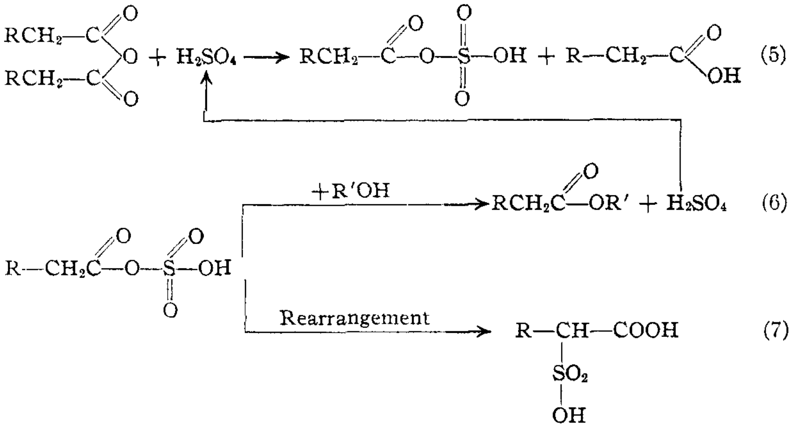

The mixed anhydride of sulfuric and the aliphatic acid may react with the material to be acylated, liberating a molecule of sulfuric acid which again may react with a molecule of aliphatic anhydride, and the acylation cycle may be repeated or the mixed anhydride may rearrange to a sulfoaliphatic acid, thus removing the sulfuric acid from further participation in the acylation.

The authors wish to express their appreciation to Dr. William J. Priest of these Laboratories for his assistance in the kinetic interpretation of these data.

Summary

The rate of formation of sulfoaliphatic acids by reaction of sulfuric acid with aliphatic anhydrides at 40° has been measured, using small amounts of sulfuric acid in various concentrations of acetic, propionic and *n*-butyric anhydrides in the corresponding acids.

The rate of disappearance of sulfate ion follows the first-order reaction equation and is related to the concentration of the aliphatic anhydride. The relation between the experimental results and the mechanism of the reaction is discussed.

A mechanism of acylation in the presence of sulfuric acid catalyst is suggested.

ROCHESTER, N. Y. RECEIVED FEBRUARY 19, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Diene Addition Products to Diaroylethylenes and their Transformation Products. II

BY ROGER ADAMS AND R. B. WEARN[1]

In a recently published article[2] it was shown that butadiene, 2,3-dimethylbutadiene and cyclopentadiene undergo an essentially quantitative addition to dibenzoylethylene with formation of dibenzoylcyclohexenes (I). Syntheses from these adducts were developed for the corresponding dibromo addition products (II), dihydroisobenzofurans (V), isobenzofurans (IV), *o*-dibenzoylbenzenes (VI), oxido-tetrahydronaphthalenes (VII) and substituted naphthalenes (VIII). A comparison of the procedures used with those previously known for the same compounds was discussed. The series of reactions is illustrated by formulas I–VIII.

In this paper, analogous reactions between the *trans* forms of di-*p*-chlorobenzoyl, di-*p*-toluyl and dimesitoyl ethylenes and butadiene, 2,3-dimethylbutadiene and cyclopentadiene are reported in order to demonstrate the extent of applicability of these methods in preparative work Butadiene and cyclopentadiene added quantitatively to all three of the diaroyl ethylenes with formation of 4,5-diaroyl cyclohexenes (I). 2,3-Dimethylbutadiene also added to all except the dimesitoylethylene. Apparently, in this case, steric influences prevent the addition from taking place.

The cyclopentadiene addition products could in no case be converted to furans, possibly on account of the strains involved. Similarly, the dimesitoylethylene and butadiene adduct did not form a furan, due probably to steric influences.

The reactions discussed below, except for the addition of bromine to the original adducts, the 4,5-diaroyl cyclohexenes (I), apply merely to the products formed from di-*p*-chlorobenzoylethylene and di-*p*-toluylethylene with butadiene and 2,3-dimethylbutadiene.

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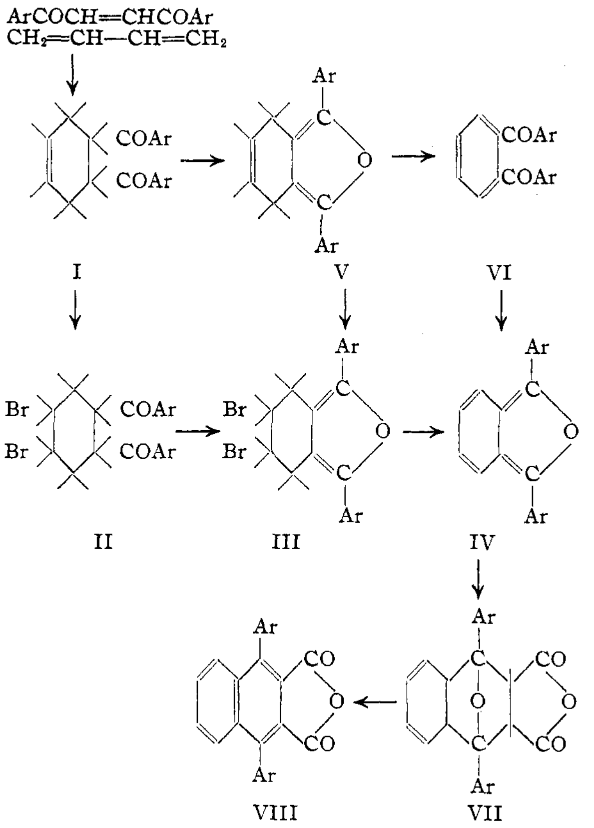
[1] An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Adams and Gold, THIS JOURNAL, **62**, 56 (1940). See also Adams and Geissman, *ibid.*, **61**, 2083 (1939).



The 4,5-diaroyl cyclohexenes (I) add bromine quantitatively in chloroform solution to give 1,2-dibromo-4,5-diaroyl cyclohexanes (II).

The 4,5-diaroyl cyclohexenes (I) are converted quantitatively by means of acetic anhydride and a little phosphoric acid to 1,3-diaryl-4,7-dihydroisobenzofurans (V).

The 1,2-dibromo-4,5-diaroyl cyclohexanes (II) are unaffected by treatment with acetic anhydride and phosphoric acid but by means of acetyl chloride containing a little sulfuric acid, a reagent shown by Lutz[3] to be more effective than the former, are converted to the corresponding 1,3-diaryl-5,6-dibromo-4,5,6,7-tetrahydroisobenzofurans (III). These latter products when derived from 2,3-dimethylbutadiene derivatives are stable but when derived from butadiene derivatives partially decompose and oxidize upon attempts to recrystallize with formation of *o*-diaroyl benzenes. It is worthy of note that the dibromo compounds formed by addition of bromine to the adducts from butadiene or 2,3-dimethylbutadiene and unsubstituted dibenzoylethylene are not closed to furans by acetyl chloride and sulfuric acid.

The 1,3-diaryl-5,6-dibromo-4,5,6,7-tetrahydroisobenzofurans (III) also could be prepared by direct addition of bromine to the 1,3-diaryl-4,7-dihydroisobenzofurans but the yields were poor.

o-Diaroyl benzenes (VI) are formed quantitatively from the 1,3-diaryl-4,7-dihydroisobenzofurans (V) by treatment of the latter with two moles of bromine followed immediately by sodium acetate in acetic acid and then with water.

Activated zinc and alkali convert the *o*-diaroyl benzenes (VI) to 1,3-diarylisobenzofurans (IV). The yields are usually excellent but depend upon the length of time of reduction, which varies from compound to compound. If the reduction is carried too far, the yield falls. The derivatives of butadiene in all cases reduce more rapidly than those from dimethylbutadiene.

The 1,3-diarylisobenzofurans (IV) when derived from 2,3-dimethylbutadiene also can be formed from the 1,3-diaryl-5,6-dibromo-4,5,6,7-tetrahydroisobenzofurans (III) merely by treatment with sodium acetate, acetic acid and acetic anhydride. The dibromotetrahydroisobenzofurans derived from butadiene, however, do not undergo this reaction

The addition of maleic anhydride to the 1,3-diarylisobenzofurans (IV) proceeds very smoothly to give 1,4-diaryl-1,4-oxido-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydrides (VII). The 1,3-diarylisobenzofurans containing 5,6-dimethyl groups give two isomeric oxido compounds. One is stable only in cold benzene and changes to a lower melting form when crystallized from hot benzene.

Dehydration of the 1,4-diaryl-1,4-oxido-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydrides (VII) with dry hydrogen chloride yields 1,4-diaryl-2,3-naphthalic anhydrides (VIII).

The dihydroisobenzofurans (V) and the isobenzofurans (IV) produce a blue-green fluorescence in solution.

The compounds prepared, with the methods of purification, melting points, yields and analyses are given in Tables I–IV.

Experimental

Addition of Diaroylethylenes to Dienes—General Procedure for Preparing Dibenzoyl Cyclohexenes (I).—To a solution of 40 g. (1 mole) of di-*p*-chlorobenzoylethylene in 1 liter of dry benzene was added 21.5 g. (2 moles) of crude 2,3-dimethylbutadiene (prepared by distilling pinacol from a small amount of hydrobromic acid). After refluxing overnight, the solvent was evaporated

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[3] Lutz, This Journal, **48**, 2916 (1926).

TABLE I

4,5-DIAROYL CYCLOHEXENES

a = di-*p*-chlorobenzoylethylene[a]
b = di-*p*-toluylethylene[a]
c = dimesitoylethylene[a]

1 = butadiene
2 = 2,3-dimethylbutadiene
3 = cyclopentadiene

Reactants	4,5-Diaroyl cyclohexene	Crystalline form, white	Solvent for crystn.	M. p. (cor.), °C.	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
a, 1	4,5-Di-*p*-chlorobenzoyl-	Plates	Ethanol–acetone	125	92	$C_{20}H_{16}O_2Cl_2$	66.86	4.49	67.14	4.64
b, 1	4,5-Di-*p*-toluyl-	Needles	Ethanol–acetone	127	89	$C_{22}H_{22}O_2$	82.98	6.97	83.16	7.43
c, 1	4,5-Dimesitoyl-	Plates	Benzene	204	80	$C_{26}H_{30}O_2$	83.38	8.07	83.01	8.27
a, 2	1,2-Dimethyl-4,5-di-*p*-chlorobenzoyl-	Plates	Acetone	151	92	$C_{22}H_{20}O_2Cl_2$	68.22	5.21	68.60	5.34
b, 2	1,2-Dimethyl-4,5-di-*p*-toluyl-[b]	Prisms	Ethanol	129	90	$C_{24}H_{26}O_2$	83.20	7.57	82.18[b]	7.59
a, 3	3,6-Endomethylene-4,5-di-*p*-chlorobenzoyl-	Needles	Ligroin	139	92	$C_{21}H_{16}O_2Cl_2$	67.94	4.35	68.45	4.42
b, 3	3,6-Endomethylene-4,5-di-*p*-toluyl-	Plates	Ligroin	106	67	$C_{23}H_{22}O_2$	83.60	6.70	83.47	6.95
c, 3	3,6-Endomethylene-4,5-dimesitoyl-	Needles	Ligroin	117	80	$C_{27}H_{30}O_2$	83.90	7.80	84.23	7.93

[a] These compounds have been prepared previously by Conant and Lutz, THIS JOURNAL, **45**, 1305 (1923). [b] Several additional analyses produced no better check on this compound, but the conversion to the corresponding dibromide and furan derivatives, which analyzed properly, is sufficient proof for its identity.

TABLE II

1,2-DIBROMO-4,5-DIAROYL CYCLOHEXANES, 1,3-DIARYL-4,7-DIHYDROISOBENZOFURANS, AND 1,3-DIARYL-5,6-DIBROMO-4,5,6,7-TETRAHYDROISOBENZOFURANS

a = 4,5-di-*p*-chlorobenzoylcyclohexene; b = 4,5-di-*p*-toluylcyclohexene; c = 4,5-dimesitoylcyclohexene; d = 1,2-dimethyl-4,5-di-*p*-chlorobenzoylcyclohexene; e = 1,2-dimethyl-4,5-ditoluylcyclohexene.

Reactant	1,2-Dibromo-4,5-diaroyl cyclohexane	Crystalline form, white	Solvent for crystn.	M. p. (cor.), °C.	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
a	4,5-Di-*p*-chlorobenzoyl-	Plates	Bz–lig.	181	92	$C_{22}H_{16}O_2Cl_2Br_2$	46.27	3.11	46.19	3.44
b	4,5-Di-*p*-toluyl-	Plates	Bz–lig.	177	90	$C_{22}H_{22}O_2Br_2$	55.25	4.64	55.17	4.68
c	4,5-Dimesitoyl-	Needles	Bz–lig.	202	95	$C_{26}H_{30}O_2Br_2$	58.47	5.66	58.55	5.88
d	-1,2-Dimethyl-4,5-di-*p*-chlorobenzoyl-	Hexagons	Ethanol	173	92	$C_{22}H_{20}O_2Cl_2Br_2$	48.29	3.69	48.72	3.82
e	-1,2-Dimethyl-4,5-di-*p*-toluyl-	Needles	Ligroin	184	90	$C_{22}H_{22}O_2Br_2$	56.93	5.18	56.67	5.20
	1,3-Diaryl-4,7-dihydroisobenzofuran	Needles								
a	1,3-Di-*p*-chlorophenyl-	Yellow	Bz–lig.	215	97	$C_{20}H_{14}OCl_2$	70.39	4.13	70.32	4.27
b	1,3-Di-*p*-tolyl-	Yellow	Bz–lig.	210	99	$C_{22}H_{20}O$	87.96	6.71	88.40	6.81
d	1,3-Di-*p*-chlorophenyl-5,6-dimethyl-	Green-yellow	Benzene	236	97	$C_{22}H_{18}OCl_2$	71.55	4.91	71.68	5.30
e	1,3-Di-*p*-tolyl-5,6-dimethyl-	Green-yellow	Benzene	237	95	$C_{24}H_{24}O$	87.76	7.37	87.48	7.23
	1,3-Diaryl-5,6-dibromo-4,5,6,7-tetrahydroisobenzofuran	Needles								
d	1,3-Di-*p*-chlorophenyl-	Pale green	Benzene	179	88	$C_{22}H_{18}OCl_2Br_2$	49.95	3.43	50.15	3.52
e	1,3-Di-*p*-tolyl-	Pale green	Benzene	166	81	$C_{24}H_{24}OBr_2$	59.01	4.95	59.19	5.05

TABLE III

1,2-DIAROYLBENZENES AND THE CORRESPONDING 1,3-DIARYLISOBENZOFURANS

a = 1,3-di-*p*-chlorophenyl-4,7-dihydroisobenzofuran
b = 1,3-di-*p*-tolyl-4,7-dihydroisobenzofuran
c = 1,3-di-*p*-chlorophenyl-5,6-dimethyl-4,7-dihydroisobenzofuran
d = 1,3-di-*p*-tolyl-5,6-dimethyl-4,7-dihydroisobenzofuran

Reactant	1,2-Diaroylbenzene	Crystalline form, white	Solvent for crystn.	M. p. (cor.), °C.	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
a	1,2-Di-*p*-chlorobenzoyl-[a]	Needles	EtOH–acetone	167–168	96	$C_{20}H_{12}O_2Cl_2$	...	..	...	..
b	1,2-Di-*p*-toluyl-[b]	Needles	EtOH–acetone	191	95	$C_{22}H_{18}O_2$	...	..	...	..
c	1,2-Di-*p*-chlorobenzoyl-4,5-dimethyl-	Plates	Ligroin	168–169	97	$C_{22}H_{16}O_2Cl_2$	68.94	4.21	69.07	4.35
d	1,2-Di-*p*-toluyl-4,5-dimethyl-	Plates	Ethanol	164	96	$C_{24}H_{22}O_2$	84.18	6.48	83.90	6.48
	1,3-Diarylisobenzofuran	Yellow								
a	1,3-Di-*p*-chlorophenyl-[c]	Leaflets	Ligroin	199–200	60	$C_{20}H_{12}OCl_2$	...	..	...	..
b	1,3-Di-*p*-tolyl-[d]	Leaflets	Ligroin	125	62	$C_{22}H_{18}O$	...	..	...	..
c	1,3-Di-*p*-chlorophenyl-5,6-dimethyl-	Needles	Benzene	213	70	$C_{22}H_{16}OCl_2$	71.82	4.40	72.01	4.50
d	1,3-Di-*p*-tolyl-5,6-dimethyl-	Plates	Benzene	186	75	$C_{24}H_{22}O$	88.31	6.78	88.20	7.16

[a] Reported by Blicke and Patelski, m. p. 167–168°, THIS JOURNAL, **58**, 273 (1936). [b] Reported by Bauer, m. p. 190–191°, *Arch. Pharm.*, **247**, 220 (1909). [c] Reported by Blicke and Patelski, m. p. 199–200°, note (*a*). [d] Reported by Guyot and Valette, m. p. 125°, *Ann. chim. Phys.*, **23**, 363 (1911).

TABLE IV

1 4-DIARYL-1,4-OXIDO-1,2,3,4-TETRAHYDRONAPHTHALENE-2,3-DICARBOXYLIC ANHYDRIDES AND THE CORRESPONDING 1,4-DIARYL-2,3-NAPHTHALIC ANHYDRIDES

a = 1,3-di-*p*-chlorophenylisobenzofuran
b = 1,3-di-*p*-tolylisobenzofuran
c = 1,3-di-*p*-chlorophenyl-5,6-dimethylisobenzofuran
d = 1,3-di-*p*-tolyl-5,6-dimethylisobenzofuran

Reactant	1,4-Diaryl-1,4-oxido-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride	Crystalline form, white	Solvent for crystn.	M. p. (cor.), °C.	Yield, %	Formula	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
a	1,4-Di-*p*-chlorophenyl-	Needles	Bz–lig.	264–266	94	$C_{24}H_{14}O_4Cl_2$	66.02	3.23	66.28	3.58
b	1,4-Di-*p*-tolyl-	Needles	Bz–lig.	256–258	92	$C_{26}H_{20}O_4$	78.77	5.09	78.95	5.27
c	1,4-Di-*p*-chlorophenyl-6,7-dimethyl-	Needles	Cold Bz	292–293		$C_{26}H_{18}O_4Cl_2$	67.02	3.89	67.34	4.13
			Hot Bz	270–272	95	$C_{26}H_{18}O_4Cl_2$	67.02	3.89	66.84	4.03
d	1,4-Di-*p*-tolyl-6,7-dimethyl-	Needles	Cold Bz	285–286	93	$C_{28}H_{24}O_2$	79.23	5.70	79.34	5.94
			Hot Bz	267–268						
	1,4-Diaryl-2,3-naphthalic anhydride									
a	1,4-Di-*p*-chlorophenyl-	Leaflets	Benzene	304–305[a]	61	$C_{24}H_{12}O_3Cl_2$	68.75	2.89	68.22	3.04
b	1,4-Di-*p*-tolyl-	Leaflets	Benzene	293–295[a]	55	$C_{26}H_{18}O_3$	82.52	4.80	82.18	4.99
c	1,4-Di-*p*-chlorophenyl-6,7-dimethyl-	Leaflets	Acetic acid	321–323[a]	57	$C_{26}H_{16}O_3Cl_2$	69.71	3.60	70.11	3.82
d	1,4-Di-*p*-tolyl-6,7-dimethyl-	Leaflets	Acetic acid	338–340[a]	68	$C_{28}H_{22}O_3$	82.74	5.46	82.56	5.52

[a] Bloc Maquenne.

until the resulting volume was 70 cc. On cooling the 1,2-dimethyl-4,5-di-*p*-chlorobenzoylcyclohexene crystallized.

By this procedure, di-*p*-chlorobenzoyl and di-*p*-toluyl ethylenes were added to butadiene, 2,3-dimethylbutadiene, and cyclopentadiene. Dimesitoylethylene was added to butadiene and cyclopentadiene but did not react (even under pressure in a sealed tube) with 2,3-dimethylbutadiene (see Table I).

Bromination of Dibenzoyl Cyclohexenes.—One mole of bromine was added to a saturated chloroform solution of 4,5-di-*p*-chlorobenzoylcyclohexene at 0°. The crude 1,2-dibromo-4,5-di-*p*-chlorobenzoylcyclohexane separated from a benzene–ligroin mixture.

By this procedure, the dibromo derivatives (II) of all the diaroyl cyclohexenes derived from butadiene and 2,3-dimethylbutadiene were prepared (see Table II).

Conversion of *o*-Diaroyl Cyclohexenes to the Corresponding Dihydroisobenzofurans (V).—To a suspension of 25 g. of 1,2-dimethyl-4,5-di-*p*-chlorobenzoylcyclohexene in 200 cc. of hot acetic anhydride was added 0.5 g. of sirupy phosphoric acid. The insoluble furan began to crystallize immediately, but the mixture was refluxed for five minutes. On cooling, the 1,3-di-*p*-chlorophenyl-5,6-dimethyl-4,7-dihydroisobenzofuran crystallized quantitatively.

By this method 1,3-di-*p*-tolyl-, 1,3-di-*p*-chlorophenyl-, and 1,3-di-*p*-tolyl-5,6-dimethyl dihydroisobenzofurans were also prepared. Under the same conditions, 1,3-dimesitoylcyclohexene and the 3,6-endomethylene-4,5-diaroyl cyclohexenes would not close to form furans (see Table II).

Preparation of 1,3-Diaryl-5,6-dibromo-4,5,6,7-tetrahydroisobenzofurans (III).—(a) A saturated solution of 9.2 g. of 1,2-dimethyl-1,2-dibromo-4,5-di-*p*-chlorobenzoylcyclohexane in acetyl chloride was heated to boiling. Several drops of concentrated sulfuric acid was added, and the solution was boiled for several minutes. It became dark colored, due to charring by the acid. The sides of the flask were scratched vigorously with a glass rod, and greenish needles of the 1,3-di-*p*-chlorophenyl-5,6-dibromo-5,6-dimethyl-4,5,6,7-tetrahydroisobenzofuran separated.

By this method, the corresponding di-*p*-tolyl compound also was prepared. The 1,2-dibromo-4,5-diaroylcyclohexanes (II) (without the 1,2-methyl groups) were closed to the furans under the same conditions, but pure products could not be isolated on account of their ready oxidation in solution to the *o*-dibenzoyl benzenes (VI) (see Table II).

(b) To a saturated solution of 1 g. (1 mol) of 1,3-di-*p*-chlorophenyl-4,7-dihydroisobenzofuran in chloroform at 0° was added slowly a solution of 0.49 g. (1 mol) of bromine in 2 cc. of chloroform. The product was isolated by concentrating the solvent to small volume.

By this procedure the corresponding di-*p*-tolyl compound was prepared. Due to unsatisfactory yields in both cases, this method was discarded in favor of the above (a).

Conversion of Diaryl-dihydroisobenzofurans to Corresponding *o*-Dibenzoyl Benzenes (VI).—To a suspension of 10 g. (1 mol) of 1,3-di-*p*-chlorophenyl-5,6-dimethyl-4,7-dihydroisobenzofuran in a hot solution of 20 g. of sodium acetate (anhydrous) in 400 cc. of glacial acetic acid was slowly added 8.7 g. (2 mols) of bromine. The mixture was kept boiling throughout this addition (ten minutes) and then refluxed for twenty minutes longer. Water was added until a considerable precipitate was formed in the boiling solution, and the mixture was allowed to cool. The crude 1,2-dimethyl-4,5-di-*p*-chlorobenzoylbenzene was filtered and recrystallized.

By the same method 1,2-dimethyl-4,5-di-*p*-toluyl, *o*-di-*p*-chlorobenzoyl-, and *o*-di-*p*-toluyl benzenes were prepared (see Table III).

Conversion of *o*-Diaroyl Benzenes to the Corresponding Isobenzofurans (IV).—A suspension of 5 g. (1 mol) of 1,2-dimethyl-4,5-di-*p*-chlorobenzoylbenzene in 200 cc. of absolute ethanol was heated to boiling. A solution of 5 g. of sodium hydroxide in 5 cc. of water was added to the mixture. Refluxing was continued until the solution became dark reddish-brown (from one-half to one and one-half hours). At this point, 5 g. of active zinc dust (prepared by washing with dilute hydrochloric acid followed by water) was added and refluxing continued for twenty minutes. At the end of this time, the color changed from dark red to bright fluorescent yellow. The hot solution was then filtered, 50 cc. of acetic acid was added, and the mixture was heated to boiling. Hot water was added until crystals began to form. Boiling was continued for several minutes, and then the solution was cooled. The product was 1,3-di-*p*-chlorophenyl-5,6-dimethylisobenzofuran.

By the same method the 1,3-di-*p*-tolyl-5,6-dimethyl-, 1,3-di-*p*-tolyl-, and 1,3-di-*p*-chlorophenyl-substituted isobenzofurans were prepared. The change of color at the end of the reduction did not always take place, so the length of time for reduction, which apparently varied with the activity of the zinc, had to be estimated in each case.

Addition of Maleic Anhydride to Isobenzofurans (VII).—To a solution of 6 g. (1 mol) of 1,3-di-*p*-chlorophenyl-5,6-dimethylisobenzofuran in 200 cc. of benzene was added 1.8 g. (1.1 mols) of maleic anhydride. The reaction was complete in about five minutes in cold solution, as indicated by the sudden disappearance of fluorescence. The solvent was evaporated at room temperature under reduced pressure, and crystals of 1,4-di-*p*-chlorophenyl-1,4-oxido - 6,7 - dimethyl - 1,2,3,4 - tetrahydronaphthalene-2,3-dicarboxylic anhydride separated.

When this compound was crystallized from hot benzene solution, a lower melting isomer was obtained. This isomer was also obtained when the original addition was carried out in hot solution.

By this method the maleic anhydride adducts of 1,3-di-*p*-tolyl-5,6-dimethyl-, 1,3-di-*p*-chlorophenyl-, and 1,3-di-*p*-tolyl-substituted isobenzofurans were also prepared. These products were crystallized from hot solutions and no attempt was made to isolate the higher melting isomers except in the case of 1,3-di-*p*-tolyl-5,6-dimethylisobenzofuran (see Table IV).

Dehydration of Oxido Tetrahydro Naphthalic Anhydrides (VII) to Form the Corresponding Naphthalic Anhydrides (VIII).—A suspension of 2 g. of 1,4-di-*p*-chlorophenyl - 1,4 - oxido - 6,7 - dimethyl - 1,2,3,4 - tetrahydronaphthalene-2,3-dicarboxylic anhydride in 200 cc. of absolute methanol was saturated with dry hydrogen chloride gas. The gas was bubbled through the solution slowly to keep it saturated while it was refluxed for two hours. The mixture was then evaporated to dryness. After addition of 50 cc. of 30% aqueous potassium hydroxide and 200 cc. of ethanol, the mixture was refluxed for six hours. The solution was then cooled and acidified. The precipitate was filtered off and purified by dissolving in potassium hydroxide, followed by reprecipitation by acid. The crude 1,4-di-*p*-chlorophenyl-6,7-dimethyl-2,3-naphthalic anhydride was crystallized from hot acetic acid.

By the same method the 1,4-di-*p*-tolyl-6,7-dimethyl-, 1,4-di-*p*-chlorophenyl-, and 1,4-di-*p*-tolyl-substituted 2,3-naphthalic anhydrides were also prepared (see Table IV). Benzene was a more suitable solvent for crystallization of the last two compounds.

Summary

The new methods reported in a previous paper[2] for the preparation of dihydroisobenzofurans, isobenzofurans, *o*-dibenzoyl benzenes, and aryl- and alkyl-substituted naphthalenes from the butadiene and dimethylbutadiene adducts of dibenzoylethylene were shown to work equally well for the di-*p*-chlorobenzoyl and di-*p*-toluyl ethylenes.

Cyclopentadiene added in good yield to di-*p*-chlorobenzoyl, di-*p*-toluyl, and dimesitoyl ethylenes.

Dimesitoylethylene formed an adduct with butadiene, but did not react with 2,3-dimethylbutadiene.

The dimesitoylethylene adduct to butadiene and all of the adducts from cyclopentadiene could not be converted to furans by the usual procedures.

URBANA, ILLINOIS

RECEIVED MARCH 11, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WASHINGTON AND LEE UNIVERSITY AND HYNSON, WESTCOTT AND DUNNING, INC.]

The Halogenation of Salicylic Acid

BY LARKIN HUNDLEY FARINHOLT, A. P. STUART* AND DANIEL TWISS

The preparation of polyhalogenated salicylic acids was attempted for several reasons. In the first place, the compounds might have valuable physiological properties and, in the second place, the order in which the halogen atoms enter the available positions is interesting from a theoretical point of view.

The mono- and disubstituted halogen derivatives of salicylic acid have been prepared by previous investigators by the addition of the free halogens to a solution of salicylic acid in a suitable medium. Nothing is known, however, concerning the tri- and tetrahalogenated salicylic acids which form the subject of this investigation.

Starting with 3,5-diiodosalicylic acid prepared according to Woollett and Johnson,[1] numerous methods were applied with the object of obtaining higher iodinated derivatives, but with negative results in each case. The following methods were attempted: (I) refluxing diiodosalicylic acid

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[1] "Organic Syntheses," Vol. XIV, 1934, p. 52.