The melting point of a mixture of this solid and authentic 3,8-dinitro-2,4-dimethyldibenzofuran (IX) (m.p. 231–232°) was 231–232° (micro-melting stage).

The solid (0.55 g.) recovered from the mother liquor of recrystallization was recrystallized using the James method[19]; however, no analytically pure isomers were obtained. Additional quantities of IX were separated, together with a small amount of (0.08 g.) of a product melting at 226–227° which depressed the melting point when admixed with IX. A second product, m.p. 245–246°, seemed to be present in significant amounts, and the analysis suggests that it is an isomer of IX.

Anal. Calcd. for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52. Found: C, 59.27; H, 3.46.

Dinitration of 3-nitro-2,4-dimethyldibenzofuran. 3-Nitro-2,4-dimethyldibenzofuran (0.60 g., 0.0025 mole) was added to cold (ice bath) fuming nitric acid (6 ml.). The ice bath was removed, and after 1 hr. at room temperature, the mixture was added to 50 ml. of water and ice. The resulting white solid was washed free of acid, dried, and recrystallized from benzene. There was obtained 0.49 g. (60%) of colorless tetragonal crystals, which melted at 250–252°. The melting point was raised to 254–255° by additional recrystallization from benzene.

Anal. Calcd. for $C_{14}H_9O_7N_3$: C, 50.76; N, 2.73. Found: C, 51.05; H, 2.77.

The analysis establishes this product to be a trinitro derivative, and subsequent experiments suggest structure X.

Mononitration of 3,8-dinitro-2,4-dimethyldibenzofuran. 3,8-Dinitro-2,4-dimethyldibenzofuran (IX, 0.10 g., 0.00029 mole), derived from VIII, was nitrated as described above. The crude product (m.p. 250–251°) was recrystallized from benzene, and 0.07 g. (62%) of colorless tetragonal plates, m.p. 253–254°, was obtained. A mixture melting point of this material and that described above was 254–255°.

Nitration of 2,4-dimethyldibenzofuran with fuming nitric acid. (a). 2,4-Dimethyldibenzofuran (II, 0.60 g., 0.0036 mole) was added slowly (5 min.) to cold (ice bath) fuming nitric acid (6 ml.). The mixture was allowed to stand for 5 min., was poured onto ice, and the solid was collected and washed free of acid. Recrystallization of this product from benzene gave 0.24 g. (25% yield) of nearly colorless, tetragonal crystals melting at 245–246°. The melting point was raised to 253–254° (0.16 g. recovery) after further recrystallization from benzene. This material was identical to the trinitro isomer (m.p. 254–255°, mixture m.p. 254–255°) designated structure X, obtained by dinitration of VII or mononitration of IX.

The residue from the mother liquor was recrystallized from ethanol (James[19] method), and a second trinitro derivative was isolated. This product melted at 210°.

Anal. Calcd. for $C_{14}H_9O_7H_3$: C, 50.71; H, 2.73. Found: C, 50.90, 51.23; H, 3.15, 2.94.

(b) In another experiment impure II (0.480 g.), containing some phenol V was nitrated essentially as described above. The principal product, insoluble in 80 ml. of boiling ethanol, melted at 231–232°, and was identified as 3,8-dinitro-2,4-dimethylbenzofuran (IX, m.p. and mixture m.p. 231–232°).

Anal. Calcd. for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52. Found: C, 58.41 3.57.

Nitration of 2,4-dimethyldibenzofuran with concentrated nitric acid. Nitration of II (0.60 g., 0.0036 mole) with concentrated nitric acid (10 ml.) was carried out at ice bath temperature and the mixture was allowed to stand at 25° for 12 hr. The product (0.85 g.) melted at 106–136° and was not resolved by crystallization (benzene). A new dinitro derivative (colorless needles, 0.05 g., 6%, m.p. 251°) of II was isolated.

Anal. Calcd. for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52. Found: C, 58.78; H, 3.52.

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Neighboring Group Reactions. III. Structural and Stability Relationships between Two Geminally-substituted γ-Lactones

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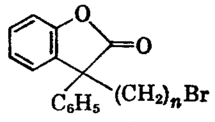
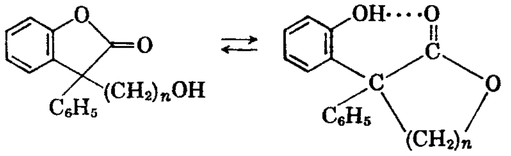
During the study of the chemical behavior of the two bromides Ia,b (and the corresponding chlorides), there was isolated from each homolog a product with elementary composition corresponding to the replacement of the halogen by hydroxyl.[1] The product obtained from Ia was a solid m.p. 159–161°, and the one derived from Ib (or the corresponding chloride) was an oil, b.p. 193–195° (1 mm.), n_D^{25} 1.5830. The main purpose of this work was to show by both chemical and spectral means that the solid product has structure IIIa and the liquid, structure IIb. Semiquantitative infrared studies were also carried out to provide an estimate of the interconvertibility within these two lactone systems.



Ia. $n = 2$.
Ib. $n = 3$.



IIa, $n = 2$.
IIb, $n = 3$.
IIIa, $n = 2$.
IIIb, $n = 3$.

The chemical evidence merely serves to show that the products are indeed lactones, and that no skeletal rearrangements have occurred during their formation. Thus, treatment of IIb with methanolic potassium hydroxide gave a potassium salt of an acid which on acidification yielded an unstable hydroxy acid that slowly reverted to the original lactone; and, by the action of hydrobromic acid, IIb was readily converted to the bromide Ib. Treatment of IIIa with hydrobromic acid likewise

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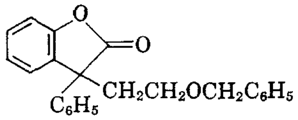
(19) C. James, *J. Am. Chem. Soc.*, 30, 184 (1908).

(1) H. E. Zaugg, R. W. DeNet, and R. J. Michaels, *J. Org. Chem.*, 26, (1961).

led to the corresponding bromide Ia; and hydrogenolysis of the benzyloxyethyl compound IV produced IIIa in good yield.


IV

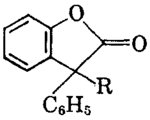
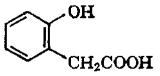
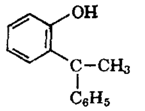
The only compelling evidence for the structural assignments to these lactones derives from their infrared spectra. The single carbonyl peak at 5.54 μ shown by IIb (5.25% in chloroform; 0.10-mm. cell) requires assignment of the benzofuranone structure to it.[2] The absence of appreciable absorption at 5.54 μ in the spectrum of IIIa (either 0.525% in chloroform in a 1.0-mm. cell, or 1.75% in a 0.30 mm. cell) rules out the presence of a 2-benzofuranone ring system. The skeletal requirements derived from the foregoing chemical evidence then force assignment of structure IIIa. Furthermore, its infrared spectrum is consistent with this structure if the provision of predominant intramolecular hydrogen-bonding is added. The normal[3] carbonyl absorption at 5.65 μ exhibited by saturated γ-lactones appears only as a shoulder. The main peak appears at 5.74 μ and represents a shift due to the predominance of an intramolecularly[4] hydrogen bonded species. Consistent with this view, a typical nonbonded OH peak is present at 2.78 μ, but is dominated by a broad band at 3.0 μ characteristic of many bonded phenolic groups.[5]

Supporting evidence for these structural assignments also comes from ultraviolet spectra. Casual inspection of Table I suffices to show a much closer spectral similarity among the chosen models of known structure than there is between the two lactones in question.[6]

To estimate the degree of interconvertibility within each pair of lactone systems (*i.e.*, IIa⇆IIIa, and IIb ⇄ IIIb), IIb and IIIa were both examined spectroscopically under conditions which favor equilibration. In neither case was any change noted in the carbonyl region of the infrared spectrum (0.025-mm. barium fluoride cell) when a 15% solution in dry methanol containing a catalytic amount of sodium methoxide was kept at 40° for forty-eight hours. Using synthetic mixtures of IIb and IIIa and assuming that the carbonyl absorbance of the hypothetical IIa would be as great as that of IIb, and IIIb as great as IIIa, it was estimated that as little as 2% of each of the isomeric lactones would have been detected had they been formed under these conditions. From this it follows that IIIa is favored over IIa and IIb over IIIb by equilibrium constants greater than 49 and by free energy differences (at 25°) greater than 2.3 kcal. If one makes the reasonable assumption that the stability of the lactone ring in the hypothetical IIa is about the same as that of IIb, then it also follows that the γ-lactone IIIa is more stable than the δ-lactone IIIb by a free energy factor greater than 4.6 kcal. per mole.

TABLE I

ULTRAVIOLET SPECTRA IN 95% ETHANOL

Compound	λ_{max}mμ	ϵ_m	λ_{min}mμ	ϵ_m
A. Benzofuranones 				
R				
H	279	1360	276	1090
	272	1520	250	725
$—(CH_2)_2Cl$	279	1500	276	1300
	272	1730	254	868
$—(CH_2)_3Br$ (Ib)	278	1390	275	1120
	271	1570	253	776
$—(CH_2)_3OH$ (IIb)	278	1345	275	1040
	270	1490	253	705
B. *o*-Substituted phenols				
	280^a	2200		
	274	2370	242	122
	280^a	2420		
	275	2740	243	470
IIIa	280^a	2450		
	275	2700	248	472

[a] Shoulder.

EXPERIMENTAL[7]

3-(β-Benzyloxyethyl)-3-phenyl-2-benzofuranone (IV). To a solution of the sodium derivative of 3-phenyl-2-benzofuranone [prepared in the usual manner[1] from 58.8 g. (0.28 mole) of the benzofuranone and 13.0 g. (0.286 mole) of a 53% mineral oil dispersion of sodium hydride] in 250 ml. of dry dimethylformamide was added in one portion, 48.8 g. (0.286

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[2] The carbonyl absorption of every 2-benzofuranone of known structure reported in this and the accompanying papers[1] fell in the range 5.53–5.55 μ.

[3] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen & Co., Ltd., London, 1958, p. 178.

[4] The spectrum does not vary with changes in concentration.

[5] A. E. Martin, *Nature*, 166, 474 (1950).

[6] Attempts to demonstrate the presence of a phenolic hydroxyl group in IIIa and its absence in IIb, by measuring the effect of increased *p*H on the position of the absorption maxima, were equivocal. The expected bathochromic shift was indeed observed for IIIa, but even in dry methanolic sodium methoxide, a similar but less marked, shift occurred with IIb. This indicated that either a rapid ring-opening of IIb took place, probably as a result of traces of moisture unavoidably present at the high dilutions necessary, or that methoxide ion itself opened the benzofuranone ring to give an equilibrium concentration of phenoxide anion–methyl ester. In any case, the shift observed with IIb, unlike that of IIIa, was not immediately reversed on acidification.

[7] Melting points and boiling points are uncorrected.

mole) of benzyl β-chloroethyl ether.[8] After stirring and heating the mixture on the steam bath for 19 hr., the dimethylformamide was removed by distillation under reduced pressure, and the cooled residue was treated with 250 ml. of cold water. Insoluble oil was taken up in ether and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave a thick oil which, on fractionation, gave 29 g. (30%) of IV, b.p. 208–213° (0.3 mm.), n_D^{25} 1.5920, m.p. 64–66° (from hexane), $\lambda_{max}^{CHCl_3}$ 5.55 μ (> C=O).

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85; O, 13.94. Found: C, 80.09; H, 5.91; O, 14.00.

2-(o-Hydroxyphenyl)-2-phenyl-4-hydroxybutyric acid γ-lactone (IIIa). A solution of 5 g. (0.0145 mole) of IV in 100 ml. of ethanol was hydrogenated at 55–60° and 40 lb. of pressure for 16 hr. using 2.5 g. of 5% palladium-charcoal catalyst. After recovery of the catalyst by filtration, the ethanol was removed using a rotating evaporator under reduced pressure. The solid residue (3.6 g., 97%), m.p. 146–151°, was recrystallized twice from benzene to give 2.8 g. (76%) of pure IIIa, m.p. 159–161°, identical (mixed melting point and infrared spectrum) with the material obtained from Ia[1]; $\lambda_{max}^{CHCl_3}$ (μ) 2.78(w), 3.0(w) (broad), 5.65(m) (shoulder), 5.74(s), 6.21(w), 6.33(w), 6.76(m), 7.29(m).

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; O, 18.88. Found: C, 75.72; H, 5.47; O, 18.53.

Refluxing 2.3 g. (0.009 mole) of IIIa for 18 hr. with a mixture of 10 ml. of 48% hydrobromic acid and 25 ml. of glacial acetic acid gave a quantitative yield of 3-(β-bromoethyl)-3-phenyl-2-benzofuranone (Ia) identified by mixed melting point and infrared spectral comparison with the authentic material.[1]

3-(γ-Hydroxypropyl)-3-phenyl-2-benzofuranone (IIb). The fraction (5.3 g.), b.p. 200–201° (1.5 mm.), obtained as an appreciable by-product in the preparation[1] of ethyl 5-phenyl 2,3,4,5-tetrahydro-1-benzoxepin-5-carboxylate by treatment of 3-(γ-chloropropyl)-3-phenyl-2-benzofuranone with sodium ethoxide, was dissolved in 10 ml. of a 10% solution of potassium hydroxide in methanol. After standing overnight, a solid potassium salt (5.3 g.) crystallized. It was collected by filtration and dried. This was dissolved in a little water and acidified with dilute hydrochloric acid. The precipitated oil (3.5 g.) quickly solidified and was collected at the filter, washed with chloroform, and dried, m.p. 113–114° (gas evolution). The infrared spectrum, λ_{max}^{Nujol} 5.93 μ (> C=O), and analysis were consistent with the structure, 2-(o-hydroxyphenyl)-2-phenyl-5-hydroxyvaleric acid.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34; O, 22.35. Found: C, 71.88; H, 6.35; O, 21.79.

Attempts to recrystallize this acid were unsuccessful. After standing in chloroform for several days it reverted spontaneously to the chloroform-soluble benzofuranone IIb, $\lambda_{max}^{CHCl_3}$ 5.54 μ (>C=O). Pure IIb was obtained by removal of the chloroform by evaporation and distillation of the residue, b.p. 193–195° (1 mm.), n_D^{25} 1.5830; λ_{max}^{CHCl} (μ) 2.74(w), 3.30(w), 3.38(w), 3.45(w), 5.54(s), 6.17(w), 6.24(w), 6.68(w), 6.77(m), 6.83(s), 6.91(w).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; O, 17.89. Found: C, 76.33; H, 6.13; O, 18.03.

Refluxing 2 g. (0.0075 mole) of the benzofuranone IIb with hydrobromic acid in acetic acid as described above for the lactone IIa gave 1.9 g. (77%) of 3-(γ-bromopropyl)-3-phenyl-2-benzofuranone (Ib), m.p. 92–94°, identified by infrared spectrum and mixed melting point with an authentic specimen.[1]

Spectra. The infrared spectra were determined using a Perkin-Elmer Model 137-G Grating Infracord, and the ultraviolet spectra using a 1-cm. cell in a Cary Model 11 recording spectrophotometer.

Acknowledgment. Mr. George Stone performed the hydrogenolysis reaction, Mr. E. F. Shelberg was responsible for the microanalyses, and Mr. Fred Scheske provided technical assistance for the infrared studies.

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Ultraviolet Spectra of Unsaturated Cyclic Nitriles

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A study of the ultraviolet spectra of a number of unsaturated aliphatic nitriles[1] led to the following rules as regards the effects of substituents on wave length: unsubstituted, 203; α- or β-monosubstituted, 205 ± 3; α,β- or β,β-disubstituted, 210 ± 3; and α,β,β-trisubstituted, 216 ± 2 mμ. Only one cyclic nitrile (1-cyanocyclohexene) was included in this study, and the ultraviolet spectra of a number of unsaturated cyclic nitriles are now considered (see Table I). These include present determinations and data taken from the literature.[2]

The α,β-disubstituted six-membered ring nitriles had their maxima at *ca.* 210 mμ, the same as that of the cyclic compounds.[1] The second maximum reported for 1-cyano-4-isopropylcyclohexene (at 271 mμ)[2e] was not observed in the other cases and may be due to an impurity (the intensity of the maximum at 212 mμ was also significantly lower). A band has been detected at 270 mμ in nitriles, but its intensity was extremely low ($A_m < 10^{-3}$).[3]

α,β-Disubstituted five-membered ring nitriles, however, had their maximum at 215–220 mμ. Similar bathochromic shifts have been noted in other five-membered endocyclic compounds[2a,4] and have been attributed[2a] to ring strain. The variation in the wave length of the maximum of these nitriles reflects the varying strain in their rings. 1-Cyano-

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