagents. The results,

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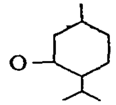
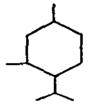
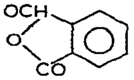
*For Part VI see ref. 1.

TABLE 1

COMPETITIVE DISPLACEMENT OF ALKOXY AND ACYLOXY IN 3-SUBSTITUTED PHTHALIDES BY ORGANOCADMIUM REAGENTS (eqn. (1))

| R | X | R' | (II) (%) | (III) (%) |
|---|---|---|---|---|
| H | $OCH_3$ | $CH_3$ | 2[a] | 91 |
| H | $OC_2H_5$ | $CH_3$ | 1[a] | 85 |
| $C_6H_5$ | $OC_2H_5$ | $C_2H_5$ | | 87[b] |
| $C_6H_5$ | $OCH(CH_3)_2$ | $C_2H_5$ | | 19[b] |
| $C_6H_5$ | $OCH(CH_3)_2$ | $C_6H_5$ | | [c] |
| H | O  | $CH_3$ | | 61[d], 97[e] |
| H | $OCOCH_3$ | $CH_3$ | 30, 57[a]<br>0[g] | [f] |
| $CH_3$ | $OCOCH_3$ | $CH_3$ | 44[g] | |
| H | $OCOCH_2O$  | $CH_3$ | 38, 13 | [h] |
| H | $OCOCH(C_6H_5)CH_2CH_3$ | $CH_3$ | | [i] |
| H |  | $CH_3$ | trace[a,k] | 22[j] |

[a] Determined by NMR analysis with dioxane as internal standard; all other values based on weight of isolated product. [b] Ref. 2. [c] o-benzoylbenzoic acid, 72%. [d] 16.5 h. [e] 45 h. [f] Starting material 42%, 33% (NMR analysis). [g] Ref. 7. [h] Starting material 36%, 33% (NMR analysis). [i] Starting material 57%, 2-phenylbutanoic acid, 14%. [j] Starting material 73%. [k] The earlier report (ref. 7) that 3-methylphthalide is formed in quantitative *yield is very apparently in error.*

assembled in Table 1, show the variations in (I) and the extent of formation of (II) and (III).

## EXPERIMENTAL

### 3-(−)-*Menthoxyphthalide*

Phthalaldehydic acid (25 g, 0.17 mole) and 26 g (0.17 mole) of (−)-menthol were refluxed in benzene for 48 h. The benzene solution was cooled, extracted with three 25-ml portions of saturated $NaHCO_3$, dried ($MgSO_4$), the benzene distilled, and the last traces of benzene evaporated on a watch glass. The solidified benzene residue was recrystallized from isopropyl alcohol, yielding 27 g (55%) of a white solid. Two more recrystallizations from the same solvent produced a white solid, m.p. 123.5–125.0°; IR (double mull): 1760 (C=O) and 2800–3000 (C–H); NMR ($CDCl_3$): 0.70–4.00 (m, 19,$-OC_{10}H_{19}$), 6.41 (d, 1, $J$ 6.0 Hz, –CHO–) and 7.30–7.91 ppm (m, 4). (Found: C, 74.86; H, 8.45. $C_{18}H_{24}O_3$ calcd.: C, 74.97; H, 8.39%.)

### 3-(2-*Phenylbutyryloxy*)*phthalide*

2-Phenylbutyryl chloride[3] (17 g, 0.092 mole) was added dropwise over 15 min to 14 g (0.092 mole) of phthalaldehydic acid in 150 ml of anhydrous pyridine*. The reaction mixture was stirred at 70° for 8 h.

The mixture was filtered and the filtrate poured into 100 ml of cold water. From the water/pyridine mixture, refrigerated overnight, 4.8 g (18%) of crude solid was collected. The solid was taken up in boiling methanol. Some insoluble material was removed by filtration and the filtrate cooled to room temperature. After removal of a second portion of solid and refrigeration of the filtrate, 2.5 g (9%) of a white solid, m.p. 78.0–79.0°, was collected; IR (double mull): 1755 and 1780 (C=O); NMR ($CCl_4$): 0.88 [t,3,–O–C(O)–C–C–$CH_3$], 1.95 [octet, 2, –O–C(O)–C–$CH_2$–], 3.51 [t, 1, –O–C(O)–CH–C–C], 7.22 [s, 5, –O–C(O)–($C_6H_5$)–C–C], 7.32 [s, 1, –CH–O–C(O)–] and 7.39–7.88 ppm (m, 4). (Found: C, 72.90; H, 5.54. $C_{18}H_{16}O_4$ calcd.: C, 72.96; H, 5.44%.)

### 3-[(–)-*Menthoxyacetoxy*]*phthalide*[1]

Phthalaldehydic acid (28.7 g; 0.191 mole) was dissolved in 112 ml of anhydrous pyridine and 27.8 g (0.191 mole) of 3-(–)-menthoxyacetyl chloride[4] was added over $\frac{1}{2}$ h. The reaction mixture was stirred magnetically at room temperature for 0.3 h and then at 77° for 1.0 h.

The reaction mixture, when cool, was poured into 700 ml of cold water, the resulting mixture being stored in the refrigerator overnight. A colored solid (16.9 g) was collected.

This solid, in addition to 9.4 g from a similar experiment, was taken up in boiling 95% ethanol. Some insoluble material was removed by filtration and the filtrate cooled to room temperature. After removal of a second portion of yellow solid and refrigeration of the filtrate, 19.9 g of material was obtained. Two recrystallizations from 95% ethanol yielded 13.4 (33%) of a white solid, m.p. 85–86°; $[\alpha]^{24}_{578}$ $-71.8\pm0.0$ (*c* 2.2, $C_2H_5OH$); $-70.7\pm0.0$ (*c* 2.3, $C_2H_5OH$); IR (double mull): 1775 and 1780 (C=O); NMR ($CCl_4$): 0.50–3.50 [series of multiplets, 19, –O–C(O)–C–O–$C_{10}H_{19}$], 4.13 [s, 2, –O–C(O)–$CH_2$–O–], 7.38 [s, 1, –CH–O–C(O)–] and 7.50–8.00 ppm (m, 4). (Found: C, 69.47; H, 7.67. $C_{20}H_{26}O_5$ calcd.: C, 69.34; H, 7.57%.)

### *o*-(1-*Methoxyethyl*)*benzoic acid*

Methylcadmium chloride was prepared as above from 130 ml of ether, 1.3 g (0.054 g-atom) of magnesium 7.7 g (0.054 mole) of methyl iodide, and 9.9 g (0.054 mole) of cadmium chloride. To the cadmium reagent was added, over 1 h, 4.4 g (0.027 mole) of 3-methoxyphthalide[6,7] in 35 ml of ether. The reaction mixture was stirred at reflux temperature for 4 h.

The reaction complex was worked up as before, using 192 ml of 6% $H_2SO_4$, five 50-ml portions of ether, two 20-ml portions of saturated $NaHSO_3$, six 40-ml portions of saturated $Na_2CO_3$, two 40-ml portions of saturated NaCl, and anhydrous $MgSO_4$. The ether was removed by rotary evaporation. NMR analysis of the oily residue with dioxane as an internal standard indicated 0.062 g (1.6%) of 3-methylphthalide.

From acidification of the $Na_2CO_3$ layer with concentrated HCl, 4.4 g (91%)

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*Commercial grade pyridine was stirred over anhydrous barium monoxide at reflux temperature for 58.5 h and then at room temperature for 49 h.

of a white solid, m.p. 111.0–111.5°, was collected; IR (double mull): 1690 (C=O); NMR ($CDCl_3$): 1.53 [d, 3, *J* 6 Hz, $-C(CH_3)-O-$) 3.30 (s, 3, $-C-O-CH_3$), 5.37 (q, 1, *J* 6 Hz, $-CH-O-$) and 7.19–8.20 ppm (m, 4). (Found: C, 66.65; H, 6.79. $C_{10}H_{12}O_3$ calcd.: C, 66.65; H, 6.71%.)

### *o-(1-Ethoxyethyl)benzoic acid*

Methylcadmium chloride was prepared in 125 ml of ether from 1.9 g (0.076 g-atom) of magnesium, 11 g (0.076 mole) of methyl iodide, and 14 g (0.076 mole) of cadmium chloride. To the cadmium reagent was added, over 1 h, 6.8 g (0.038 mole) of 3-ethoxyphthalide[5,6] in 70 ml of ether. The reaction mixture was stirred at reflux temperature for 4.5 h.

The reaction mixture was poured into 48 ml of 6% $H_2SO_4$ containing ice. The reaction flask was rinsed with 2 g $H_2SO_4$ in 15 ml water. The layers were filtered and separated. The aqueous layer was extracted with five 40-ml portions of ether. The combined ether solution was washed with two 15-ml portions of saturated $NaHSO_3$, six 30-ml portions of saturated $Na_2CO_3$, one 30-ml portion of saturated NaCl, dried ($MgSO_4$), and the ether removed on the rotary evaporator. NMR analysis of the oily residue with dioxane as an internal standard indicated 0.073 g (1.3%) of 3-methylphthalide.

From acidification of the $Na_2CO_3$ layer with concentrated HCl, 6.3 g (85%) of a white solid, m.p. 73.5–74.5°, was collected; IR (double mull): 1695 (C=O); NMR ($CCl_4$): 1.17 (t, 3, *J* 6.5 Hz, $-C-O-C-CH_3$), 1.45 (d, 3, *J* 6.5 Hz, $-C(CH_3)-O-$), 3.39 (q, 2, *J* 6.5 Hz, $-C-O-CH_2-$), 5.42 (q, 1, *J* 6.5 Hz, $-CH-O-$), and 7.10–8.17 ppm (m, 4). (Found: C, 67.97; H, 7.31. $C_{11}H_{14}O_3$ calcd.: C, 68.02; H, 7.27%.)

### *Reaction of 3-isopropoxy-3-phenylphthalide and phenylcadmium chloride*

The phenylcadmium reagent was prepared from 2.7 g (0.11 g-atom) of magnesium, 17.6 g (0.11 mole) of bromobenzene, 22.3 g (0.12 mole) of cadmium chloride, 150 ml of ether and 125 ml of benzene.

To the phenylcadmium reagent was added dropwise, over a period of ½ h, 15 g (0.056 mole) of 3-isopropoxy-3-phenylphthalide[2] in 75 ml of dry benzene. The mixture was stirred at reflux for 2 h. The reaction mixture was worked up as usual employing 0.7 *M* $H_2SO_4$ containing ice, three 30-ml portions of benzene, five 50-ml portions of 10% $Na_2CO_3$ and anhydrous $Na_2SO_4$. After distillation of the benzene, an oily residue remained whose IR spectrum was similar to that of 3-isopropoxy-3-phenylphthalide.

The $Na_2CO_3$ extracts were acidified with concentrated HCl. This resulted in recovery of 9.2 g (72%) of a white solid, m.p. 124–127°. The IR spectrum was identical to that of *o*-benzoylbenzoic acid.

In a similar experiment, except that the reflux period was 16 h, 9.3 g (72%) of *o*-benzoylbenzoic acid, m.p. 126.5–128.0° (benzene) was obtained.

### *o-[1-(−)-Menthoxyethyl]benzoic acid*

Methylcadmium chloride was prepared from 3.2 g (0.13 g-atom) of magnesium, 19 g (0.13 mole) of methyl iodide, 24 g (0.13 mole) of cadmium chloride, 130 ml of ether, and 225 ml of benzene. To the cadmium reagent was added, over a period of ½ h, 19 g (0.065 mole) of 3-(−)-menthoxyphthalide in 60 ml of benzene. An additional

30 ml of benzene was added, and the reaction mixture was refluxed and stirred for 7.0 h. It was stirred an additional 9 h without external heating.

The cooled reaction mixture was treated in the above manner with 99 ml of 6% $H_2SO_4$ containing ice, four 40-ml portions of benzene, four 50-ml portions saturated $NaHCO_3$, two 50-ml portions saturated NaCl, two 30-ml portions saturated $NaHSO_3$, and anhydrous $MgSO_4$. From the benzene solution, 12.0 g (61%) of a white solid, m.p. 171–174°, was collected in six fractions.

A portion of the solid, m.p. 171–174°, was recrystallized (benzene), producing a white solid, m.p. 173.5–174.5° ; IR (double mull): 1720 (C=O) and 2850–3000 (C–H); NMR ($C_6H_6$): 0.80–3.40 (series of multiplets, $-O-C_{10}H_{19}$), 1.55 (d, 3, $-C-CH_3$), 5.92 (q, 1, $-CH-C-$), and 7.97 ppm (two closely overlapping triplets). (Found: C, 75.11; H, 9.19. $C_{19}H_{28}O_3$ calcd.: C, 74.96; H, 9.27%.)

Slow acidification of the $NaHCO_3$ extract resulted in a precipitate (0.7 g). The IR spectrum resembled that of the material from the neutral layer.

In a similar experiment with a 45-h reaction time, 22 g (97%) of *o*-[1-(−)-menthoxyethyl]benzoic acid was isolated.

### *Reaction of* 3-*acetoxyphthalide and methylcadmium chloride*

Methylcadmium chloride was prepared from 50 ml of ether, 0.44 g (0.018 g-atom) of magnesium, 2.6 g (0.018 mole) of methyl iodide, and 3.3 g (0.018 mole) of cadmium chloride. To this was added, over a period of 50 min, 1.8 g (0.0091 mole) of 3-acetoxyphthalide[7]. The reaction mixture was stirred at reflux temperature for 4 h. The reaction mixture was worked up as above employing 64 ml of 6% $H_2SO_4$, five 40-ml portions ether, two 15-ml portions saturated $NaHSO_3$, six 30-ml portions saturated $Na_2CO_3$, two 30-ml portions saturated NaCl, and anhydrous $MgSO_4$. The ether was removed on the rotary evaporator. NMR analysis of the residue with dioxane as an internal standard indicated 0.30 g (30%) of 3-methylphthalide and 0.41 g (42%) of starting material.

In a similar experiment, 1.8 g (57%) of 3-methylphthalide and 1.0 g (33%) of starting material were obtained.

No solid precipitated after acidification of the $Na_2CO_3$ layer with concentrated HCl and refrigeration of the acidified solution in either experiment.

### *Treatment of* 3-[(−)-*menthoxyacetoxy*]*phthalide with methylcadmium chloride*

The Grignard reagent was prepared in 225 ml of ether from 1.8 g (0.072 g-atom) of magnesium turnings and 10.3 g (0.072 mole) of methyl iodide. To this reagent was added, portion-wise and with stirring, 13.2 g (0.072 mole) of anhydrous cadmium chloride. After 0.25 h of additional stirring, a negative Gilman test[9] was noted.

To the methylcadmium chloride was added dropwise, over a period of 50 min, 12.5 g (0.036 mole) of 3-[(−)-menthoxyacetoxy]phthalide {$[\alpha]^{24}_{578}$ −71.8±0.0 (*c* 2.2, $C_2H_5OH$); −70.7±0.0 (*c* 2.3, $C_2H_5OH$)} in 125 ml of ether. After the addition the mixture was stirred at reflux for 4.0 h.

The reaction mixture was treated as usual with 190 ml of 6% $H_2SO_4$, five 40-ml portions ether, two 15-ml portions saturated $NaHSO_3$, six 40-ml portions saturated $Na_2CO_3$, and two 40-ml portions saturated NaCl. Acidification of the $Na_2CO_3$ extract produced no insoluble material.

The ether layer was dried ($MgSO_4$) and the solvent removed. The neutral residue was fractionally distilled, producing 7.0 g of a colorless liquid, b.p. 78.5–96.5° (0.7 mm). This was subsequently shown to be a mixture of 3-methylphthalide and an unknown component.

The liquid was dissolved in 36 ml of ether and 12 ml of 10% NaOH added. This was allowed to stand at room temperature for 4 days with intermittent shaking. The layers were separated and the aqueous layer extracted with ten 10-ml portions of ether. The aqueous layer was acidified with concentrated HCl and heated on the steam bath slowly for 1 h. It was extracted with eight 10-ml portions of ether. The combined ether layer was extracted with two 5-ml portions of saturated $Na_2CO_3$, dried ($MgSO_4$), the solvent removed, and the residue distilled, producing two fractions (38%).

(1). 1.40 g, b.p. 101° (0.9 mm); $[\alpha]^{24}_{578}$ $+1.99\pm0.00$ (*c* 6.8, $CH_3OH$); $[\alpha]^{26}_{578}$ $+2.43\pm0.08$ (*c* 6.8, $CH_3OH$); IR (neat): 1760 (C=O); NMR (neat): 1.67 (d, 3, *J* 7 Hz, $-C-CH_3$), 5.71 (q, 1, *J* 7 Hz, $-CH-C$) and 7.40–8.00 ppm (m, 4);

(2). 0.62 g, b.p. 102–103° (0.9 mm); $[\alpha]^{25}_{578}$ $+2.29\pm0.00$ (*c* 7.4, $CH_3OH$), $+2.27\pm0.07$ (*c* 7.3, $CH_3OH$); IR (neat): 1760 (C=O); NMR ($CCl_4$): 1.61 (d, 3, *J* 6.5 Hz, $-C-CH_3$), 5.60 (q, 1, *J* 6.5 Hz, $-CH-C$) and 7.30–7.90 ppm (m, 4).

The product from both fractions was comparable to an authentic sample of (±)-3-methylphthalide[7] on the basis of IR, NMR and TLC.

NMR analysis of the original neutral residue with dioxane as an internal standard indicated the presence of 36% of starting material. Recrystallization (95% EtOH) of the distillation residue, 36 g (29%), resulted in 0.5 g of white crystals, m.p. 84–85°, $\{[\alpha]^{32}_{578}$ $-70.9\pm0.3$ (*c* 2.5, $C_2H_5OH$); $-69.2\pm0.1$ (*c* 2.6, $C_2H_5OH$)$\}$.

In a similar experiment from starting material with $[\alpha]^{24}_{D}$ $-68.3\pm0.1$ (*c* 2.2, $C_2H_5OH$); $-69.6\pm0.1$ (*c* 2.7, $C_2H_5OH$), 0.34 g (13%) of 3-methylphthalide was isolated, b.p. 80–83° (0.6 mm); $[\alpha]^{24}_{578}$ $+2.18\pm0.00$ (*c* 5.4, $CH_3OH$); $+1.56\pm0.10$ (*c* 2.5, $CH_3OH$); the IR and NMR spectra were similar to those above.

The residue from the fractional distillation amounted to 2.0 g (33%) consisting primarily of starting material.

### *Reaction of* 3-(2-*phenylbutyryloxy*)*phthalide and methylcadmium chloride*

Methylcadmium chloride was prepared from 19 ml of ether, 0.41 g (0.017 g-atom) of magnesium, 2.42 g (0.017 mole) of methyl iodide, and 3.1 g (0.017 mole) of cadmium chloride. To the cadmium reagent was added 2.5 g (0.0085 mole) of 3-(2-phenylbutyryloxy)phthalide in 60 ml ether, and the mixture was stirred under reflux for 4 h. It was worked up in the usual manner from 48 ml of 6% $H_2SO_4$, four 25-ml portions ether, two 15-ml portions saturated $NaHSO_3$, six 15-ml portions saturated $NaHCO_3$, two 15-ml portions of saturated NaCl, and $MgSO_4$; the ether was removed on the rotary evaporator. The residue, 1.4 g (57%) crystallized spontaneously. The IR and NMR spectra indicated that it was identical to the starting material.

Acidification of the $NaHCO_3$ washings with concentrated HCl resulted in the collection of 0.19 g (14%) of a white solid, m.p. 41–43°. It was identified by IR and NMR spectra as 2-phenylbutyric acid.

### *Reaction of di*-3-*phthalidyl ether and methylcadmium chloride*

Methylcadmium chloride was prepared from 100 ml of ether, 0.5 g (0.021

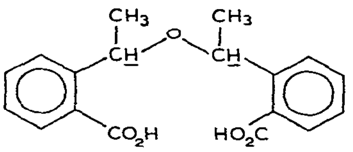
g-atom) magnesium, 2.92 g (0.021 mole) of methyl iodide, and 3.8 g (0.021 mole) of cadmium chloride. To the cadmium reagent was added all at once 2.9 g (0.010 mole) of di-3-phthalidyl ether[7,8]. After being stirred at reflux for 0.75 h, the reaction complex became so thick that stirring was no longer possible. It was allowed to stand at room temperature for 95.5 h.

To the reaction mixture was added 32 ml of 6% $H_2SO_4$ containing ice. From the hydrolyzed mixture, 2.1 g (73%) of an off-white solid, m.p. 205–212°, was collected. The IR spectrum was identical to that of di-3-phthalidyl ether. The liquid layers of the filtrate were separated and the aqueous layer extracted with five 50-ml portions of ether. The combined ether solution was washed with two 15-ml portions of saturated $NaHSO_3$, six 30-ml portions of $Na_2CO_3$, two 30-ml portions of saturated NaCl, dried ($MgSO_4$), and the ether removed. After precipitation with chloroform and then carbon tetrachloride of an additional 0.11 g (4%) of starting material, the brown filtrate was concentrated and shown to contain 3-methylphthalide (NMR).

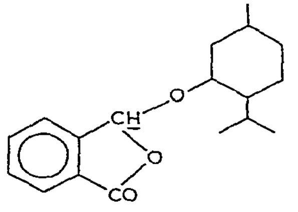
Acidification of the $Na_2CO_3$ layer with concentrated HCl and refrigeration of the acidified solution produced 0.7 g (22%) of a white solid, m.p. 205–214°; IR (double mull): 1690 (C=O); NMR (DMF): 1.46 (t, 6, J 6 Hz, $-C-CH_3-O-C-CH_3$), 5.43 (septet, 2, J 6 Hz, $-CH-C-O-CH-C$) and 7.10–8.00 ppm (m, 8). (Found: C, 68.78; H, 5.92. $C_{18}H_{18}O_5$ calcd.: C, 68.78; H, 5.77%.)

## RESULTS AND DISCUSSION

Several interesting conclusions are evident from the experimental results. The displacement of acyloxy is strongly favored over that of alkoxy. This clarifies an earlier, puzzling observation[7] that 3-alkoxyphthalides [(I), X = OMe, OEt] afforded the corresponding displacement products (II) in negligible amounts, even though the starting materials could not be recovered. We have reinvestigated these cases and confirmed our expectations that the major products are acids (III). A particularly striking instance of ring-opening by displacement of acyloxy is the formation of the dicarboxylic acid (IV) from methylcadmium reagent and di-3-phthalidyl ether (Table 1, last entry). The structural assignment is based on analysis and the IR spectrum, but especially on the NMR spectrum, which shows the methinyl protons [underlined in structure (IV)] to be diastereotopic[10]. The C-3 diastereotopic protons in 3-menthoxyphthalide (V) likewise are evident from the NMR resonance doubling.



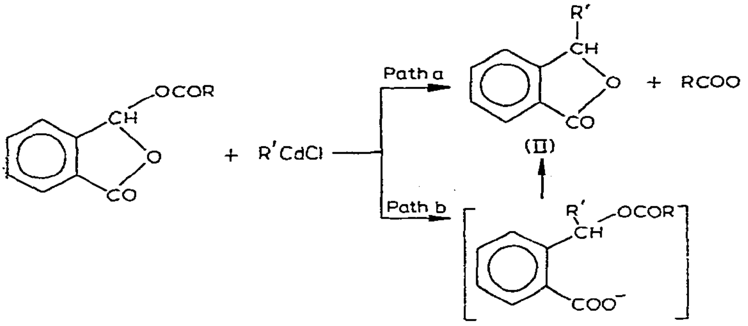
(IV)



(V)

Bulky 3-alkoxy substituents impede ring-opening, as shown by the more extensive reaction of 3-ethoxy- over 3-isopropoxyphthalides. A change of the other 3-substituent in (I) from H to $C_6H_5$, however, seems to have little effect.

In a phthalide substrate containing two acyloxy groups [(I), X = acyloxy] the "exocyclic" group is lost preferentially, the phthalide structure being preserved in the product. The formation of (II) could occur "directly", as represented in path a, or by "double acyloxy displacement", via path b. The latter is attractive because it would account for the formation of (III) by the first step of path b, the subsequent cyclization being unfavored because of the nature of the leaving group. Although one cannot distinguish between paths a and b on the basis of present knowledge, the retention of optical activity in (II) (see ref. 1 and experimental) requires that the steps be concerted in any case. The possibility that the phthalide (I) reverts to the parent *o*-acylbenzoic acid before reaction with organocadmium compound occurs [eqn. (3)] is ruled out by the stereoselectivity of the displacement with 3-[(−)-menthoxyacetoxy]phthalide[1].



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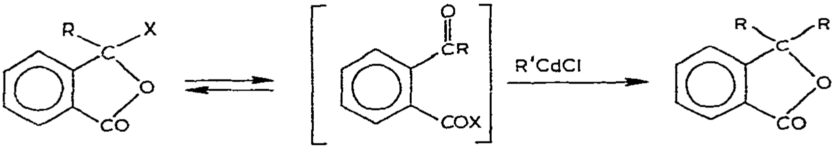

(3)

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