Radical Anions of *o*-Dicarbonylbenzenes and Phthalides

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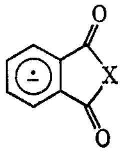
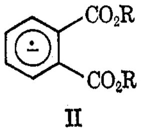
The esr spectra of radical anions of *o*-acylbenzoates (IV), alkyl *o*-acylbenzoates (V), phthalide, and 1-indanone are reported, and the spin distributions are discussed. Electrolytic reduction of alkyl *o*-acylbenzoates give V, and at higher potential mixtures of the 1,3 indandione obtained by Claisen condensation and IV. 3-Alkoxyphthalides give V, by an alkoxide-catalyzed cleavage. The hydrogens at C_3 of phthalide are rapidly replaced by deuterium in DMSO-d_6, as are those at C_2 of 1-indanone, but the C_3 hydrogens of 1-indanone do not exchange.

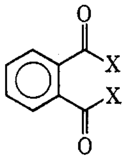
In an earlier esr study of the effect of carbonyl substitution on its spin delocalization properties, we reported esr spectra of several derivatives of phthalic anhydride radical anion (I), including the species with X = O, CR^-, and NR.[1] These substitutions resulted in rather small differences in spin density distribution. A symmetry node in the odd electron molecular orbital passes through the "X" position, resulting in very low spin density at X, minimizing the effect of substitution.



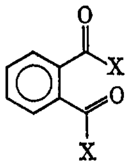
I



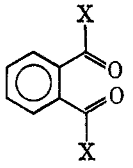
II



A

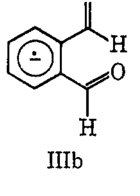


B



C

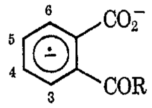
The effect of having ortho ester carbonyls was investigated with dimethyl and diethyl phthalate radical anions (II).[2] Although the carbonyl groups are no longer held planar with the ring, and rotational isomerism about the carbonyl oxygen bonds should lead to three different isomers (A–C) for II, only a "symmetrical" spectrum, showing equal splittings at both alkoxy groups, and two sets of equivalent ring splittings, was observed.[2] Stone and Maki[3] showed several years ago that the lifetime of rotamer B of *o*-phthalaldehyde anion (IIIb) was long on the esr time scale, and that only this rotamer was observable.[4] That different ring splittings ought to be observed for different rotamers of various types of carbonyl groups is indicated by the unsymmetrical spectra of benzaldehyde and acetophenone, and the different spectra observed for two ester carbonyl rotamers for fumeric ester anions.[5]



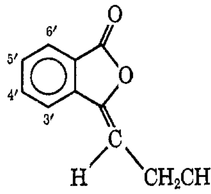
IIIb

The work reported here was undertaken to investigate the effects of having two different types of carbonyls ortho to each other on the spin distribution in the radical anion.

Results

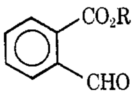


IV



1, 4′-*tert*-butyl

2, 5′-*tert*-butyl



3

o-Acylbenzoate Anions.—Electrolytic reduction of *o*-acylbenzoic acids in DMSO containing 0.05 *M* tetrabutylammonium perchlorate (used throughout this study) inside the esr cavity gave esr spectra which we assign to the expected *o*-acylbenzoate dianion radicals IV on the basis of splitting constants. The same esr spectra were observed as the ultimate products of electrolytic reduction of esters and pseudoesters of *o*-acylbenzoic acids, and of alkylidine phthalides. This is consistent with our earlier observation of formation of the half ester dianion radicals from phthalates and fumarates.[2] The formyl splitting in IV (R = H) was assigned by deuteration, but the 4- and 5-*tert*-butyl compounds were used to assign the H_3 and H_5 ring splittings. Since phthalic anhydride is the most convenient starting material for these systems, specific ring deuteration would be inconvenient. We did not assign the small H_4 and H_6 splittings, which are very similar in magnitude. The *tert*-butylated radicals IV were generated from 4′- and 5′-*tert*-butylphthalide (**1** and **2**), prepared as a mixture by Perkin condensation of 4-*tert*-butylphthalic anhydride with butyroyl anhydride and sodium butyrate. In contrast to similar mixtures of ring *tert*-butylated *o*-acyl esters and pseudoesters, **1** and **2** proved to be conveniently separated by tlc. The largest ring splitting was shown to be $a(H_5)$ (para to the acyl substituent), and the next largest ring splitting was not at the 4′ position, as would be the case if both carbonyl groups were effective in spin de-

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[1] S. F. Nelsen, *J. Amer. Chem. Soc.*, **89**, 5256, 5925 (1967); see also R. E. Sioda and W. S. Koski, *ibid.*, **89**, 475 (1967).

[2] S. F. Nelsen, *Tetrahedron Lett.*, 3395 (1967).

[3] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 199 (1963).

[4] We have repeated this work in DMSO using *intra muros* generation and did not have the problems of signal instability mentioned.[3] Although we were able to resolve the sixth splitting constant (splittings of 4.58, 3.67, 2.95, 2.19, 0.47, and 0.14 were observed), lines attributable to IIIa or IIIc were not observed.

[5] Reference 2. The suggestion of ref 2 that the two radicals observed for dialkyl maleates or fumerates are cis and trans forms about the C=C bond is clearly incorrect; the two species are present in too similar concentrations. Both must be trans, and ester carbonyl rotamers are observed.

TABLE I

ESR SPLITTINGS (GAUSS) FOR O-ACYLBENZOATE DIANION RADICALS (IV) AND RELATED COMPOUNDS

Registry no.	Compd reduced[a]	Radical observed	R	$a(H_4)$ and $a(H_6)$	$a(H_5)$	$a(H_3)$	a_R
40496-67-1	A, B, C	IV	H	0.96, 1.09	6.03	4.02	8.80 (1 H_α)
40496-68-2	A, C	4-*t*-Bu-IV	H	1.03	6.18	4.06	9.11 (1 H_α)
40496-69-3	C	IV	D	0.95, 1.05	6.15	3.90	1.31 (1 D_α)
40496-70-6	A, B, D	IV	CH_3	1.13, 1.25	6.41	4.04	7.52 (3 H_β)
40496-71-7	A, B, D	IV	CH_2CH_3	1.01, 1.13	6.49	3.80	6.33 (2 H_β) 0.13 (3 H_γ)
40496-72-8	D	4-*t*-Bu-IV	$CH_2CH_2CH_3$	1.16	6.49	3.79	6.18 (2 H_β) 0.31 (2 H_γ)
40496-73-9	D	5-*t*-Bu-IV	$CH_2CH_2CH_3$	1.13, 1.13		4.00	6.73 (2 H_β)[b]
40496-74-0	A, B, D	IV	$CH(CH_3)_2$	1.06, 1.06	6.52	3.98	1.30 (1 H_β) 0.05 (6 H_γ)
40496-75-1	A, B	IV	OCH_3	~0.9	7.53	3.77	~0.9 (3 H)
40496-76-1	A, B	IV	OCH_2CH_3	0.74, 1.00	7.51	3.79	~0.74 (2 H)
		$[PhCHO]\cdot^-$[c]		0.75, 1.31	6.47	3.39, 4.69	8.51 (1 H_α)
		$[PhCOCH_3]\cdot^-$[c]		0.88, 1.07	6.60	3.71, 4.25	6.73 (3 H_β)

[a] A, benzoic acid; B, normal ester **3**; C, pseudoester **4**; D, alkylidine phthalide. [b] A splitting for many hydrogens of about 0.17 G for the *tert*-butyl group was observed. Presumably the γ splitting was about twice this. [c] Reference 6.

TABLE II

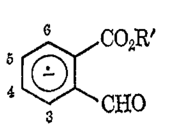
ESR SPLITTINGS OF ALKYL o-FORMYLBENZOATE ESTER RADICAL ANIONS (V)

Registry no.	Compd reduced[a]	Radical (R′)	$a(H_4)$ and $a(H_6)$	$a(H_5)$	$a(H_3)$	$a(H_\alpha)$	$a(R')$
40496-77-3	A, B, C	V (CH_3)	0.97 (2 H)	4.37	1.47	6.00	0.64 (3 H)
40496-78-4	A, B, D	V (CH_2CH_3)	0.97 (2 H)	4.26	1.45	5.72	0.56 (2 H)
40496-79-5	B	V-α-*d* (CH_2CH_3)	0.97 (2 H)	4.26	1.45	0.88 (1 D)	0.55 (2 H)
40496-80-8	C	V ($CH(CH_3)_2$)	0.96, 1.04	4.45	1.54	6.01	0.31 (1 H)
40496-81-9	B	4-*t*-Bu-V (CH_3)	0.93	4.13	1.55	5.90	0.60 (3 H)

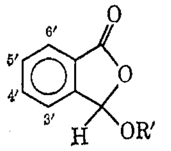
[a] A, Alkyl ester **3**; B, 3-alkoxyphthalide (pseudoester, **4**); C, 3-ethoxyphthalide plus alcohol; D, **3** (R′ = CH_3) plus ethanol.

localization. We therefore assign structure IV to these radicals. The protonated form, with one acid and one acyl substituent, would be expected to give a spectrum more closely related to those of the diester anions II. Splitting constants for IV, benzaldehyde,[6] and acetophenone[6] are summarized in Table I.

Alkyl o-Acylbenzoate Radical Anions.—Reduction of alkyl 2-formylbenzoates (**3**) gave well-resolved esr spectra, to which we assign structure V. We obtained identical spectra starting with the related 3-alkoxyphthalides (pseudoesters) (**4**). After reduction at high potentials, the spectra corresponding to V faded, and were replaced by IV. The splittings observed are summarized in Table II.



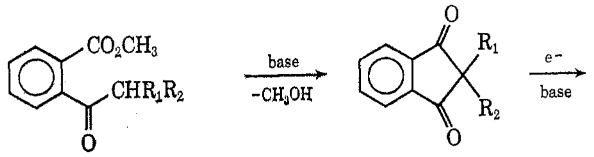
V



4

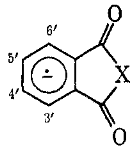
From the spectrum generated from **4-3-*d***, the formyl hydrogen splitting is the largest one, and that from 4-*tert*-butyl-**3** (R′ = CH_3) showed that the larger ring splitting was not that para to the ester group. The only reasonable assignment is that with $a(H_6) > a(H_3)$, which was used in Table II.

Reduction of Alkyl o-Acylbenzoates.—Reduction of methyl o-acylbenzoates 6 and 7 initially gave complex spectra which we were unable to analyze. The spectra were broadened, especially at the high-field end. Rotational isomerism, possibly with intermediate rotation rates, comparable to the splittings, leading to broadening, might be responsible for these complex spectra, but this point remains to be elucidated. Ester **8** did give an analyzable spectrum on reduction, and the observed splittings of 6.92, 5.27, 1.82, 1.39, and 0.13 (4 H) G seem compatible with the simple radical anion, $[\mathbf{8}]\cdot^-$.



6, $R_1 = R_2 = H$
7, $R_1 = H$; $R_2 = CH_3$
8, $R_1 = R_2 = CH_3$

9



I

At higher potentials, the initial spectra from **6–8** faded and were replaced by the spectra of the related benzoate dianions IV and, in addition, a second radical. This second radical proved to be the related I radical, which had been previously observed from electrolytic reduction of the 1,3-diketohydrindans.[1] These radicals logically arise by base-catalyzed intramolecular Claisen condensation to **9**, followed by further reduction (and deprotonation, if possible). Isopropylidine phthalides **1** and **2** both gave 4′-*tert*-butyl-I (X = $C^-CH_2CH_3$) under these conditions. The spectra of the I derivatives observed appear in Table III.

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(6) N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 732 (1964).

TABLE III

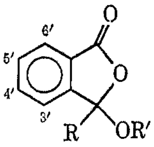
ESR SPECTRA OF 1,3-DIKETOHYDRINDAN ANION DERIVATIVES (I)

Registry no.	Compd reduced	X	$a(H_4)$	$a(H_3)$	a(X)
40488-41-3	**6**	CH^-	2.50	0.16	0.77 (1 H)
40488-42-4	**7**	CCH_3^-	2.64	0.17	1.32 (3 H)
40488-43-5	**1, 2**	$CCH_2CH_3^-$(4′-*t*-butyl)	2.27 (1 H)	0.24	0.89 (2 H)
40496-82-0	**8**	$C(CH_3)_2$	2.62	0.10	0.10 (6 H)
40496-83-1	**7**[a]	$CHCH_3$	2.63	0.08	2.26 (1 H)

[a] See text.

Interestingly, reduction of **7** usually gave a fleeting, intermediate radical which was rapidly replaced by I (X = C^-CH_3), which had the splittings expected for I (X = $CHCH_3$), to which it is assigned in Table III. I (X = CMe_2) is an excellent model for the latter species. Although the outer lines in the nine-line patterns caused by the 3,6 hydrogens plus the two methyl groups of I [X = $C(CH_3)_2$] were little larger than noise, the observed intensity ratios make it clear that the splittings for both types of hydrogen were 0.1 G: observed (in per cent of central peak, from center to edge of multiplet), 100, 80.5, 39.2, 11.9, ?; calculated for six equivalent H, 100, 85, 30, 5, 0; calculated for eight equivalent H, 100, 80, 40, 11.4, 1.4. Thus both the ring splittings in the transient symmetrical radical from **7** fit well for the structure being I (X = $CHCH_3$), as assigned.

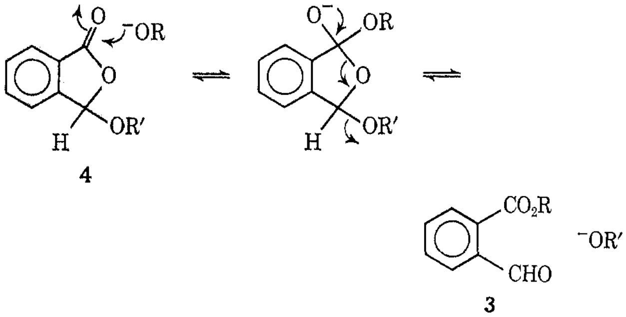
Radicals from the Reduction of 3-Alkoxyphthalides.—As mentioned previously, reduction of 3-alkoxyphthalides gave radical V, followed at higher potential by radical IV. We used this observation to prepare the formyl deuterated IV and V radicals, since phthalic anhydride is cheaply reduced to 3,3-dideuteriophthalide, and **12** can be prepared by bromination and solvolysis (see Experimental Section). By adding excess alcohols to the mixture of electrolyte and alkoxyphthalide, the esr spectrum of the alcohol-exchanged o-formylbenzoate V was obtained (see Table II). The normal methyl ester exchanged rapidly with added ethanol during reduction, but the exchange reaction of isopropyl alcohol and methyl o-formylbenzoate was quite sluggish. When 3-methoxyphthalide (**10**) was electrolyzed in the presence of isopropyl alcohol, V [R′ = $CH(CH_3)_2$], the isopropyl alcohol-exchanged formylbenzoate anion, was the first radical to be observed. Under the same conditions, reducing methyl o-formylbenzoate remained unchanged, even after 1 hr of electrolysis. This requires that observing V (R′ = CH_3) upon reduction of **10** (R′ = CH_3) is not the result of an intramolecular rearrangement of $[\mathbf{10}]\cdot^-$, and strongly suggests to us that alkoxide-catalyzed cleavage of the 3-alkoxyphthalide is observed. Reduction of **14** gave the same broadened spectrum as reduction of the normal ester, but in this case we detected a prior species which we believe to be the pseudoester radical anion from the similarity of its splittings [7.62, 4.89, 1.11, 0.40 (4 H)] to those of phthalide anion radical.



10, R = H; R′ = CH_2 **13**, 4′-*t*-Bu, R = H; R′ = CH_3

11, R = H; R′ = CH_2CH_3 **14**, R = CH_3; R′ = CH_3

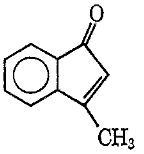
12, R = D; R′ = CH_2CH_3



4

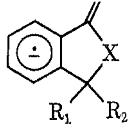
3

Another base-catalyzed reaction was unfortunately observed in our attempts to generate the radical anion of o-diacetylbenzene. The major radical produced had splittings of 7.93 (3 H), 1.92, 1.39, 1.88, 0.81, and 0.52 G, and can only correspond to the radical anion of 3-methylindenone (**15**), the dehydrated aldol product. Its multitude of lines obscured the spectra of at least one other species present in low concentration sufficiently to preclude analysis.



15

Phthalide and 1-Indanone Radical Anions.—As models for the closed form of 3-alkoxyphthalides, and also for benzene rings conjugated to planar ester and ketone carbonyl groups, we determined the esr spectra of the radical anions of phthalide (VI, X = O) and 1-indanone[7] (VI, X = CH_2). Our results appear in Table IV.



VI

Since the 13.4-G splitting hydrogens of VI (X = CH_2; R = H) rapidly exchanged upon reduction in DMSO-d_6, these may be confidently assigned to the hydrogens at C_2. The C_3 hydrogens did not exchange even after 2 hr of continuous reduction; so there is a huge difference in exchange rate at the two positions. In contrast, the C_3 hydrogens of phthalide exchange

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[7] G. A. Russell and G. R. Stevenson, *J. Amer. Chem. Soc.*, **93**, 2432 (1971).

TABLE IV

ESR SPLITTINGS OF PHTHALIDE AND 1-INDANONE RADICAL ANIONS

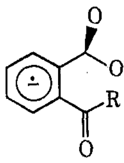
Registry no.	Radical	$a(H_3')$	$a(H_4')$	$a(H_5')$	$a(H_6')$	$a(H_3)$	Other
34507-52-3	VI (X = CH_2; R = H)	0.16	6.92	1.47	5.69	1.60	13.40 (2 H)
40496-85-3	VI (X = CD_2; R = H)	0.16	6.88	1.46	5.60	1.59	1.99 (2 D)
40496-86-4	VI (X = O; R = H)	0.31	7.79	1.37	5.66	6.25	
40496-87-5	VI (X = O; R = D)	0.31	7.79	1.39	5.69	0.95 (2 D)	
40488-44-6	4′-*t*-Bu-VI (X = O; R = H)	Obscured		1.62	~6.25	~6.25	(0.17-*t*-Bu)
40488-45-7	5′-*t*-Bu-VI (X = O; R = H)	0.15	7.73		5.91	6.77	
40488-46-8	VI (X = O; R_1 = H; R_2 = CH_3)	Unobsd	8.07	1.31	5.89	5.89 (1 H)	Unobsd

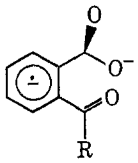
with solvent rapidly under our conditions, as was verified both by washing the label out of 3,3-dideuterio material by reducing in DMSO, and exchanging it into protio material, using DMSO-d_6.

Discussion

The splittings of Table I show that the carboxylate group is not effective at delocalizing spin; in fact, an ortho carboxylate actually forces spin onto the acyl group [comparing IV (R = H) with benzaldehyde ketyl, and IV (R = CH_3) with acetophenone ketyl]. Similar effects have been noted previously for nitro anions.[8] This suggests that one negative charge is essentially localized in the carboxylate group, which is twisted at a large angle to the ring, and has a minimal effect on the benzaldehyde-type π system. The splittings of the alkyl *o*-formylbenzoates of Table II show that substantially more spin density is present in the ester carbonyl of V than in the carboxylate carbonyl of IV. The a_3 splitting, meta to the ester carbonyl, is distinctly lower in V than in IV, and the methoxy splitting of V (R′ = CH_3) is 70% as large as that of IV (R′ = OCH_3), where the ester is the principal function stabilizing the aromatic anion radical. When the *o*-formyl group of V (R′ = CH_3) is replaced by an *o*-isobutyryl group, [**8**]$\cdot^-$, significantly more spin density is present in the ring and less at the methoxy group. Apparently, two large acyl substituents are more twisted from the plane of the ring, and at least the ester accepts less spin density.

We only saw one isomer for the *o*-acylbenzoates of Table I, although we would expect to be able to see different splittings for ring carbonyl isomers, if they were both present in substantial amounts. This is perhaps not surprising for the *o*-formylbenzoates, for the oxygen anti isomer IVa is favored both on steric grounds and on the basis of charge repulsion (maximum separation of the negatively charged oxygens). That these factors are not the only important ones has been shown by Stone and Maki.[3] No explanation was offered for *o*-phthalaldehyde anion existing only as IIIb, whereas IIIa is the favored one considering steric and charge repulsion factors. The suggestion of Bauld and coworkers[9] that a carbonyl carbon remains positively charged, even in the radical anion, would reverse the electrostatic argument for III, and give a rationale for IIIb being the observed form. In the case of IV, which has a full negative charge on the carboxylate, IVa would remain the prediction. From the similarity of the ring splittings for IV (R = CH_3) and IV [R = $C(CH_3)_2$], it is difficult to support the contention that they have different configurations at the carbonyl group. The question of whether IVa or IVb (or an equilibrating mixture) is observed remains unanswered.


IVa


IVb

We were able to detect a minor species with very similar splittings to the major one in the wings of the V (R′ = CH_2CH_3) spectrum reported in Table II. We suggest that this minor species is the other ester conformation, but do not know how to even guess which is which. The complex spectra mentioned for alkyl *o*-acylbenzoates seem certain to be caused by rotamers, perhaps interconverting ones.

The 3.9 ratio of $a(H_3)$ for the anion radicals from phthalide (VI, X = O) and indanone (VI, X = CH_2) seems surprising at first, considering the substantial similarity of the ring splittings. We suggest that the increased $a(H_3)$ for phthalide anion arises principally from the fact that the C_3–H_3 bond can hyperconjugate simultaneously with the π orbital at C_2' and that at oxygen. McLachlan calculations show that the coefficient signs at both atoms are the same, so that the proper "spin density" in an $a(H_3) = Q\rho$ McConnell equation should be $[c(2') + c(0)]^2$ where c(i) is the coefficient at atom i.[10] Since the McLachlan spin density at oxygen is sensitive to the heteroatom parameters chosen, and no set of these parameters is generally suitable for many compounds, we have not attempted to devise sets which would fit our single observed splitting. It is worth mentioning that the $a(H_3)$ for 1-indanone appears anomalously low compared to $a(H_6')$, because the spin densities at $c(2')$ and $c(6')$ are the same except for an inductive effect. Since McLachlan calculations appear not to be very good in predicting such effects (one gets into the problem of making up parameters which are clearly not transferable from compound to compound), this statement may not be correct, but we wish to point out that the unusually large spin density at the C_2 hydrogens might have a cancelling effect on $a(H_3)$ in phthalide.

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[8] P. Ludwig, T. Layoff, and R. N. Adams, *J. Amer. Chem. Soc.*, **86**, 4568 (1964).

[9] N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967).

[10] D. H. Wiffen, *Mol. Phys.*, **6**, 223 (1963).

Unfortunately, we do not have at our disposal a sophisticated enough scheme of calculating what is expected for the splittings of IV–VI as a function of geometry to give a quantitative interpretation of the observed splittings, but we believe that the data could prove valuable in testing future methods of calculating spin densities for heteroatomic systems.

The observation that the hydrogens at C_3 of phthalide exchange in seconds, whereas those of 1-indanone do not exchange in hours, is a striking one, and must mean that there is a huge difference in the acidity of the C_2 and C_3 hydrogens in 1-indanone.[11] Our result represents a substantial contrast to that of Dubois and Dodin,[11e] who observed competitive oxidation of the carbons α to the carbonyl and those α to the ring in *p*-alkylacetophenones using HMPA–*tert*-butoxide–air. They, then, observed vinylogous enolization at the para position competing with ordinary enolization.

Experimental Section

A Varian A-60A instrument was used for nmr spectra, a Varian E.3 or E.15 for esr spectra, and an AEI MS.9 for mass spectra. Vpc separations used a 5-ft 15% Cargowax 20M on Chromosorb W column in a Varian Aerograph A.90.P-3 (thermal conductivity detector) instrument.

Commerical samples of phthalaldehyde and *o*-acetylbenzoic acid were employed. The preparations of Kariyone and Shimizu[12] were used for the alkylides and phthalides used, and *o*-isobutyrylbenzoic acid. 3-Methylphthalide was prepared by zinc-hydrochloric acid reduction of *o*-acetylbenzoic acid,[13] and purified by vpc. *o*-Diacetylbenzene was prepared by chromic acid oxidation of commercial 1,4-dimethylnaphthalene,[14] and crystallized from pentane–CCl_4, mp 41–42° (lit.[14] mp 39–40°). Methyl *o*-acylbenzoates **6**, **7**, and **8** were prepared from the acids and diazomethane.[15] None of the corresponding 3-methoxyphthalides were detected by nmr.[15]

3-Methoxyphthalide (**10**) was prepared as a mixture with the normal ester when phthalaldehydic acid was refluxed both in methanolic HCl and in thionyl chloride, followed by removal of excess reagent and addition of alcohol at 0°. Refluxing the acid with methanol and concentrated sulfuric acid gave a mixture of **10** and methyl phthalaldehyde dimethyl acetal [nmr (CCl_4) δ aromatic multiplet (4 H), 5.98 (s, 1 H), 2.83 (s, 3 H), 3.26 (s, 6 H); mass spectrum consistent]. Pseudoester **10** was separated by tlc or vpc, mp 43–44° (lit.[15] mp 44°).

3-Ethoxyphthalide (**11**), uncontaminated by the normal ester, was prepared from 3-bromophthalide[16] by dissolving it in absolute ethanol and crystallizing the product from alcohol, mp 66–67° (lit.[15] mp 68°).

4′-*tert*-Butylphthalide was prepared as a mixture with the 5′ isomer by zinc–acetic acid reduction[17] of 4′-*tert*-butylphthalic anhydride.[18] We were unsuccessful at tlc separation (silica gel PF-254 plates), but the 4′ isomer was isolated by crystallization:[19] mp 70–72°; nmr ($CDCl_3$) δ 7.48, 7.63, 7.75, 7.90 (aromatic multiplets, 3 H total), 5.28 (s, 2 H), 1.37 (s, 9 H). The 5′ isomer was only separated in small amounts by vpc, and had the same nmr as the 4′ isomer except in the aromatic region.

4′-*tert*-Butyl-3-methoxyphthalide (**13**).—Bromination of 5.7 g of the phthalide with 6.2 g of bromine,[16] followed by distillation, gave the 3-bromophthalide [bp 131–137° (0.23 mm), contaminated with 5% phthalide by nmr], which was added to 1.6 g of sodium methoxide in 25 ml of methanol, and stirred for 12 hr. After solvent removal, dissolution in ether, washing with water, drying with sodium sulfate, and trituration of the residue with pentane, the solid product was recrystallized from heptane:[19] mp 100–101°; nmr ($CDCl_3$) aromatic multiplet (3 H), δ 6.32 (s, 1 H), 3.66 (s, 3 H), 1.37 (s, 9 H). The best proof of position of *tert*-butylation we have for compounds in this series is the esr spectrum of the *o*-formylbenzoate dianion, which clearly shows that the proton meta to the formyl substituent is the missing one.

Phthalide-*3,3*-d_2 was prepared in low yield (2 g) but high deuteration by treating 10 g of phthalic anhydride with 30 g of zinc dust, 16 ml of D_2O (99.8%), and 80 ml of acetic anhydride at 120° for 16 hr, and subliming the residue, mp 75–77°; no C_3 hydrogen was detected by nmr.

3-Ethoxyphthalide-*3-d*.—The 3 bromide was prepared from 2 g of dideuteriophthalide and 2.6 g of bromine,[16] bp 92–97° (0.4 mm), 1.6 g. The deuteriobromide was stirred with absolute ethanol and sodium carbonate for 14 hr and distilled, bp 87–95° (0.15 mm). Crystallization from CCl_4–pentene gave material melting at 63–64°; no C_3 hydrogen was detected by nmr.

4′- and 5′-*tert*-butyl-3-propylidinephthalides were prepared by heating 5 g of 4-*tert*-butylphthalic anhydride and 4 g of butyric anhydride at 155–160°, adding 2.5 g of sodium butyrate over a 30-min period, and, after 1 hr, raising the temperature to 175–180° for 5 hr.[20] After cooling, addition of 25 ml of water, extraction into carbon tetrachloride, and drying over sodium sulfate, the solvent and starting materials were distilled off. The residue was separated by tlc on PF-254 silica gel plates (CCl_4) to give the 5′ isomer[21] (**2**) as the fastest moving band, and the 4′ isomer[21] as the next band; both were oils. The nmr spectra of the two isomers were indistinguishable [δ 5.49 (t, 1 H), 2.45 (m, 2 H), 1.38 (s, 9 H), 1.15 (t, 3 H)] except in the aromatic region, where the 4′ isomer showed the least split aromatic proton at the higher field end of the aromatic multiplets, and the 5′ isomer had the least split proton at the lower field end, as might have been predicted. Once again the esr spectra of the benzoate dianion radicals confirm the positional assignments. The cis double bond isomers were observed as slower moving bands on the tlc plate, but were not of interest in this work.

Esr spectra were determined by *intra muros* generation, using the Varian flat electrolysis cell, half filled with mercury, and DMSO containing 0.05 *M* tetrabutylammonium perchlorate as supporting electrolyte. A Heath 0.25-V dc power supply was used to apply potential. Voltage was adjusted to give the best attainable esr spectra, but we did not control the potential, or measure $E°$ values for our starting materials. Many of the radicals observed by us were products of complex base-catalyzed reactions, and frequently we used applied potentials beyond those for solvent breakdown.[22] Bases are obviously generated under these conditions. The splitting constants of Tables I–IV are estimated to be ±0.05 G for splittings under 2 G, and ±0.1 G for larger splittings.

Registry No.—Phthalide-*3,3*-d_2, 40496-88-6; phthalic anhydride, 85-44-9; 3-ethoxyphthalide-*3-d*, 40496-89-7; 3-bromophthalide-*3-d*, 40496-90-0; 4′-*tert*-butyl-3-propylidinephthalide, 40496-91-1; 5′-*tert*-butyl-3-propylidenephthalide, 40496-92-2; 4-*tert*-butylphthalic anhydride, 40496-93-3.

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