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The Reaction of Benzene, Chlorine and Maleic Anhydride. An Interception Reaction

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A reaction of free radical type between benzene, chlorine and maleic anhydride to yield α-phenyl-α'-chlorosuccinic anhydride has been observed. Dehydrohalogenation of the product provides a convenient synthesis of phenylmaleic anhydride.

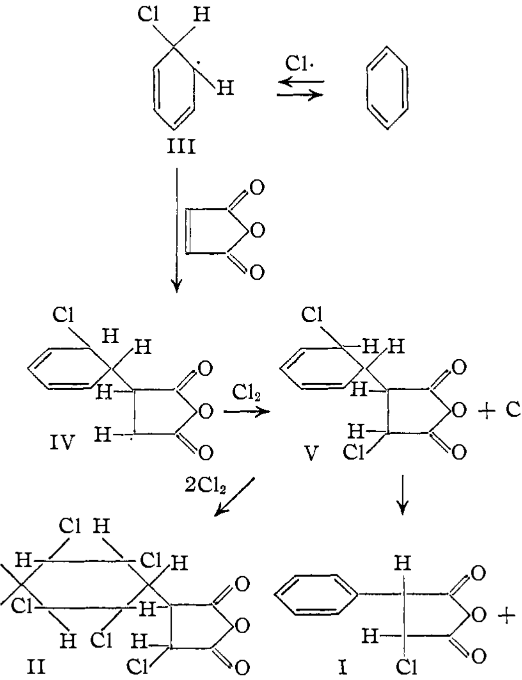
The photochlorinations of benzene to yield benzene hexachloride and of maleic anhydride to yield the α,α'-dichlorosuccinic anhydride are well known reactions which have frequently been carried out in these laboratories without any particular complications. It was therefore considered somewhat surprising when it was observed that the photochlorination of a solution of maleic anhydride in benzene resulted in the evolution of a large quantity of hydrogen chloride. Examination of the product revealed the presence of α-phenyl-α'-chlorosuccinic anhydride (I) and a material believed to be α-(2,3,4,5,6-pentachlorocyclohexyl)-α'-chlorosuccinic anhydride (II). Only trace amounts of the simple chlorine addition products of benzene and of maleic anhydride were present.

The reaction proceeds by a free radical chain mechanism as evidenced by its dependence upon peroxide or light for initiation and by its inhibition by molecular oxygen. Since both benzene and maleic anhydride normally undergo simple chlorine addition by similar photochemical chain reactions, it would appear that the above products result from the interception of one of the normal chlorination free radicals by the third reactant. The term "interception reaction" would be useful to identify this type of process as opposed to simple chlorination.

It is probable that the first step in the reaction is the photo- or peroxide-induced dissociation of a chlorine molecule. The resulting chlorine atoms may then attack the unsaturation either in the benzene ring or in the maleic anhydride. Assuming that the benzene is attacked, the resulting chlorocyclohexadiene radical (III) is then intercepted by the maleic anhydride to produce radical IV. The addition of resonance-stabilized radicals to maleic anhydride has been observed[1] previously and provides some basis for preference of this mechanism over one in which the initial attack of the chlorine atom would be on the maleic anhydride. The final step in the free radical chain consists of reaction of radical IV with molecular chlorine to yield compound V and regeneration of a chlorine atom.

Compound V may either undergo dehydrochlorination to produce α-phenyl-α'-chlorosuccinic anhydride (I) or may react with two moles of chlorine to yield compound II. Since many dienes do not require light for chlorination, it might be expected that the latter reaction would be favored by high concentrations of molecular chlorine. This has been observed in that the rapid addition of chlorine and the use of low intensity light have led to increased yields of II. Furthermore, reaction at 75° gave a weight ratio of I to II, some 50% higher than when operating at 32°. This indicated that the dehydrochlorination of V to I is more temperature dependent than the chlorination of V to II.

Some work has been done on the extension of the interception reaction to other reactants. The reaction of maleic anhydride and chlorine with aromatics other than benzene appears to be quite general. However, some compounds (nitrobenzene, benzonitrile) fail to react and others (phenol, anisole) undergo ionic chlorination so readily that only simple chlorination products result. Intermediate types of aromatics (chlorobenzene, benzotrichloride, methyl benzoate, toluene) were used with varying degrees of success. The reaction with toluene (carried out at 40–50°) was entirely analogous to the other reactions in that tolyl rather than benzylchlorosuccinic anhydride was obtained. Since positional isomerism in the aromatic ring made the isolation of pure compounds difficult, evidence of the interception reaction was based solely upon oxidation to the substituted benzoic acids.



The use of simple olefins in place of maleic anhydride usually results in simple ionic chlorination of the olefin. Some of the less reactive olefins do give interception types of reaction, and use of this fact was made in the synthesis of phenyl-

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(1) J. B. Conant and B. F. Chow, THIS JOURNAL, 55, 3475 (1933); W. G. Bickford, G. S. Fisher, F. G. Dollear and C. E. Swift, *J. Oil Chemists Soc.*, 25, 251 (1948).

chloromaleic anhydride by the reaction of benzene, chlorine and chloromaleic anhydride.

The study of other halogenation reagents in the reaction revealed that sulfuryl chloride gave yields of interception products comparable to those obtained with chlorine, whereas no reaction occurred when bromine was used.

While the reaction of benzene, chlorine and maleic anhydride would appear to be quite similar to the reaction of nitriles, halogens and olefins described in the literature,[2] there would appear to be a fundamental difference in that the latter does not require photo or peroxide initiation and has been assumed to proceed by a carbonium ion rather than a free radical mechanism.

The fundamental structure of α-phenyl-α'-chlorosuccinic anhydride (I) was determined by dehydrohalogenation to yield phenylmaleic anhydride. The fact that the phenyl group and the chlorine atom are not attached to the same carbon atom was established by bromination of the dimethyl ester of I followed by dehydrohalogenation and saponification to yield phenylchloromaleic anhydride. Had the phenyl group and the chlorine atom been attached to the same carbon atom, only phenylbromomaleic anhydride could have resulted. The only problem not solved in regard to the structure of I was whether the chlorine and the phenyl group have a *cis* or a *trans* relationship.

The structure of II is open to some question. The tendency of materials present in the reaction mixture to dehydrohalogenate and the large number of *cis–trans* isomers possible have thus far prevented isolation of a pure crystalline compound. There is no doubt that the distillation technique employed resulted in dehydrohalogenation and that the product isolated was probably 2,3,4,5,6, pentachlorocyclohexylmaleic anhydride rather than II. The presence of a pentachlorocyclohexyl ring is based upon the fact that dehydrohalogenation followed by oxidation yields dichlorobenzoic acids.

The interception reaction of benzene, chlorine and maleic anhydride followed by dehydrochlorination of I provides a convenient route for the synthesis of phenylmaleic anhydride. While the overall conversions are somewhat low (30–35%), even when pure I is not isolated, the availability of the starting materials and the simplicity of the process make the route attractive.

Acknowledgment.—The authors are indebted to Dr. William E. Burt and Mr. John P. Napolitano who first carried out the anomalous reaction of benzene, chlorine and maleic anhydride.

Experimental

Reaction of Benzene, Chlorine and Maleic Anhydride.—A 500-ml. Pyrex flask was equipped with inlet gas bubbler, stirrer, thermometer and a reflux condenser which in turn exhausted to a water scrubber for evolved hydrogen chloride. The flask was then charged with a solution of 88 g. (0.9 mole) of maleic anhydride in 281 g. (3.6 moles) of benzene. The mixture was heated to and maintained at 70°, illuminated by two General Electric (CG 401 CX) sunlamps, and 64 g. (0.9 mole) of chlorine passed in through the sintered glass bubbler over a 2.2-hour period. Upon completion of the chlorine addition, nitrogen was bubbled through the solution to remove dissolved hydrogen chloride. Titration of a sample of the water from the hydrogen chloride scrubber indicated the presence of 0.55 mole of acid. Excess benzene was removed from the reaction product by distillation at atmospheric pressure, the distillation being stopped when the pot temperature reached 120°. Application of aspirator vacuum removed last traces of volatiles to yield 190 g. of a viscous liquid which in subsequent experiments is designated as "crude chlorination product."

Effect of Light and Oxygen on Reaction.—This experiment was carried out using the same equipment and quantities of reagents as above. While adding chlorine with the reaction exposed to the sunlamps, the solution was observed to be virtually colorless. When the lamps were turned off, the reaction rapidly became yellow from unreacted chlorine. The solution rapidly decolorized upon resuming illumination.

The free radical chain mechanism was also indicated by the fact that when a slow flow of oxygen was introduced into the chlorine feed, rapid coloration resulted. The solution became colorless again upon discontinuing the oxygen flow.

α-Phenyl-α'-chlorosuccinic Anhydride (I).—The crude chlorination product obtained from the reaction of benzene, chlorine and maleic anhydride was added to 135 ml. of ether and upon cooling to 0°, 66 g. of a white solid melting at 90–98° was obtained. Successive recrystallizations from benzene and from ether ultimately gave 34 g. (18%) of I melting at 103–104.5°.

Anal. Calcd. for $C_{10}H_7O_3Cl$: Cl, 16.8. Found: Cl, 17.3.

Dehydrohalogenation of (I) to Phenylmaleic Anhydride.—A 5.8-g. (0.0276 mole) portion of I was mixed with 0.05 g. of Norit A and the mixture heated in an oil-bath at 130° for ten minutes during which time hydrogen chloride evolution was apparent. The mixture was then treated with hot benzene. Cooling and filtration yielded 3.31 g. (85% conversion) of phenylmaleic anhydride melting at 119.5–120.5°. Identification was effected by mixed melting point and by comparison of the infrared spectrum with that of an authentic sample of phenylmaleic anhydride.

α-Phenyl-α'-chlorosuccinic Acid.—A sample of I was placed on a watch glass and exposed to moist air in the room for 16 days. The melting point of the product was 174–175° (with gas evolution).

Anal. Calcd. for $C_{10}H_9O_4Cl$: Cl, 15.6; neut. equiv., 114.2. Found: Cl, 15.6; neut. equiv., 117.

Monomethyl Ester of α-Phenyl-α'-chlorosuccinic Acid.—A solution of 0.75 g. of I in 20 ml. of methanol was allowed to react for one hour at room temperature. Evaporation of the methanol under reduced pressure yielded a white solid which upon recrystallization from benzene gave 0.68 g. (79%) of white crystals melting at 148–151°.

Anal. Calcd. for $C_{11}H_{11}O_4Cl$: Cl, 14.63. Found: Cl, 14.9.

Dimethyl Ester of α-Phenyl-α'-chlorosuccinic Acid.—A solution of 10.5 g. (0.05 mole) of I in 50 ml. of methanol was allowed to stand at room temperature for 45 minutes. The excess methanol was distilled under vacuum and the residue refluxed for 15 minutes with 75 ml. of thionyl chloride. After evaporating the thionyl chloride at aspirator pressure, 50 ml. of methanol was added to the residue and the solution let stand at room temperature for 30 minutes. Volatiles were removed from the mixture by warming slightly at aspirator pressure and the diester obtained by a single recrystallization of the residue. The 7.0 g. (55%) of white crystals were found to melt at 69–71°.

Anal. Calcd. for $C_{12}H_{13}O_4Cl$: Cl, 13.82. Found: Cl, 14.2.

Conversion of Dimethyl α-Phenyl-α'-chlorosuccinate to Phenylchloromaleic Anhydride.—A solution of 5.0 g. (0.02 mole) of dimethyl α-phenyl-α'-chlorosuccinate and 3.19 g. (0.02 mole) of bromine in 150 ml. of carbon tetrachloride was illuminated at reflux with a General Electric sunlamp (CG 401 CX) for 50 hours. During the reaction hydrogen bromide was evolved slowly. The red oil obtained upon distillation of the solvent was refluxed for 1.5 hours with 50 ml. of 1.2 *N* ethanolic potassium hydroxide. After diluting with water, the alcohol was removed by distillation. The aqueous solution was then acidified, extracted with ether, the ether evaporated and the residue sublimed to yield two

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[2] T. L. Cairns, P. J. Graham, P. L. Barrick and R. S. Schreiber, *J. Org. Chem.*, **17**, 751 (1951).

grams of sublimate which, upon recrystallization from isooctane and from ether, gave phenylchloromaleic anhydride as white crystals, m.p. 81–81.5°.[3]

Anal. Calcd. for $C_{10}H_5O_3Cl$: neut. equiv., 104.3. Found: neut. equiv., 108.

This material was identical with that produced in the following experiment as evidenced by mixed melting point and by a comparison of infrared spectra.

Interception Reaction of Benzene, Chlorine and Chloromaleic Anhydride.—The reaction was carried out in the same apparatus as for the analogous reaction with maleic anhydride except that three sunlamps were used for illumination. A 56-g. (0.8 mole) portion of chlorine was added to a solution of 106 g. (0.8 mole) of chloromaleic anhydride in 250 g. (3.2 moles) of benzene over a four-hour period while the reaction mixture was maintained at 75°. Distillation of the product yielded a 47-g. fraction boiling at 90 to 195° (4 mm.). By means of caustic extraction and subsequent acidification the fraction was split into a neutral and an acidic fraction. The caustic-insoluble portion (23 g.) appeared to be largely benzene hexachloride.

Anal. Calcd. for $C_6H_6Cl_6$: Cl, 73.2. Found: Cl, 71.1.

The caustic-soluble portion (17 g.) was sublimed and recrystallized from isoöctane and from ether to yield phenylchloromaleic anhydride,[3] m.p. 83–83.5°, identical with that produced in the preceding experiment.

Anal. Calcd. for $C_{10}H_5O_3Cl$: Cl, 17.0; neut. equiv., 104.3. Found: Cl, 17.7; neut. equiv., 103.5.

Study of Reaction By-products.—An 80-g. sample of crude reaction product (*i.e.*, after stripping benzene from the reaction product of benzene, chlorine and maleic anhydride) was placed in a claisen flask and rapidly distilled at reduced pressure using a bunsen burner as a heat source. Although some hydrogen chloride was evolved a fair separation of products was obtained. The first fraction (28 g., b.p. 120° at 3 mm.) consisted largely of maleic anhydride. The second fraction (91 g., b.p. 120–190° at 3 mm.) contained the α-phenyl-α'-chlorosuccinic anhydride. The residue (60 g.) could be distilled (b.p. 192–210° at 2 mm.) but in this case was used without distillation. The material was a tacky yellow glass and all attempts to effect crystallization were unsuccessful.

Anal. Calcd. for $C_{10}H_7O_3Cl_5$ (2,3,4,5,6-pentachlorocyclohexylmaleic anhydride): Cl, 50.3; neut. equiv., 176.5. Found: Cl, 49.0; neut. equiv., 176.

A 19.5-g. portion of the residue was dissolved in 50 ml. of benzene and added to 200 ml. of 10% aqueous sodium hydroxide. The benzene was distilled to leave a homogeneous residual solution. After diluting to 500 ml. with water, 50 g. of solid potassium permanganate was added in small amounts with vigorous stirring. The addition caused the temperature to rise from 50 to 93°. At this point the manganese dioxide was removed by filtration and oxidation completed by treating the filtrate at 90° with an additional 5 g. of potassium permanganate. The mixture was again filtered, decolorized by the addition of sodium bisulfite, and the *p*H lowered to the phenolphthalein end-point by the addition of 12 *N* hydrochloric acid. The solution was evaporated to two-thirds of its original volume, acidified, and extracted with ether. Evaporation of the ether extract yielded 6 g. (57%) of mixed dichlorobenzoic acids as a white solid. After sublimation the material had a melting range of 140–180°.

Anal. Calcd. for $C_7H_4O_2Cl_2$: neut. equiv., 191. Found: neut. equiv., 185.

Fractional crystallization from water–acetone yielded 1.0 g. of 3,4-dichlorobenzoic acid, m.p. 201.5–202.5°.

Anal. Calcd. for $C_7H_4O_2Cl_2$: Cl, 37.2; neut. equiv., 191. Found: Cl, 36.1; neut. equiv., 190.

Peroxide-catalyzed Reaction.—A solution of 234 g. (3.0 moles) of benzene and 88 g. (0.9 mole) of maleic anhydride was shielded from light and maintained at 75 to 80° over a three-hour period while 64 g. (0.9 mole) of chlorine and 4.36 g. (0.018 mole) of benzoyl peroxide dissolved in 78 g. (1.0 mole) of benzene were added simultaneously. The reaction evolved 0.525 mole of hydrogen chloride. After distilling the excess benzene, the remaining material was rapidly distilled to yield 85 g. (45%) of α-phenyl-α'-chlorosuccinic anhydride (b.p. 120° at 2 mm. to 190° at 6 mm.).

Anal. Calcd. for $C_{10}H_7O_3Cl$: Cl, 16.8. Found: Cl, 17.2.

A sample of the material was dissolved in ether, triethylamine added, and the resultant triethylamine hydrochloride removed by filtration. After evaporating the ether from the filtrate, recrystallization from toluene yielded phenylmaleic anhydride (m.p. and mixed m.p. with authentic material 120°).

There was also obtained a precut consisting of 30 g. of impure maleic anhydride and a 57-g. residue.

Reaction of Benzene, Sulfuryl Chloride and Maleic Anhydride.—During a 10-hr. period 2.5 g. (0.01 mole) of benzoyl peroxide was added to a refluxing solution of 74 g. (0.75 mole) of maleic anhydride, 234 g. (3.0 moles) of benzene and 101 g. (0.75 mole) of sulfuryl chloride. Distillation of the product yielded 70 g. (44%) of an α-phenyl-α'-chlorosuccinic anhydride fraction (b.p. 130–195° at 15 mm.).

Anal. Calcd. for $C_{10}H_7O_3Cl$: Cl, 16.9. Found: Cl, 15.0.

Recrystallization from ether gave pure material (m.p. 102–104°) which did not depress the melting point of sample obtained from the reaction of chlorine, benzene and maleic anhydride.

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(3) G. K. Almström, *Ann.*, **411**, 378 (1916), reports phenylchloromaleic anhydride to melt at 83–84°.