[Contribution from the McPherson Chemical Laboratory of The Ohio State University]

I. Addition Reactions of Arylalkanes and Maleic Anhydride Occurring by Chain Processes

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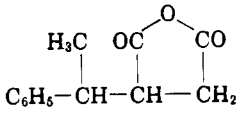
Received July 6, 1956

Substituted succinic anhydrides may be prepared by thermal addition of maleic anhydride to arylalkanes (such as 2-methylnaphthalene, fluorene, and isopropylbenzene, etc.) having hydrogen atoms attached to positions that are *alpha* to the aromatic nuclei.[2] Thus, reaction of ethylbenzene and maleic anhydride at 250–350° results in formation of 3-phenyl-1,2-butanedicarboxylic anhydride(I).[3] The addition reactions are catalyzed by iodine, sulfur, and copper bronze;[2a] they are also accelerated by benzoyl peroxide at 100°[4] or by ultraviolet light.[4a] On the basis of the accelerative effects of initiators[4] and the ratio of the number of molecules of adduct formed to that of initiator consumed, it is apparent[4a] that addition of an arylalkane to maleic anhydride occurs by a homolytic chain process involving (1) attack by the decomposition products of the initiator on the arylalkane to give the α-arylalkyl radical, (2) addition of the arylalkyl radical to the carbon-carbon double bond of maleic anhydride, and (3) reaction of the intermediate arylalkylsuccinyl radical with the parent hydrocarbon by hydrogen transfer to yield the arylsuccinic anhydride and an α-arylalkyl radical.



$C_6H_5-\overset{H_3C}{CH}-\overset{OC-O-}{CH}-\overset{CO}{CH_2}$

I

Since it is possible to conveniently scrutinize by kinetic methods[1] the reactions of arylalkanes and maleic anhydride in the presence of di-*tert*-butyl peroxide, it was desired to (1) obtain additional information concerning the effect of structure of an arylalkane on the scope and specificity of its reaction with maleic anhydride, (2) investigate the kinetics of addition of maleic anhydride to various *ortho, meta,* and *para*-substituted arylalkanes,[1] and (3) determine the influences of ring size and strain on reactions of homologous arylcycloalkanes with maleic anhydride. The present communication is concerned primarily with the first of the listed objectives.

The reactions of *o, m,* and *p*-xylenes, respectively, with maleic anhydride and di-*tert*-butyl peroxide were investigated first to determine the effect of methyl groups on the addition processes. *p*-Xylene and maleic anhydride (mole ratio of 27.8:1) react slowly at 150° in the absence of an initiator in that addition was only 16 per cent complete after 3 hours. The inhibitor action of hydroquinone and the subsequent accelerative effects of di-*tert*-butyl peroxide on reaction of *p*-xylene and maleic anhydride are illustrated in Figure 1. Both *p*- and *m*-xylenes underwent rapid addition of maleic anhydride in the presence of di-*tert*-butyl peroxide (mole ratio of 1.6:0.10:0.007) at 150° (Table I) to give 3-(*p*-tolyl)-1,2-propanedicarboxylic acid (II, 99%)[5] and 3-(*m*-tolyl)-1,2-propanedicarboxylic acid (III, 79%)[5] upon hydrolysis of the reaction mixtures. *m*-Xylene reacted with maleic anhydride at a slightly lower rate than did *p*-xylene.[6] The structure assigned to II was based on its analysis and the similarity of its properties with those previously reported.[4a] the structure of III was established from its analysis, neutral equivalent and oxidation to isophthalic acid (87%).

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(1) Abstracted in part from a Ph.D. dissertation presented by Harold C. Barker to the Graduate School of The Ohio State University, 1951.

(2) (a) Binapfl, French Patent 775,363 (Dec. 27, 1934); German Patent 607,380 (Jan. 2, 1935); German Patent 623,338 (Dec. 21, 1935); (b) Barnett, Goodway, Higgins, and Lawrence, *J. Chem. Soc.*, 1224 (1934); (c) Clar, *Chem. Ber.* Proof, 859 (1942); (d) Alder, Pascher, and Vagt, *Ber.*, **75**, 1501 (1942) and (e) Alder and Wolff, *Ann.*, **576**, 182 (1952).

(3) The adduct is capable of existing in two *d, l* pairs.

(4) (a) Bickford, Fischer, Dollear, and Swift, *J. Am. Oil Chem. Soc.*, **25**, 251 (1948); (b) Beavers, British Patent 668,574 (March 19, 1952).

(5) Based on maleic anhydride reacted. The percentages of maleic anhydride consumed in formation of II and III after 5 hours were 76 and 73 respectively. Further absorption of maleic anhydride occurred very slowly because most (>99%) of the initiator had been decomposed (the half life of di-*tert*-butyl peroxide at 150° is 0.71 hours; Technical Brochure No. S-9987, Shell Development Co., Emeryville, Calif.); addition could be reinitiated, however, upon introduction of fresh di-*tert*-butyl peroxide. In most of the systems investigated additional initiator was not added and reaction was essentially terminated after 70–85% of the maleic anhydride had been consumed.

(6) (a) These reactions are kinetically reproducible and are first order with respect to maleic anhydride for up to 50–60% reaction.[1] In reactions of *p*- and *m*-xylenes with maleic anhydride and di-*tert*-butyl peroxide (mole ratio of 30.6:1.0:0.034) at 135 ± 0.15°, the chain lengths of addition range from 160 to 180 and from 75 to 105, respectively, for up to 40% absorption of maleic anhydride.[1] (b) The chain lengths were based on the mechanism proposed in ref. 4a and the rate constant for decomposition of di-*tert*-butyl peroxide at 135°; Raley, Rust, and Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1948).

TABLE I

REACTION OF MALEIC ANHYDRIDE WITH SUBSTITUTED ALKYLBENZENES

Alkylbenzene	Product[a]	Maleic Anhydride % reacted, 5 hours	Yield, %[b, c]	m.p., °C.[d]	Carbon		Hydrogen		Neut. equiv	
					Calc'd	Found	Calc'd	Found	Calc'd	Found
p-Xylene	3-(*p*-Tolyl)-1,2-propanepropanedicarboxylic acid	76	99	114–115[e]	64.85	64.83	6.35	6.45	111.1	110.6
m-Xylene	3-(*m*-Tolyl)-1,2-propanedicarboxylic acid[f]	73	79(63)[g]	128–129	64.85	64.89	6.35	6.42	111.1	112.4
o-Xylene	3-(*o*-Tolyl)-1,2-propanedicarboxylic acid[h]	60	43[i]	171–172[j]	64.85	64.79	6.35	6.44	111.1	112.0
p-Chlorotoluene	3-(*p*-Chlorophenyl)-1,2-propanedicarboxylic acid[k]	75	44(30)[g] (70)[l]	131.5–132.5	54.44	54.50	4.57	4.73	121.3	121.0
m-Chlorotoluene	3-(*m*-Chlorophenyl)-1,2-propanedicarboxylic acid[m]	—	39[l]	134–135	54.44	54.25	4.57	4.72	121.3	122.9
o-Chlorotoluene	3-(*o*-Chlorophenyl)-1,2-propanedicarboxylic acid[n]	—	73[l]	157.5	54.44	54.49	4.57	4.77	121.3	122.7
p-Methoxytoluene	3-(*p*-Methoxyphenyl)-1,2-propanedicarboxylic acid[o]	72	38[p](17)	100–101[o]	60.49	60.64	5.92	6.02	119.1	120.0
p-Isopropyltoluene	3-Methyl-3-(*p*-tolyl)-1,2-butanedicarboxylic acid[q]	85	89(67)[g]	188–189[r]	67.18	67.45	7.25	7.21	125.2	126.0
p-Ethylisopropylbenzene	3-Methyl-3-(*p*-ethylethylphenyl)-1,2-butanedicarboxylic acid[q]	88	99(>51)[g]	182–184	68.16	68.72	7.63	7.62	132.2	131.0
p-Ethyltoluene	3-(*p*-Tolyl)-1,2-butanedicarboxylic acid[s]	85	65(25)[t]	161–162	66.09	66.28	6.87	6.54	118.1	118.0

[a] Reactions were usually effected at 150° with the arylalkane, maleic anhydride, and di-*tert*-butyl peroxide in a mole ratio of 10–15:1:0.007. The anhydrides obtained were usually isolated as dicarboxylic acids. [b] Based on initial product isolated from reaction and on maleic anhydride consumed after 5 hours. [c] The acids obtained from initial precipitation were acceptably pure except in cases where they may exist in 2 racemic modifications. [d] Corrected melting points. [e] Lit.[4a] m.p. 114–115°. [f] Oxidized to isophthalic acid (87%); m.p. 343–345°; lit., m.p. 345–347° [Baeyer, *Ann.*, **276**, 258 (1893)]. [g] Minimum yield of analytical samples (the products were usually crystallized twice from water or aqueous methanol). [h] A relatively large excess of *o*-xylene was used (see Experimental), and the adduct was first isolated as the anhydride by distillation at reduced pressure. [i] The yield of anhydride. [j] Lit.[9b] m.p. 170–172°. [k] Oxidized to *p*-chlorobenzoic acid (38%); m.p. 243–245°; no depression of an authentic sample. [l] Min. yield when the alkylbenzene (0.34 mole) and di-*tert*-butyl peroxide (0.007 mole) were added in 5 hours to the alkylbenzene (3.30 mole) and maleic anhydride (0.102 mole) at 140–145°; the subsequent reaction period was 12 hours at 140–145°. The percentage of maleic anhydride consumed was not determined. [m] Oxidized to *m*-chlorobenzoic acid (62%), m.p. 155.6–156.5°; no depression by an authentic sample. [n] Oxidized to *o*-chlorobenzoic acid (59%), m.p. 141.0–142.5°; no depression by an authentic sample. [o] Lit.[10] m.p. 101°. [p] Isolated initially as the potassium acid salt of 3-(*p*-methoxyphenyl)-1,2-propanedicarboxylic acid, m.p. 216–220°, after partially acidifying the alkaline reaction product. [q] Oxidized to 3-methyl-3-(*p*-carboxyphenyl)-1,2-butanedicarboxylic acid (36%), m.p. 227–228°; lit.[4a] m.p. 227–228.5°. [r] Lit.[4a] m.p. 192–193°. [s] Footnote 3. [t] Yield of one racemate after 4 recrystallizations of the crude product from benzene; the minimum percentage of one racemate in the crude product was 39%.

In the reaction of *o*-xylene, maleic anhydride, and di-*tert*-butyl peroxide, maleic anhydride was absorbed incompletely and considerably slower than in comparable experiments with the isomeric xylenes.[1] The expected adduct (after hydrolysis), 3-(*o* - tolyl)-1,2-propanedicarboxylic acid, was obtained in only 5–10% yields, and the length of the chain reaction (13–19) was much shorter than that for *m*- and *p*-xylenes. In this reaction system however, adducts were continually formed which separated from solution. The structures of the heterogeneous solid products could not be determined but, on the basis of their properties (see Experimental), it appears that one *o*-xylyl radical has been incorporated with more than one unit of maleic anhydride, possibly as in IV[7,8]. Some measure of practical control over the undesirable

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(7) The dimunition in rate of reaction and the added incorporation of maleic anhydride possibly arise from steric influences of the *o*-methyl group as expressed in the hydrogen transfer reaction of the *o*-xylylsuccinyl radical with *o*-xylene and (or) addition of the *o*-xylyl radical to maleic anhydride.

(8) (a) Similar products are obtained from tetralin, maleic anhydride, and di-*tert*-butyl peroxide at 150°.[1] (b) Hydrindane and tetralin react with maleic anhydride at 250–280° in the presence of iodine to give complex involatile products along with the 2 racemates each of α-hydrindylsuccinic anhydride and of α-tetralylsuccinic anhydride.[2e] (c) Dioxane, maleic esters, and benzoyl peroxide form adducts containing 3–6 units of succinic anhydride per unit of dioxane (Marvel, Prill, and DeTar, *J. Am. Chem. Soc.*, **69**, 52 (1947).

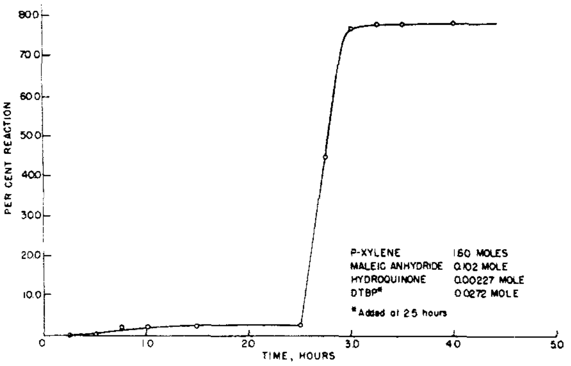
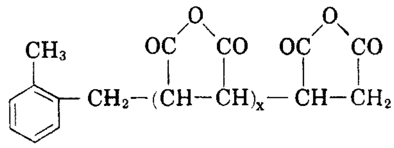


FIG. 1. THE EFFECTS OF HYDROQUINONE AND DI-*tert*-BUTYL PEROXIDE ON REACTION OF *p*-XYLENE AND MALEIC ANHYDRIDE AT 150°.

competitive reactions was obtained by using relatively high ratios of *o*-xylene to maleic anhydride and minor amounts of initiator. Reaction of *o*-xylene, maleic anhydride and di-*tert*-butyl peroxide (mole ratio of 8.3:0.05:0.007) at 150° thus gave 3-(*o*-tolyl)-1,2-propanedicarboxylic anhydride (V) in 43% yield; 1,2-di-*o*-tolylethane[9a] was also obtained as a minor product of this reaction system. The structure of V was assigned on the basis of its conversion to 3-(*o*-tolyl)-1,2-propanedicarboxylic acid[9b] and its corresponding anilic acid.[9b]



IV

A study was made of the addition reactions of maleic anhydride with *p*-methoxytoluene and with *o*-, *m*-, and *p*-chlorotoluenes, respectively. With di-*tert*-butyl peroxide at 140–150°, homolytic addition occurs satisfactorily, and the products isolated after hydrolysis are the nuclear-substituted benzylsuccinic acids[10] (Table I). In experiments with the chlorotoluenes and maleic anhydride, the reactions were effected at relatively high dilution, and the initiator was added slowly and continually[11] to the reactants (see Experimental). Under such conditions reaction of *o*-chlorotoluene and maleic anhydride at 140–145° gave, after hydrolysis, 3-(*o*-chlorophenyl)-1,2-propanedicarboxylic acid in at least 73 per cent yield. Efforts to alkylate maleic anhydride with *p*-tolunitrile were unsuccessful.[1]

A series of internal competitive experiments was conducted in which *p*-isopropyltoluene, *p*-ethylisopropylbenzene, and *p*-ethyltoluene were reacted with maleic anhydride and di-*tert*-butyl peroxide to determine the relative reactivities of primary, secondary and tertiary α-hydrogen atoms in the addition processes. The adducts isolated from reactions of *p*-isopropyltoluene and of *p*-isopropylethylbenzene were derived from attack on the tertiary hydrogen atoms of the isopropyl groups; the adducts, after hydrolysis to their substituted succinic acids (Table I), were 3-methyl-3-(*p*-tolyl)-1,2-butanedicarboxylic acid[12] (67% min. yield) and 3-methyl-3-(*p*-ethylphenyl)-1,2-butanedicarboxylic acid (VI, 51% min. yield). The structure of VI was established from its analysis, neutral equivalent, and oxidation to 3-methyl-3-(*p*-carboxyphenyl)-1,2-butanedicarboxylic acid[4a] by potassium permanganate.

Addition of *p*-ethyltoluene to maleic anhydride occurred (mainly) by attack on a secondary hydrogen atom of the arylalkane to give 3-(*p*-tolyl)-1,2-butanedicarboxylic acid[3,8b] (VII, Table I) upon hydrolysis of the reaction products. The structure assigned to VII was based on its comparison with an identical product prepared by an independent route. Synthesis of VII was initiated by condensing *p*-methylacetophenone and diethyl succinate in the presence of potassium *tert*-butoxide to give the half-esters of 3-(*p*-tolyl)-2-butene-1,2-dicarboxylic acid (VIII).[13] Conversion of VIII into its dibasic acids (IX, an isomeric mixture) was effected by alkaline hydrolysis and subsequent acidification. Hydrogenation of the Stobbe dicarboxylic acids (IX) over platinum oxide and subsequent crystallization[3,8b] of the products from benzene and from ethanol-water gave material identical with VII.[14]

EXPERIMENTAL

Reagents and general techniques. The arylalkanes (>99% purity), *p*-methoxytoluene (pure grade), *p*-tolunitrile, and the *o*-, *m*-, and *p*-chlorotoluenes (pure grade) were rectified

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[9] (a) Carre, *Bull. soc. chim.*, **5**, 489 (1909); (b) Chakravarti, *J. Indian Chem. Soc.*, **20**, 393 (1943).

[10] 3-(*p*-Methoxyphenyl)-1,2-propanedicarboxylic acid has been prepared previously by an independent route; Haworth, Jones, and Way, *J. Chem. Soc.*, 10 (1943).

[11] This technique allows formation of adducts under relatively smaller initiator concentrations than in the usual procedure.

[12] Prepared previously from reaction of *p*-isopropyltoluene, maleic anhydride, and benzoyl peroxide at 100° and subsequent hydrolysis.[4a]

[13] (a) Johnson and Jones, *J. Am. Chem. Soc.*, **69**, 792 (1947) report that Stobbe condensation of *p*-methylacetophenone and diethyl succinate yielded an isomeric mixture (VIII) of the half esters of the 3-(*p*-tolyl)-2-butene-1,2-dicarboxylic acids (and possibly of 3-(*p*-tolyl)-3-butene-1,2-dicarboxylic acid); the components and the composition of the product were not determined however. (b) The formation of a mixture of geometric and position isomers in this Stobbe condensation did not affect the proof of structure of VII since the olefinic centers were removed in a subsequent hydrogenation step.

[14] Reaction of arylalkanes and maleic anhydride to give substituted succinic acids may offer special advantage over the usual methods of synthesis involving Stobbe condensation of aryl carbonyl compounds and diethyl succinate and subsequent hydrogenation of the reaction product; Johnson and Daub, *Org. Reactions*, **6**, 1 (1951).

in efficient columns and stored under nitrogen. The *p*-chlorotoluene also was fractionally crystallized twice at 0°. The maleic anhydride (C.P.) was recrystallized from acetone (C.P.) and from chloroform (C.P.) and dried under a vacuum; m.p. 53.0–53.5°, lit.[15] m.p. 53.0°. The di-*tert*-butyl peroxide (tech.) was fractionally distilled.

Mixtures of the arylalkane, maleic anhydride, and di-*tert*-butyl peroxide (mole ratio of 10–15:1:0.007) were heated to 150° in a glass flask equipped with a stirrer, condenser, and drying tube. Special precautions were taken to protect the reaction mixture from atmospheric gases in experiments of kinetic significance. The consumption of maleic anhydride was determined from aliquot samples by titrating the unreacted maleic anhydride in the presence of the arylalkylsuccinic anhydride by iodimetric methods[16] (di-*tert*-butyl peroxide does not interfere). The reaction mixture was heated until the amount of maleic anhydride consumed became essentially constant. The addition product was usually isolated upon extracting the reaction mixture with aqueous potassium hydroxide and then acidifying the aqueous extract with hydrochloric acid. The crude succinic acids may crystallize slowly upon cooling the acidic aqueous extract; often 2–3 days were required before solidification of the acids was complete. The crude products that did not solidify were usually crystallized satisfactorily from benzene. If insufficient acid is added to the alkaline extract, potassium acid salts of the arylalkylsuccinic acids may be precipitated. No thorough studies were made to obtain maximum yields of addition products; the higher molecular weight products of addition were not identified. There were considerable losses of products in the recrystallization operations. A typical procedure is described for reaction of *p*-ethyltoluene and maleic anhydride. The reactions of maleic anhydride with *o*-chlorotoluene and *o*-xylene are described because they involve particular procedures.

Reaction of p-ethyltoluene and maleic anhydride. A stirred mixture of *p*-ethyltoluene (112 g., 0.94 mole), maleic anhydride (10.0 g., 0.102 mole), and di-*tert*-butyl peroxide (1.0 g., 0.007 mole) was heated at 150 ± 2° for 5 hours; reaction was 83% complete after this period. The mixture was extracted with aqueous potassium hydroxide (15 g. in 100 ml.). Acidification of the alkaline extract with hydrochloric acid resulted in separation of an oily product. The oil was dissolved in warm acetone and benzene was added. The solution was concentrated, filtered through anhydrous sodium sulfate, and allowed to stand at 5°. After several days the product separated in finely-divided white crystals (12.9 g., 65% yield based on maleic anhydride consumed), m.p. 115–125°; upon four recrystallizations from benzene and then from ethanol-water (30:70), 3-(*p*-tolyl)-1,2-butanedicarboxylic acid[3, 17] (VII, Table I, 5.0 g., 38.5% of the initial crude product) was obtained, m.p. 161–162°. Further recrystallization of the acid from ethanol-water (30:70), acetic acid-water (30:70), and benzene–petroleum ether did not alter its melting point.[3, 17]

Synthesis of 3-(p-tolyl)-1,2-butanedicarboxylic acid.[3, 17] Condensation of *p*-tolyl methyl ketone and diethyl succinate by potassium *tert*-butoxide gave the partly crystalline monoethyl esters of 3-(*p*-tolyl)-2-butene-1,2-dicarboxylic acid and its possible isomers (VIII, 57%).[13] Saponification of the half-esters with aqueous potassium hydroxide and subsequent acidification of the product yielded a mixture (semi-solid) of 3-(*p*-tolyl)-butene-1,2-dicarboxylic acids (IX).

Anal. Calc'd for $C_{13}H_{14}O_4$: C, 66.70; H, 6.00; Neut. equiv., 117.1. Found: C, 66.42; H, 6.03; Neut. equiv., 116.0.[18]

The crude acids (IX, 1.0 g.) were dissolved in acetic acid and hydrogenated at 2 atmospheres over platinum oxide[19] (0.1 g.). The mixture was filtered and then was distilled; the residual oil was dissolved in benzene (200 ml.), and the solution was concentrated to a volume of 50 ml. After 24 hours at 5°, 3-(*p*-tolyl)-1,2-butanedicarboxylic acid[3, 17] (VII, 0.5 g., 50%) separated as finely-divided white crystals, m.p. 153–157°; further recrystallization from ethanol-water raised the melting point to 159.5–162°. This material did not depress the melting point of 3-(*p*-tolyl)-1,2-butanedicarboxylic acid (VII), m.p. 161–162°, obtained from reaction of *p*-ethyltoluene and maleic anhydride.

Reaction of o-chlorotoluene and maleic anhydride. Di-*tert*-butyl peroxide (1.0 g., 0.007 mole) in *o*-chlorotoluene (43.3 g., 0.34 mole) was added in 5 hours to a stirred mixture of *o*-chlorotoluene (417 g., 3.30 mole) and maleic anhydride (10.0 g., 0.102 mole) at 140–145°. The mixture was stirred for 12 hours at 140–145° and then was distilled at atmospheric pressure until most of the *o*-chlorotoluene was removed. The residue was saponified with excess aqueous potassium hydroxide and then was washed with ethyl ether. The alkaline extract was acidified with conc'd hydrochloric acid and allowed to cool. A red oil settled which crystallized to give 3-(*o*-chlorophenyl)-1,2-propanedicarboxylic acid (18.0 g., 0.074 mole, 73% based on maleic anhydride added); m.p. 150–153°. The dicarboxylic acid was crystallized from water–methanol–Darco and then benzene–heptane to yield a white analytical procuct (Table I); m.p. 157.5–157.8°.

Reaction of o-xylene and maleic anhydride. A stirred mixture of *o*-xylene (881 g., 8.3 moles), maleic anhydride (5.0 g., 0.051 mole), and di-*tert*-butyl peroxide (1.0 g., 0.007 mole) was heated at 150 ± 2°; reaction of maleic anhydride was 60% complete in 5 hours. The mixture was concentrated by distillation (200 ml.) and cooled. A heterogeneous solid separated and was filtered (2.4 g.); this adduct was not identified (see subsequent Experimental). The filtrate was distilled at reduced pressure to yield, after removing the remaining xylene, a mixture (4.5 g.) boiling at 150–160° (1 mm.). The distillate was extracted with small portions of petroleum ether. The solvent was distilled from the petroleum ether extract; the resulting oil was crystallized from aqueous ethanol to give a white solid (0.77 g.) identified as 1,2-di-*o*-tolylethane, m.p. 66–67°; lit.[9a] m.p. 66–67°.

Anal. Calc'd for $C_{16}H_{18}$: C, 91.37; H, 8.62. Found: C, 91.42; H, 8.60.

The remainder of the high-boiling distillate was characterized as 3-(*o*-tolyl)-1,2-propanedicarboxylic anhydride (V, 3.4 g., 43% yield based on maleic anhydride consumed): Neut. equiv. (calc'd), 102.1; Neut. equiv. (found), 103. Conversion of V into its anilic acid was effected by reaction with aniline in hot benzene and subsequent recrystallization of the product from water, m.p. 160–161°; lit.[9b] m.p. 157–158°.

Saponification of V (0.6 g., 0.0029 mole) with aqueous potassium hydroxide (10%) and subsequent acidification of the reaction mixture with conc'd hydrochloric acid yielded a white solid after several days at 0–5°. The product was recrystallized twice from water to give 3-(*o*-tolyl)-1,2-propanedicarboxylic acid (0.2 g., 31% yield from V); m.p. 171–172°, lit.[9b] 170–172°.

The heterogeneous adduct is a white resinous brittle solid, m.p. 95–120°; upon being melted it is a viscous adhesive liquid. Distillation at reduced pressures (<0.5 mm.) resulted in its extensive decomposition. The adduct dissolves slowly in acetone and in boiling water; it is insoluble in *o*-xylene (the hot reaction mixture), benzene, ligroin, chloroform, carbon tetrachloride, ethyl ether, and water. It (*Anal.*[20] C, 60.76; H, 4.07) may be fractionally precipitated

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[15] Anschutz, *Ber.*, **12**, 2281 (1879).

[16] Kaufmann, Baltes, and Buter, *Ber.*, **70**, 903 (1937); Bickford, Krauczunas, and Wheeler, *Oil and Soap*, **19**, 23 (1942).

[17] Presumably the racemate of lesser solubility.

[18] The product analyzed was recrystallized from water, m.p. 153–155°.

[19] Adams, Voorhees, and Shriner, *Org. Syntheses*, Coll. Vol. I, 452 (1932).

[20] The composition of the crude adduct corresponds approximately to 3 units of maleic anhydride to one of *o*-xylene.

from warm acetone by adding benzene; analyses of fractions 1 and 7 are: C, 56.11; H, 4.36 and C, 57.06; H, 5.16. Oxidation of the product with aqueous potassium permanganate gave phthalic acid; hydrolysis yielded tars and amorphous materials. Formation of both V and the resinous adduct (IV) was accelerated by di-*tert*-butyl peroxide at 150° and by benzoyl peroxide at 100°; their production was retarded by hydroquinone. In typical experiments at 150° for 10 hours, reaction of 176.2 g. (1.66 mole) of *o*-xylene, 10.0 g. (0.102 mole) of maleic anhydride, and 1.0 g. (0.007 mole) of di-*tert*-butyl peroxide gave 9.4–9.6 g. of the insoluble product. The yield of the heterogeneous adduct was enhanced by increasing the concentration of the initiator or of maleic anhydride.

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