Influence of Lewis acids on the Diels–Alder reaction. II. Rearrangement of 1- and 1,4-substituted diethyl 7-oxabicyclo[2·2·1]2,5-heptadiene-2,3-dicarboxylate adducts to 4- and 4,6-substituted diethyl 3-hydroxyphthalates[1]

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Direct formation of 4- or 4,6-alkyl and aryl substituted diethyl 3-hydroxyphthalates from the correspondingly substituted Diels–Alder adducts of 2- or 2,5-substituted furans and diethyl acetylenedicarboxylate is promoted by $AlCl_3$ in CH_2Cl_2 at room temperature. The first adduct of 2,5-diphenylfuran to be isolated has been obtained from the same reaction at −20°. The aromatic compounds can be obtained alternatively by treating the adducts with BF_3 or H_2SO_4: where the adducts can be prepared by conventional means this two-step procedure has resulted in greatly improved yields. Adducts of furan and furfuryl alcohol are similarly converted to substituted phenols. HCl effected conversion only in the case of adducts carrying a bridgehead aryl substituent; in all other cases HCl added to the substituted double bond. The mechanism of the adduct rearrangement is discussed.

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Introduction

Suitably substituted Diels–Alder adducts provide the most versatile route by which a benzene ring may be formed while simultaneously introducing substituents (1). The adducts usually possess a six-membered carbocyclic ring containing one or two double bonds and may have in addition a 1,4-bridge consisting of one or two carbon atoms or a heteroatom. Aromatization is induced by dehydrogenation (2), dehydrohalogenation (3), deamination (4), pyrolytic elimination of substituents (5), or a 1,4-bridge (6), or fission of a 1,4-oxygen bridge followed by loss of H_2O (7). Less general procedures for the annelation of readily available molecules to benzene rings include the catalytic trimerization of acetylenes (8), the reaction of pyrylium salts with nitromethane (9), or triphenylphosphinemethylene (10), the condensation of pyrones with Grignard reagents (11), the ketovinylation of β-dicarbonyl compounds followed by intramolecular cyclization or further reaction with β-chlorovinyl ketones (12), and the reaction of enamines with esters of acetylenedicarboxylic acid (13).

In preliminary communications (14,15) we reported that Lewis acids produced an enormous increase in the rate of formation of 1- and 1,4-substituted diethyl 7-oxabicyclo[2·2·1]2,5-heptadiene-2,3-dicarboxylates (**1**) from suitably substituted furans and diethyl acetylenedicarboxylate (DEAD), and also promoted the rearrangement of these adducts to 4- and 4,6-substituted derivatives of diethyl 3-hydroxyphthalate (**2**). Reactions using ethyl propiolate behaved similarly (15). Subsequently, other workers have reported that the dimethyl ester corresponding to **1** (R_1 = 4-methoxyphenyl; R_2 = H) rearranged to the analogue of **2** (R_1 = 4-methoxyphenyl; R_2 = H) in the presence of warm acetic acid (16).[4]

This paper discusses in full the mechanism and experimental conditions for the conversion of **1** to **2**. The derivatives **2** prepared in this way, with one exception **2***a*, contain *three different types* of substituents, one of which is a phenolic hydroxyl group. Diels–Alder reactions using dienes such as 2-acetoxyfuran (17), 1,4-diacetoxybutadiene (5), and substituted 4-hydroxy-α-pyrones (18) have been used previously to introduce a phenolic hydroxyl substituent, but these methods seem to be of limited scope as compared to our method. The substituent migrations which occur in the transformation of **1** to **2**, although not particularly new from a chemical standpoint, are nevertheless the first to be reported in the direct formation of benzene derivatives from Diels–Alder adducts. High yields of **2** and the possibility of increasing the number of types of substituents

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[4] During the final stages of preparation of this manuscript Vogel and co-workers published (30) an account of work closely related to that previously reported by us (14,15) and by Ayres and Smith (16). Their work involved acid-catalyzed rearrangement of a variety of methyl or methoxyl-substituted oxanorbornadienes. The spectral data reported for compounds analogous to **2***b* and **2***e* are in full agreement with our own data.

TABLE I

Proton magnetic resonance data for **1**, **2**, and derivatives

	τ							$J_{p,q}$(Hz)			
Compound	OCH_2CH_3(J = 7.0)	OH*	R_1, R_2	H_1	H_4	H_5	H_6	4,5	4, 6	5,6	Sub-spectra; other resonances
1*a*	5.74(q)†, 8.69(t)			4.34(m)		2.78(m)					$A(H_1)\ X(H_6)\ X'(H_5)\ A'(H_4)$ $J_{4,5} + J_{4,6} = 2.1$ Hz
1*b*‡	5.70(q), 5.77(q), 8.68(t), 8.72(t)		8.23(CH_3, d)		4.44(q)	2.83(m)		2.1	0.1	5.3	$A(H_5)\ B(H_6)\ X(H_4)$ $\Delta\nu_{5,6} = 12.5; J_{H5,CH3} = 0.4$ Hz
1*c*	5.70(q), 5.75(q), 8.68(t), 8.69(t)	7.0(s)	5.74(CH_2, s)		4.34(q)	2.85(m)		2.2	0.1	5.0	$A(H_5)\ B(H_6)\ X(H_4)$ $\Delta\nu_{5,6} = 10.8$ Hz
1*d*	5.76(q), 5.92(q), 8.73(t), 8.93(t)		2.60(C_6H_5, m)		4.19(q)						$A(H_5)\ B(H_6)\ X(H_4)$ $J_{4,5} + J_{4,6} = 2.2$ Hz; H_5,H_6 in C_6H_5 multiplet
1*e*‡	5.74(q), 8.68(t)		8.20($2CH_3$, s)			3.05(s)					
1*f*	5.92(q), 8.93(t)		2.50($2C_6H_5$, m)			2.40(s)					
2*a*	5.71(q), 5.73(q), 8.63(t), 8.67(t)	−0.33(s)			2.50 − 3.10(m)						$A(H_4)\ B(H_5)\ C(H_6)$
2*b*‡	5.63(q, 4H), 8.63(t), 8.65(t)	−0.83(s)	7.78(CH_3, d)		2.91(q)			8.7			$A(H_4)\ B(H_5)$§ $\Delta\nu_{4,5} = 19.2; J_{H5,CH3} = 0.4$ Hz
2*d*	5.62(q), 5.97(q), 8.67(t), 9.04(t)	−1.07(s)	2.66(C_6H_5, s)		2.75(q)			8.7			$A(H_4)\ B(H_5)$§ $\Delta\nu_{4,5} = 19.8$ Hz
2*e*‡	5.63(q), 5.64(q), 8.60(t), 8.65(t)	−1.01(s)	7.77, 7.80 ($2CH_3$, s)			2.85(s)					$J_{H5,CH3} = 0.4$ Hz
2*f*‖	5.58(q), 5.92(q), 8.67(t), 9.05(t)	−1.58(s)	2.55($2C_6H_5$ + H_5, m)								
3	5.48(q), 8.53(t)	−0.80(s)			2.61(q)			8.7			$A(H_4)\ B(H_5)$§ $\Delta\nu_{4,5} = 15.2; J_{H4,CH2} < 0.2$ Hz 4.83 τ (CH_2, s)
4*g*¶		3.20(s)	7.46, 7.66 ($2CH_3$, s)			2.64(s)					
4*h***			7.43, 7.65 ($2CH_3$, s)			2.42(s)					5.92 τ (OCH_3, s)
4*i*¶		2.08(s)	2.50($2C_6H_5$, m)			2.21(s)					
5	5.68(q), 5.70(q), 8.68(t, 6H)					2.82(s)					7.63, 7.84 τ ($2CH_3$, s); 7.74 τ ($OCOCH_3$, s)
6**		1.43(s), 4.73(t), 5.50(t)				3.17(s)					5.23, 5.52 τ ($2CH_2$, d); 7.78, 7.87 τ ($2CH_3$, s)

*Hydroxyl protons were replaceable by deuterium.

†s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Average τ values are reported for multiplets.

‡References in parentheses give parameters for dimethyl ester and diacid of **1***b* (27, 28, 30), **1***e* (28, 30), and **2***b*, *e* (30), as well as dimethyl ester of **1***a* (26).

§H_5 occurs at lower field than H_4 in **2***b* and **2***d*; H_4 is at lower field than H_5 in **3**.

‖Diethyl 3-methoxy-4,6-diphenylphthalate (acetone-d_6): 5.64(q), 5.96(q), 8.66(t), 9.03(t) (OCH_2CH_3); 6.55(OCH_3, s); 2.60(11 aromatic H,m).

¶At 50°.

Acetone-d_6 (4***h*); DMSO-d_6 (**6**).

TABLE II

Overall yields of **2** and **3** obtained at room temperature from dienes and DEAD directly in the presence of $AlCl_3$,* or from **1** by treatment with BF_3† or H_2SO_4

		Addends + $AlCl_3$		**1** + BF_3 or H_2SO_4	
Diene	Reaction product	Time (h)	Yield %	Time (h)	Yield %
Furan	**2***a*	—	—	50	45
2-Methylfuran	**2***b*	72	50	0.4	90
2-Phenylfuran	**2***d*	1	50	0.2	90
2,5-Dimethylfuran	**2***e*	72	45	0.4	90
2,5-Diphenylfuran	**2***f*	1	65	0.2	40‡
Furfuryl alcohol	**3**	—	—	3.0	35

*Reactions were carried out in CH_2Cl_2 and were 0.1 *M* in addends and $AlCl_3$.

†Reactions were carried out in CH_2Cl_2 and were 0.3 *M* in **1**: the solutions were treated with excess BF_3 or H_2SO_4.

‡**1***f* could only be isolated in 40% yield but was converted to **2***f* quantitatively. Overall yield is therefore 40%.

suggests that our procedure should prove generally useful for the synthesis of a large number of benzene derivatives which would be difficult by more conventional routes.

Our studies on the formation of **1** in the presence of Lewis acids are not relevant to the present work and will therefore be published separately.

Results and Discussion

The proton magnetic resonance (p.m.r.) spectral evidence used in the structural elucidation of the compounds discussed below is detailed in Table I.

Preparation and Structures of 1

Thermal condensation of the addends (19) enabled the adducts **1***a–e* to be isolated in excellent yield. However, attempts to prepare **1***f* by heating the addends at temperatures up to 180° in a sealed tube were unsuccessful. Indeed no adducts of 2,5-diphenylfuran have been reported previously, and this can undoubtedly be attributed to a reduction in diene character as a result of extensive π-delocalization due to coplanarity of the aromatic and furan rings. Conversion of the addends to crystalline **1***f* was, however, promoted by $AlCl_3$ (see Experimental).

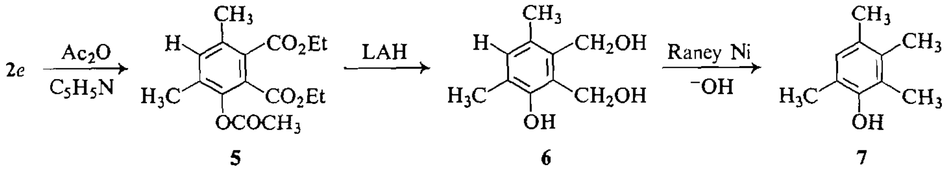
The structures of **1***a–f* were established from their p.m.r. spectra although their identity was quite clear from their mode of formation. Compounds **1***a*, *e*, and *f* belong to the symmetry group C_s and consequently gave characteristic p.m.r. signals for two chemically equivalent olefinic hydrogens, bridgehead substituents, and carbethoxy groups. The aromatic hydrogens in **1***f* gave a complex multiplet (ABCDE system? - due to asymmetry at C_1 and C_4), and the olefinic and bridgehead hydrogens of **1***a* an AXX′A′ spectrum. The unsymmetrical adducts **1***b*, *c*, and *d*, on the other hand, gave characteristic ABX systems for the two olefinic and bridgehead hydrogens as well as signals for the bridgehead substituents and two chemically non-equivalent carbethoxy groups. An interesting example of long-range spin–spin coupling across five bonds (20) (J_{H_5,CH_3} = 0.4 Hz) was observed in **1***b*.

Preparation and Structures of 2

Adducts **1***a–f* rearranged in the presence of BF_3 or H_2SO_4 in CH_2Cl_2 to compounds of type **2** or to compound **3** (see Table II).

The p.m.r. and infrared (i.r.) spectra of **2***a* and the observation that it gave 3-hydroxyphthalic acid on saponification establishes the structure as diethyl 3-hydroxyphthalate.

The unsymmetrical tetra-substituted benzene derivatives gave p.m.r. signals with chemical shifts, multiplicities, and intensities consistent with the numbers and types of hydrogens shown in structures **2***b*, **2***d*, and **3**. Each compound gave a characteristic AB pattern for two *ortho* coupled aromatic hydrogens. In two compounds, the proton giving rise to the low-field half of the AB pattern was long-range coupled (21) to the benzylic methyl (**2***b*) or methylene (**3**) hydrogens, while in all three, the proton giving rise to the high-field part of the AB system had a chemical shift consistent with the presence of an *ortho* phenolic hydroxyl group (22). A proton *ortho* to



SCHEME 1

a carbonyl function would give a signal at lower field (ca. τ 2.0) (22). This evidence together with the known structures of **1***b*, *c*, and *d* and the fact that **1***a* gave diethyl 3-hydroxyphthalate (**2***a*), requires that the compounds be diethyl 6-methyl-3-hydroxyphthalate (**2***b*), diethyl 6-phenyl-3-hydroxyphthalate (**2***d*), and 7-carbethoxy-6-hydroxyphthalide (**3**). The i.r. spectra were consistent with these structures. The structure of **3** was confirmed by its saponification to the known 7-carboxy-6-hydroxyphthalide (23).

The structure of **2***e* was established from the following evidence: (*a*) it could be converted to isodurenol (**7**) via Scheme 1; (*b*) i.r. studies on a 0.005 *M* solution of **2***e* in CCl_4 indicated intramolecular hydrogen bonded hydroxyl and ester carbonyl groups as well as a free ester carbonyl group; (*c*) it could be converted to an anhydride (**4***g*) and the phenolic hydroxyl group of this compound could be methylated (**4***h*); and (*d*) the p.m.r. spectra of **2***e*, **4***g*, **4***h*, and **7** contained signals with characteristic chemical shifts, multiplicities, and intensities for each proton type. From (*b*), (*c*), and (*d*) it can be deduced that the phenolic hydroxyl and two carbethoxy groups in **2***e* have the same relative orientation as in diethyl 3-hydroxyphthalate (**2***a*). This structural feature together with (*a*) establishes that the two methyl substituents on C_2 and C_3 of isodurenol (**7**) must have been derived from the two carbethoxy groups of **2***e*. It follows that the two remaining methyl substituents at C_4 and C_6 of isodurenol must have been the original methyl substituents which were observed in (*d*) for **2***e*. We can, therefore, state unambiguously that **2***e* is diethyl 4,6-dimethyl-3-hydroxyphthalate and **4***g* and **4***h* are 4,6-dimethyl-3-hydroxy- and 3-methoxyphthalic anhydride. Compound **6** must be 2,3-dihydroxymethyl-4,6-dimethylphenol.

The single aromatic hydrogen in **2***e*, **4***g*, and **4***h* is long-range coupled to about the same extent with both methyl substituents (21) but is not similarly coupled to the methoxyl hydrogens (24) in **4***h*. These observations provide strong evidence that the aromatic hydrogen is *ortho* to both methyl substituents in all these compounds and confirms their structures by an alternative procedure.

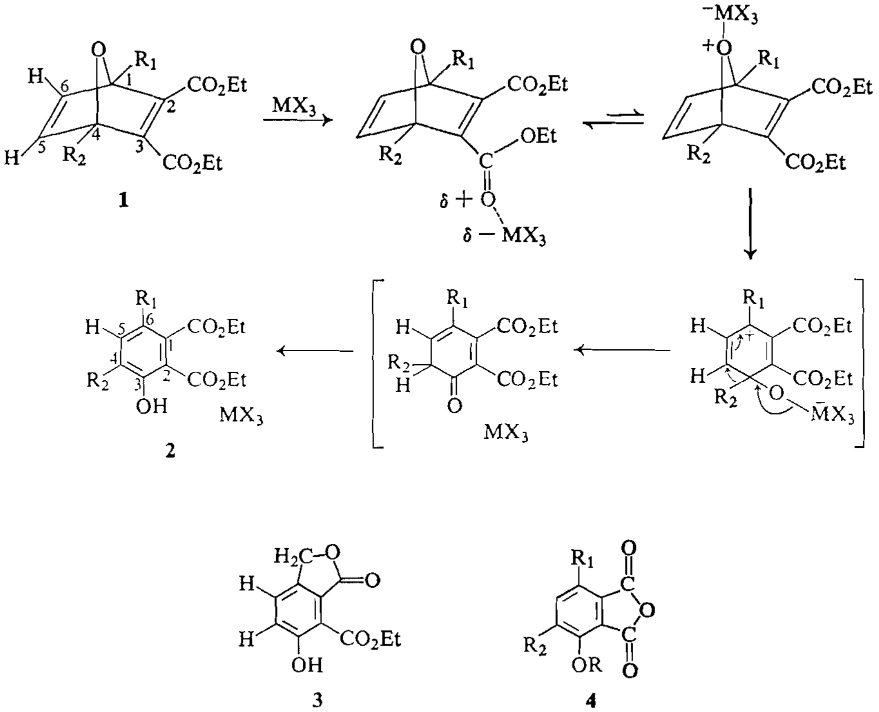
The structure of the *m*-terphenyl derivative (**2***f*) was established in a similar manner to that of **2***e* [see (*b*), (*c*), and (*d*) above]. The 11 aromatic hydrogens in **2***f* covered the range from τ 2.3 to 2.7 and no characteristic signal was observed for a single aromatic hydrogen deshielded by an *ortho* carbonyl function (ca. τ 2.0) (22). This evidence, together with the structure of the adduct (**1***f*) from which **2***f* is produced, requires that the latter be diethyl 4,6-diphenyl-3-hydroxyphthalate and **4***i* be 4,6-diphenyl-3-hydroxyphthalic anhydride.

Optimum Conditions for the Formation of 2a, b, d, e, and f and 3

Table II lists the yields of benzene derivatives (**2** or **3**) formed either directly by a one-step synthesis from the addends in the presence of $AlCl_3$ or indirectly via Diels–Alder adducts (**1**) through the action of BF_3 or H_2SO_4.

When alkyl-substituted furans or 2-phenylfuran were used as the diene component in the one-step synthesis, yields of **2** were only about 50%; no aromatic compound was formed in the case of furan or furfuryl alcohol. The lack of reaction or low yields could be attributed to extensive diene polymerization caused by $AlCl_3$ and/or precipitation of insoluble diene-$AlCl_3$ complexes. One or other of these side reactions became more dominant if the $AlCl_3$ concentration was increased. Attempts to replace $AlCl_3$ with excess BF_3 or BCl_3 also led to lower yields of product indicating that these Lewis acids also promote the side reactions. The latter were less important in the case of 2,5-diphenylfuran where yields of **2***f* as high as 75% were obtained when the addends and $AlCl_3$ were equimolar.

The side reactions could be reduced or eliminated, and the scope of the synthetic procedure increased, by first converting the addends to the



a) $R_1 = R_2 = H$
b) $R_1 = CH_3$; $R_2 = H$
c) $R_1 = CH_2OH$; $R_2 = H$
d) $R_1 = C_6H_5$; $R_2 = H$
e) $R_1 = R_2 = CH_3$
f) $R_1 = R_2 = C_6H_5$
g) $R_1 = R_2 = CH_3$; $R = H$
h) $R_1 = R_2 = R = CH_3$
i) $R_1 = R_2 = C_6H_5$; $R = H$

Scheme 2

corresponding Diels–Alder adduct (**1**) in the absence of Lewis acid. The adducts (**1***a*–*e*) could be obtained in about 95% yield and rearranged in the presence of excess BF_3 or H_2SO_4 to the corresponding benzene derivatives (**2***a*, *b*, *d*, *e* and **3**). Essentially quantitative yields (>90%) of **2***b*, *d*, and *e* could be obtained, while **2***a* and **3** were isolated in about 40% yield. Since the adduct (**1***f*) can only be isolated in about 40% yield in the presence of $AlCl_3$ the two-step procedure for forming **2***f* is inferior to the direct method although acid promotes quantitative conversion to the aromatic compound.

In the one-step procedure, rates of conversion to alkyl-substituted derivatives of **2** were slower by a factor of about 70 than for the aryl-substituted derivatives.

Boron trichloride could be used in place of BF_3 or H_2SO_4 in the two-step method, but reaction times were increased by a factor of 20 if $SnCl_4$ was used. Aluminium chloride does, of course, catalyze the rearrangement of **1** to **2** but is much less soluble in the CH_2Cl_2 solution of the adduct and in some cases precipitation of adduct-$AlCl_3$ complexes occurs.

While H_2SO_4 is generally effective as a catalyst for the rearrangement of **1** to **2** or **3**, halogen acids are not. Although anhydrous HCl effects quantitative conversion of **1***d* and **1***f* to **2***d* and **2***f*, it adds (*cis* and *trans*) to the 2,3-double bond of **1***a*, *b*, *c*, and *e*. The structures of the products and mechanisms of the addition reactions of some of these adducts (**1**) will be reported in full elsewhere.

The structures of the aromatic compounds (**2**) formed from the adducts (**1**) suggest the mechanism of rearrangement outlined in Scheme 2. Coordination or protonation of the bridge oxygen in the adduct will induce bridge cleavage which is followed by migration of the unsubstituted double bond and substituent geminal to the complexed or protonated oxygen atom. Enolization then yields **2**. Where $R_2 = H$, bridge cleavage may be followed by elimination of this proton and double bond migration.

Substituents at the bridgehead, e.g. methyl or phenyl, will facilitate reaction by inductive and resonance stabilization of the carbonium ion formed on bridge cleavage. Consequently, excellent yields of **2** were obtained from adducts carrying these substituents at the bridgehead. Moreover, the rates of conversion of phenyl-substituted adducts to the corresponding derivatives of diethyl 3-hydroxyphthalate were greater than those for alkyl-substituted adducts (see Table II). This indicates that resonance stabilization of the transition state is more significant than inductive stabilization, as would be expected. In the case of the aryl-substituted compounds the rate of HCl-promoted bridge cleavage must be greater than that of HCl addition to the double bond while the reverse is true of the alkyl-substituted derivatives.

Rearrangement of the adducts of furan (**1**_a_) and furfuryl alcohol (**1**_c_), which lack substituents at the bridgehead, to **2**_a_ and **3** occurs more slowly and lower yields are obtained. The adduct of dimethyl acetylenedicarboxylate and 2,2′-bifuryl has been reported to be stable to acid (25). In view of our results, it seems probable that cleavage of the oxygen bridge of this compound might be induced by BF_3 or H_2SO_4.

Experimental

The p.m.r. spectra were obtained on a Varian A-60A spectrometer equipped with a V-6058A spin-decoupler using $CDCl_3$ as solvent (unless stated otherwise) and tetramethylsilane as internal standard. The i.r. spectra were recorded on either a Perkin–Elmer model 521 or 237 spectrometer.

Chromatographic separations were carried out on Mallinckrodt silicic acid (100–150 mesh) using $CHCl_3$ as eluant.

Preparation of **1**_a–e_ *in the Absence of Lewis Acid*

The following adducts were prepared in the absence of solvent from the appropriate furan and diethyl acetylenedicarboxylate at 100° by the method of Alder *et al.* (19). Essentially quantitative conversion (>95%) of addends to adduct occurred in 4 h and the adducts were obtained in a pure state by chromatography.

1_a_ ($\eta_d^{23} = 1.4795$), **1**_b_ ($\eta_d^{19} = 1.4749$), **1**_c_ ($\eta_d^{23} = 1.4971$), **1**_d_ ($\eta_d^{19} = 1.5240$) and **1**_e_ ($\eta_d^{19} = 1.4680$) were obtained as yellow oils.

Preparation of **1**_f_ *in the Presence of Lewis Acid*

Two solutions containing 2,5-diphenylfuran (0.2 *M*) and DEAD (0.2 *M*) plus $AlCl_3$ (0.28 *M*) in CH_2Cl_2 were prepared separately, cooled to −20° and mixed. After 1 h at this temperature the reaction was stopped by washing the dark red reaction solution with water to remove the Lewis acid. After drying and removing the solvent the residue was triturated with petroleum ether to remove starting materials and leave the adduct as an insoluble residue.

1_f_ was obtained as needles from ether–petroleum ether in 40% yield, m.p. 103–104°.

Direct Formation of **2**_b, d, e,_ *and* _f_ *from Furans and DEAD in the Presence of* $AlCl_3$

The experimental procedure was the same as given above for the preparation of **1**_f_ except that all 3 reagents were equimolar, and the solutions were allowed to stand at room temperature until no further reaction occurred.

The reaction products were purified by chromatography or crystallization. Yields of **2** prepared in this way are given in Table II. This procedure can not be used with furan or furfuryl alcohol because of side reactions.

Using excess BF_3 or BCl_3 in place of $AlCl_3$ caused extensive diene polymerization which reduced the yields of **2**.

2_b_ was obtained as a yellow oil, $\eta_d^{19} = 1.5083$. Characteristic i.r. absorptions (liquid film): hydrogen bonded (1675 cm^{-1}) and free (1735 cm^{-1}) carbonyl functions, and hydrogen bonded hydroxyl group (broad band with maximum at 3100 cm^{-1}).

2_d_ was obtained as a yellow–orange oil, $\eta_d^{19} = 1.5630$. Characteristic i.r. absorptions (liquid film): hydrogen bonded (1675 cm^{-1}) and free (1730 cm^{-1}) carbonyl functions.

2_e_ was obtained as a yellow oil, $\eta_d^{19} = 1.5186$. Characteristic i.r. absorptions (0.005 *M* in CCl_4): hydrogen bonded (1673 cm^{-1}) and free (1731 cm^{-1}) carbonyl functions, and hydrogen bonded hydroxyl group (measured after deuteration, at 2340 cm^{-1}).

Saponification of **2**_e_ with 1 *N* KOH followed by acidification gave an acid which was sublimed at 140–145° and 0.01 mm pressure to yield **4**_g_ in virtually quantitative yield, m.p. 178–179°. Characteristic i.r. absorptions (KBr disc): anhydride carbonyls (1760 and 1830 cm^{-1}) and phenolic hydroxyl (3450 cm^{-1}).

4_g_ was converted to **4**_h_ with diazomethane in ether and the latter crystallized as colorless prisms from this solvent, m.p. 151–152°. Characteristic i.r. absorptions (KBr disc): anhydride carbonyls (1770 and 1845 cm^{-1}).

2_f_ was obtained from methanol as colorless plates, m.p. 128–129°.

Anal. Calcd. for $C_{24}H_{22}O_5$ (mol. wt. 386): C, 73.83; H, 5.68; O, 20.49. Found (390 (osmometer)): C, 73.83; H, 5.76; O, 20.37. In ethanol $\lambda\lambda_{max}$ 232 (ε 33 500), 330 (ε 6 500) mμ; 0.025 *N* NaOH in 96% ethanol 254 (ε 22 900), 287 (ε 10 700), 365 (ε 9 900) mμ. Characteristic i.r. absorptions (0.005 *M* in CCl_4): hydrogen bonded (1665 cm^{-1}) and free (1732 cm^{-1}) carbonyl functions, and hydrogen bonded hydroxyl group (measured after deuteration at 2320 cm^{-1}).

2_f_ was converted to diethyl 3-methoxy-4,6-diphenylphthalate with diazomethane in ether and crystallized from ethanol as needles, m.p. 96°.

Anal. Calcd. for $C_{25}H_{24}O_5$ (mol. wt. 404): C, 74.24; H, 5.98; O, 19.78. Found (399 (osmometer)): C, 74.13; H, 5.89; O, 19.74. In ethanol $\lambda\lambda_{max}$ 245 (ε 29 600), 294 (ε 4 150) mμ. Characteristic i.r. absorption (KBr disc): ester carbonyl (1730 cm^{-1}).

2_f_ was converted to **4**_i_ by heating it with acetic acid saturated with HBr in a sealed tube at 110–125° for 7 h. **4**_i_ crystallized from the acetic acid solution on cooling and was recrystallized from CCl_4 as needles, m.p. 190–191°.

Anal. Calcd. for $C_{20}H_{22}O_4$ (mol. wt. 316): C, 75.94; H, 3.82; O, 20.83. Found (317 (osmometer)): C, 75.24; H, 3.97; O, 20.68. In ethanol $\lambda\lambda_{max}$ 237 (ε 26 200), 300 (ε 6 370), and 355 (ε 6 300) mμ. Characteristic i.r. absorptions (KBr disc): anhydride carbonyls (1750 and 1830 cm^{-1}) and phenolic hydroxyl (3450 cm^{-1}).

Preparation of 2a, b, d, e, and f and of 3 from the Corresponding Adducts **1**

(a) In the Presence of BF_3

Solutions of the adducts in CH_2Cl_2 (0.33 *M*) were cooled in ice while saturating with BF_3 and then allowed to stand at room temperature. The reactions were stopped by removing the Lewis acid with water and the reaction products purified by chromatography or crystallization.

(b) In the Presence of H_2SO_4

Solutions of the adducts in CH_2Cl_2 were cooled in ice and a slight molar excess of concentrated H_2SO_4 added dropwise with stirring. After standing at room temperature the reactions were worked up as in (*a*).

The yields of **2** prepared in (*a*) and (*b*) are given in Table II.

2*a* was obtained as a yellow oil.

Saponification of **2***a* gave 3-hydroxyphthalic acid. Recrystallization from water gave colorless needles which on slow heating had m.p. 195–196° [reported m.p. for 3-hydroxyphthalic anhydride is 198–199° (29)]. The p.m.r. and i.r. spectra of this material were identical to those of an authentic sample of 3-hydroxyphthalic acid prepared by diazotization of 3-aminophthalic acid.

3 was obtained as colorless prisms from benzene–petroleum ether, m.p. 179–179.5°. Characteristic i.r. absorptions (KBr disc): α,β-unsaturated γ-lactone (1750 cm^{-1}) and ester (1728 cm^{-1}) carbonyls, and phenolic hydroxyl (broad band with maximum at 3200 cm^{-1}).

Saponification of **3** gave the free acid (90%), crystallized from acetone as colorless prisms, m.p. 216–217° [lit. (23) m.p. 212–213°].

Action of Hydrogen Chloride on **1***d and* **1***f*

When solutions of **1***d* or **1***f* (0.1 *M*) in CH_2Cl_2 were saturated with hydrogen chloride and left standing for 10 min at room temperature they were quantitatively (>95%) converted to **2***d* and **2***f*.

Conversion of **2***e to Isodurenol*

2*e* (8.38 g) was acetylated in 15 min at 100° with acetic anhydride (5.5 ml) in pyridine (10 ml). After working up in usual manner, **5** was obtained as a viscous oil (9.22 g, 95% yield). Characteristic i.r. absorption (liquid film): ester (1730 cm^{-1}) and phenolic acetate (1770 cm^{-1}) carbonyls.

Without further purification **5** (7.3 g) was reduced with $LiAlH_4$ (3 g) in ether (260 ml) in a nitrogen atmosphere. After standing for 1 h at room temperature and at reflux for a further 2 h the excess $LiAlH_4$ was destroyed by adding ethyl acetate (45 ml). The reaction solution was then worked up in the usual manner to yield a residue of **6** which crystallized from petroleum ether–ethyl acetate as cream colored needles (2.12 g, 50% yield), m.p. 125–128°. Characteristic i.r. absorption (KBr disc): hydroxyl (broad band, with maxima at 3350 and 3100 cm^{-1}).

6 (500 mg) was dissolved in 5% NaOH (135 ml) and Raney alloy (6 g) added in small portions with mechanical agitation. After standing for 1 h at room temperature, the mixture was heated for a further 1 h on a steam bath. The solution was then cooled, filtered, and acidified with concentrated hydrochloric acid. A colorless precipitate was collected by filtration and subsequently crystallized from petroleum ether to give **7** as colorless needles (298 mg, 72%), m.p. 79.5–81.5°. No depression in m.p. was observed on admixing with authentic isodurenol (**7**), and the i.r. and p.m.r. spectra of the synthetic material were identical to those of an authentic sample of isodurenol.

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