[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF HYMAN LABORATORIES, INC.[1]]

Dienophilic Reactions of Aromatic Double Bonds in the Synthesis of β-Substituted Naphthalenes

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RECEIVED FEBRUARY 23, 1954

Naphthalene and anthracene act as dienophiles and undergo Diels-Alder adduction with hexachlorocyclopentadiene. The principal products are II and IV, respectively, each consisting of two moles of diene and one mole of hydrocarbon. Substitution reactions, such as nitration and halogenation, of the aromatic ring of adduct II occur in the β-position, or (for chlorine only) in all four available positions. Dissociation of substituted II regenerates hexachlorocyclopentadiene and yields β-substituted naphthalenes.

While workers in the field of the diene (Diels–Alder) synthesis continue to find new systems capable of reacting as 1,3-conjugated dienes,[2,3] it has been assumed that the possibilities for uncovering new dienophiles are largely exhausted.[4]

Thus, the chemical literature of the diene synthesis fails to disclose a reaction wherein an aromatic double bond acts as a dienophile.[5] We are unable to decide from this fact whether such reactions have not been attempted because current interpretations of quantum-mechanical theories of aromatic structures often discount the olefinic nature of the aromatic double bond, or whether such reactions have been attempted but have heretofore failed because of the tendency of the dienes employed to polymerize or of the adducts formed to revert to their generators at the reaction temperatures employed.

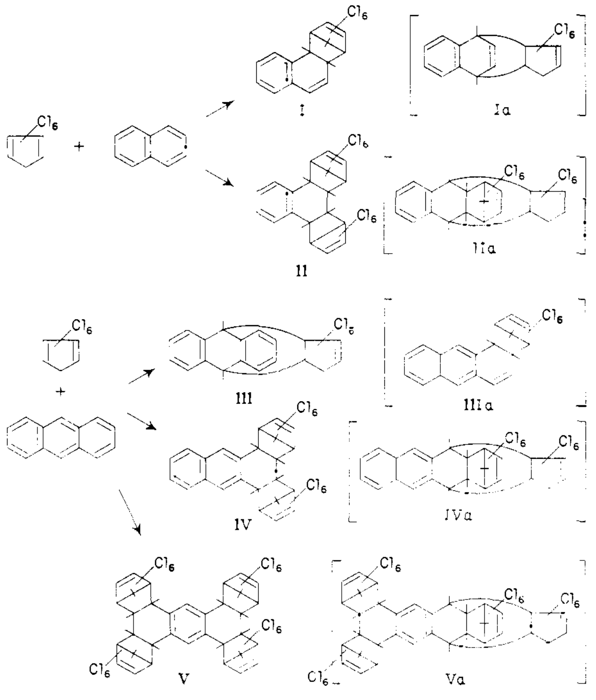

Fig. 1.—Reactions of naphthalene and anthracene with hexachlorocyclopentadiene.

It has been observed that hexachlorocyclopentadiene[6] is extremely thermostable and that in the absence of catalysts it does not decompose or react with itself. Its activity as a diene is well known.[7] These circumstances permit the use of hexachlorocyclopentadiene under conditions of time and temperature not generally possible with most dienes.

Described herein are diene reactions of hexachlorocyclopentadiene, acting as a diene, with the polycyclic aromatic hydrocarbons, naphthalene and anthracene, and the use of the resulting reaction products for further novel syntheses of substituted polycyclic aromatic compounds.

It has been found that prolonged heating of hexachlorocyclopentadiene with naphthalene and with anthracene at 160° forms the polychlorinated Diels–Alder adducts 1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (II) and 1,2,3,4,5,6,7,8,15,15,16,16-dodecachloro-1,4,4a,4b,5,8,8a,14b-octahydro-1,4;5,8-dimethanodibenz[a,c]anthracene (IV)[8] (Fig. 1) with by-product quantities of 9,10-*endo*-[hexachlorocyclopentadiene]-dihydroanthracene (III) and 1,2,3,4,5,6,7,8,10,11,12,13,14,15,16,17,19,19,20,20,21,21,22,22-icositetrachloro-1,4,4a,4b,5,8,8a,9b,10,13,13a,13b,14,17,17a,18b-hexadecahydro-1,4,5,8;10,13;14,17-tetramethanotetrabenz[a,c,h,j]anthracene (V). The compound 1,2,3,4,11,11-hexachloro-1,4,4a,10a-tetrahydro-1,4-methanophenanthrene (I) has also been produced in small amount. It will be noted that in the formation of the principal products II and IV by this Diels–Alder reaction the aromatic double bond acts as a dienophile.

Aside from its novel aspect, the reaction developed interest because of the discovery that it offered a route for a relatively facile synthesis of (a) monosubstituted naphthalenes in the β-position, (b) disubstituted napththalenes in the 2,3-position, (c) polysubstituted naphthalenes in which all substituents are confined to a single ring[9] and (d) substituted anthracenes.[10]

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[1] A portion of this work was done at the laboratories of Julius Hyman & Company, Rocky Mountain Arsenal, Denver, Colo.

[2] M. C. Kloetzel and H. L. Herzog, THIS JOURNAL, **72**, 199 (1950).

[3] M. C. Kloetzel, R. P. Dayton and H. L. Herzog, *ibid.*, **72**, 273 (1950).

[4] "Preparative Organic Chemistry" (Fiat Review of German Science, Part II, 1939–1946), p. 147 (German edition)—section written by Prof. K. Alder.

[5] For a summary of the diene (Diels–Alder) synthesis, see "Organic Reactions," Vol. IV, Roger Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1948, Chapts. I and II.

[6] (a) F. Straus, L. Kollek and W. Heyn, *Ber.*, **63B**, 1868 (1930); (b) H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946); (c) E. T. McBee and C. F. Baranauckas, *Ind. Eng. Chem.*, **41**, 806 (1949).

[7] (a) E. A. Prill, THIS JOURNAL, **69**, 62 (1947); (b) Hooker Electrochemical Co.: "Hexachlorocyclopentadiene," Technical Data Sheet No. 371, December 19, 1947; (c) U. S. Patent 2,606,910, assigned to Velsicol Corporation.

[8] U. S. Patent 2,658,926, assigned to Shell Development Co.

[9] U. S. Patent 2,658,913, assigned to Shell Development Co.

[10] This report deals principally with the synthesis of substituted naphthalenes; the work with substituted anthracenes will be reported at a later date.

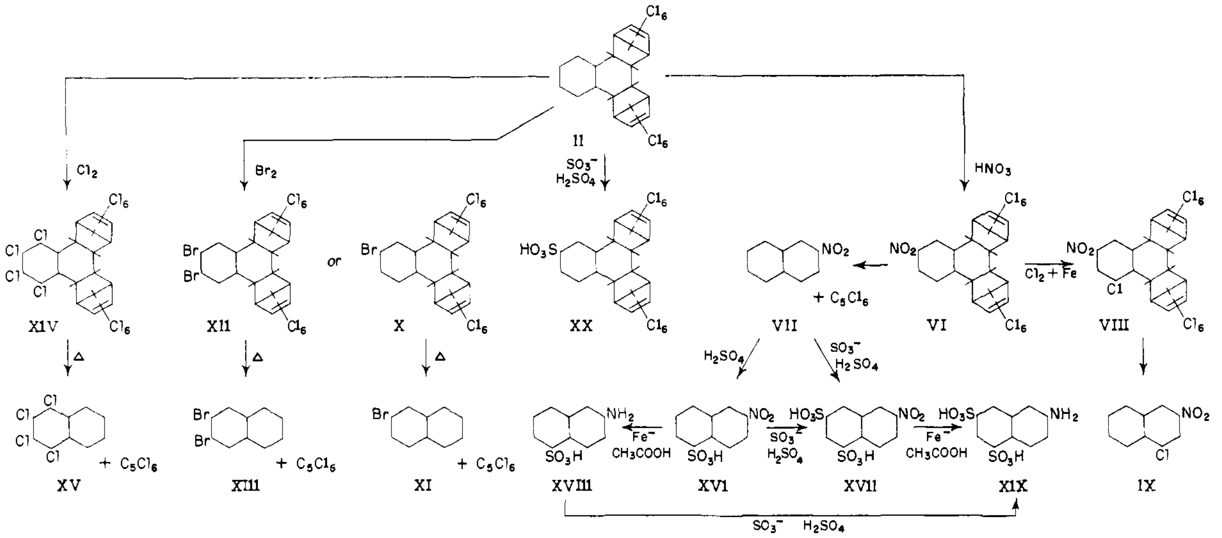

Fig. 2.—Preparation of certain substituted naphthalenes starting with II.

Substituted naphthalenes prepared in excellent yields (80–95%) by means described herein include such hitherto rare compounds as 2-nitronaphthalene (VII), 2-bromonaphthalene (XI), 2,3-dibromonaphthalene (XIII) and 1,2,3,4-tetrachloronaphthalene (XV). The ready availability of 2-nitronaphthalene permitted the synthesis of 2-naphthylamine-5-sulfonic acid (XVIII) and 2-naphthylamine-5,7-disulfonic acid (XIX) in a pure state and high yields, and leads to the economical process for the preparation of other potential dyestuff intermediates heretofore difficult to come by.

The syntheses, summarized in Fig. 2, comprise essentially three steps: (1) adduction of 2 moles of hexachlorocyclopentadiene to naphthalene to form a chlorinated polyhydrodimethanotriphenylene, (2) introduction of substituents into the aromatic ring of the adduct and (3) thermal dissociation of the adduct into hexachlorocyclopentadiene and the substituted naphthalene.

Apparently the formation of I is of a transitory nature, being followed very quickly by its adduction with another mole of hexachlorocyclopentadiene to form II.

The over-all adduction of hexachlorocyclopentadiene to naphthalene proceeds to equilibrium at a relatively slow rate. When stoichiometric quantities of the reactants are heated at 155–165°, reaction proceeds to approximately 40% of completion in 100 hours, and levels off at 75% in 350 hours. Temperatures above 165° favor reversal of the reaction, although equilibrium is achieved more rapidly.

The dissociation rate of the adducts appears to be strongly dependent on temperature. They dissociate rather slowly at 200°, but almost instantaneously above 300°. Thermal dissociation with minimal polymerization or decomposition of resulting products is best attained if the adducts are pyrolyzed in an apparatus allowing maximum heat transfer, low temperature gradients and short contact time.[11]

The presence of a benzenoid moiety in adduct II and a naphthalenoid moiety in adduct IV was determined through ultraviolet absorption studies.[12]

The discovery made during the course of the present study, namely, that hexachlorocyclopentadiene can react as a dienophile,[13] coupled with the earlier observation of Kloetzel, Dayton and Herzog[3] that naphthalene shows a detectable tendency to act as a diene, raises the possibility of the existence of compounds Ia, IIa, III, IVa and Va. Compound IIIa would be in the series I, II, IV and V, whereas III belongs to the alternate series.

While a final choice between certain of these structural forms may have to await further clarification, the following reasons impelled us to make the structure assignments which we did: (1) (a) There can be hardly a question that II is a correct structure and IIa incorrect. Structure IIa cannot explain the hindered α-positions of ring A, whereas structure II explains these readily. (b) Also, this compound shows no evidence of the presence of allylic chlorines, which would otherwise be readily demonstrable because of their lability. (c) Again, the impressive yields of diadduct obtained are at critical variance with the trace yields obtained by Kloetzel, *et al.*,[3] in treating naphthalene with maleic anhydride over an extended period. (d) Finally, IIa would have to be formed *via* Ia, which should be relatively stable because the remaining olefinic bond would be considerably hindered[14]; yet, spectroscopic examination of mother liquors of several naphthalene–hexachlorocyclopentadiene reactions has failed to show any reaction product other than the diadduct. Hence, Ia not being present in the reaction, the existence of IIa is most doubtful.

(2) Inasmuch as the existence of IIa is highly doubtful, that of Ia must therefore also be questioned (see 1d, above). It is our belief that I was produced in our experiments through the pyrolytic decomposition of II, for it possesses an unhindered olefinic bond, and would thus be converted rapidly to II during the reaction.

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(11) A continuous cracker designed for this purpose is described by J. S. Chirtel and Y. A. Tajima in a paper to be published elsewhere.

(12) Private communication, E. Clar, Univ. of Glasgow.

(13) Dr. Clar[12] has reported a 1:1 adduct of hexachlorocyclopentadiene with tetracene and with pentacene, and has stated his belief that the aromatic hydrocarbons act as dienes.

(14) K. Alder and G. Stein, *Ann.*, **501**, 1 (1933).

(3) In anthracene one is dealing with a very active diene. While IIIa could probably be produced by careful pyrolysis of IV, the appreciable yields of monoadduct obtained *directly* by the reaction of anthracene with hexachlorocyclopentadiene afford good evidence of the validity of structure III. Unfortunately, a report on the ultraviolet absorption of this compound, which might be decisive, is not available to us at this writing.

(4) The 1:2 adduct of anthracene and hexachlorocyclopentadiene can hardly be anything other than IV, in view of the great likelihood that II represents the correct formula for the 1:2 adduct of naphthalene and hexachlorocyclopentadiene. No dienic activity of anthracene beyond its normal *meso*-activity is to be expected, or has ever been reported.

(5) There is little to choose between V and Va, because our knowledge of this compound is too fragmentary. It was produced in very small yield after a protracted reaction period. The symmetrical formula V has been chosen by us as portraying a molecule built up along lines which appear to us to have been established by the diadductions II and IV. However, the surprising solubility of this tetraadduct in such a poor solvent as heptane may point to a structure less symmetrical than V.

The ultraviolet absorption spectra[15] of adducts II and IV show the primary bands typical of benzene and naphthalene, respectively. Ring A of adduct II shows the characteristic, although hindered, substitution reactions of an aromatic compound; it can be halogenated, nitrated and sulfonated. The alicyclic ring B, on the other hand, appears to be inert to substitution reactions.

Chlorine atoms attached to carbon atoms 1 and 8 of II appear to hinder substitution in what would be an analogous α-position of naphthalene. In contrast to the predominant α-substitution occurring in naphthalene, no bromine or nitro groups could be introduced in the analogous positions of II. Despite repeated trials with excess quantities of bromine or nitric acid and prolonged reaction times, substitution invariably occurred only in the β-position. These chlorine atoms, however, apparently are not bulky enough to hinder the entrance of other chlorine atoms into the α-positions.

The adduction of hexachlorocyclopentadiene with anthracene proceeded under conditions similar to those used with naphthalene. Adduct IV was the principal product isolated. The presence of a naphthalenic group, revealed by ultraviolet[12] and infrared absorption studies, offers evidence for the structure of IV to be as indicated. Although the structure of the by-product adduct III has not yet been elucidated conclusively, it does not appear that hexachlorocyclopentadiene acted as a diene in that reaction. Thus, it is thought that III may represent the first concrete instance of a reaction wherein hexachlorocyclopentadiene acts as a dienophile. This conclusion is supported by the infrared spectrum of adduct III which lacks the structural features common to the 1:2 adducts of naphthalene and anthracene with hexachlorocyclopentadiene. The adduct V was isolated in small quantities (less than 1% of theoretical yield) from the crude hexachlorocyclopentadieneanthracene reaction mixture. The extremely simple infrared spectrum of adduct V indicates that it must have a highly symmetrical structure such as that proposed.

Because adduction of naphthalene with hexachlorocyclopentadiene proceeds slowly, experiments were made to determine whether 1,2,3,4-tetrachlorocyclopentadiene-1,3 would permit a faster adduction rate. Unfortunately, the tetrachlorocyclopentadiene was found to undergo fairly rapid self-adduction and polymerization at 100[5] and hence was not practical for adductions with naphthalene

The 1,2,3,4-tetrachlorocyclopentadiene-1,3 was prepared easily by reduction of hexachlorocyclopentadiene with zinc dust and acetic acid, to yield a crystalline product melting at 60° and possessing the correct chlorine content for $C_5H_2Cl_4$. The assigned structure of the tetrachlorocyclopentadiene is inferred from the fact that the allylic chlorines of hexachlorocyclopentadiene are by far the most reactive of the six present,[16] and hence it is those chlorines that would be most susceptible to reductive displacement by hydrogen.

The ready availability of 2-nitronaphthalene by the reactions described herein prompted us to investigate its behavior toward sulfonation. Kappeler[17] reported that sulfonation of 2-nitronaphthalene with fuming sulfuric acid at ice-bath temperature yields a mixture of 2-nitronaphthalene-5 and -8-sulfonic acids. No other references appear in the literature. We found that sulfonation of 2-nitronaphthalene to the mono- and disulfonic acids is possible under a wide range of temperatures and sulfuric acid strength. Both factors appear to determine the distribution of isomers formed. The first sulfonic acid group apparently enters the 5- or 8-position and never in the nitrated ring. One might expect four monosulfonic acid isomers to be formed: 2-nitronaphthalene-5-, -6-, -7- and -8-sulfonic acids. Traces of the 6- and 7-isomers were detected in a few experiments but never in significant yields. The second acid group then enters *meta* to the first and on the same ring, in conformance with the Armstrong–Wynne rule.[18]

The 2-nitronapthalene-5-sulfonic acid (XVI), which can be prepared in high yields at 60° using concentrated sulfuric acid, is reduced readily to the valuable 2-naphthylamine-5-sulfonic acid (XVIII) This acid in turn can be sulfonated quantitatively to the important 2-naphthylamine-5,7-disulfonic acid (XIX).[19] Alternatively, XVI can be sulfonated to 2-nitronaphthalene-5,7-disulfonic acid (XVII) and then reduced to XIX. As with the work of Beretta,[20] nitration of XVI under anhydrous conditions may lead to 2,7-dinitronaphthalene-5-sulfonic acid.

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[15] The ultraviolet spectra discussed here and a tabulation of the infrared spectra have been deposited as Document number 4292 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to Chief, Photoduplication Service, Library of Congress.

[16] J. S. Newcomer and E. T. McBee, THIS JOURNAL, **71**, 946 (1949).

[17] H. Kappeler, *Ber.*, **45**, 633 (1912).

[18] H. E. Armstrong and W. P. Wynne, *ibid.*, **24R**, 718 (1891).

[19] "The Chemistry of Synthetic Dyes," Vol. I, K. Venkataraman, Academic Press, Inc., New York, N. Y., 1952, p. 193.

[20] F. Beretta, U. S. Patent 2,191,820.

Experimental

Materials.—The hexachlorocyclopentadiene (94 ± 2% purity) was supplied by Julius Hyman and Co. Division, Shell Chemical Corp., Denver, Colo.

The naphthalene used was Baker and Adamson resublimed flaked naphthalene. Other reagents were obtained through the usual chemical supply channels.

Preparation of II. Method A.—A mixture of 128 g. (1.0 mole) of naphthalene and 595 g. (2 moles) of hexachlorocyclopentadiene (92% purity) was heated in a round-bottomed flask at 155–160° for 120 hours. On heating, the flask contents formed a clear solution which darkened as the reaction progressed. At the end of the heating period, the reaction mixture was chilled in ice, whereupon a large quantity of crystalline material gradually separated from solution. The crystals were collected by suction filtration and washed on the filter with small portions of cold acetone. The resulting white crystalline II melted at 211.5–213.5° and weighed 166 g. (29.6% yield). Repeated recrystallization from heptane raised the m.p. to 214–215°.

Anal. Calcd. for $C_{20}H_8Cl_{12}$: Cl, 63.20; mol. wt., 674. Found: Cl, 62.8; mol. wt., 683.

Method B.—A mixture of 296 g. (1 mole) of hexachlorocyclopentadiene (92% purity) and 512 g. (4 moles) of naphthalene was heated in a glass flask at 150–160° for 200 hours. On heating, the flask contents formed a clear solution which darkened as the reaction progressed. At the end of the heating period the unreacted hexachlorocyclopentadiene and naphthalene were removed by vacuum distillation. During the distillation, the oil-bath temperature was not allowed to exceed 175°. The overhead of unreacted materials was collected in two fractions. The first yielded, under water aspirator vacuum, a cut boiling at 80–110° (11 mm.). The second fraction yielded, under oil-pump vacuum, a cut boiling at 60–80° (1 mm.).

The viscous red oil remaining in the distillation flask was cooled to 40° and on stirring it with 100 ml. of cold acetone, a crystalline material separated which was collected by suction filtration. The acetone solution in the filtrate was set aside for subsequent recovery of I. The solid left on the filter was washed under suction with small portions of cold acetone until the washings came through almost free of color. The crude solid thus obtained was recrystallized from heptane to yield a white crystalline product melting at 210–211°. Repeated crystallization raised the melting point to 214–215°. A yield of 295 g. (44%) was obtained.

An alternative procedure for isolating II from the crude mixture consists of diluting the crude reaction mixture while still warm (*ca.* 80–90°) with an equal volume of isopropyl alcohol, cooling to room temperature, filtering and recrystallizing the solid from heptane.

Preparation of I.—The acetone filtrate obtained in the method B workup for II described above, was heated to remove the acetone. The resulting oily residue was vacuum distilled to give a distillate of red viscous oil boiling at 90–160° (0.5 mm.). The distillate was discarded since it consisted principally of products resulting from prolonged heating of commercial hexachlorocyclopentadiene. The pot residue was vacuum distilled in an apparatus allowing relatively short-path distillation. A red gummy material (1.3 g.) boiling between 170° and 210° at 0.5 mm. pressure was collected. Crystallization of the red gum from hexane gave 0.7 g. of a white solid melting at 163–164°.

Anal. Calcd. for $C_{15}H_8Cl_6$: Cl, 53.1; mol. wt., 401. Found: Cl, 52.7; mol. wt., 354.

Preparation of 10-Nitro-1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (VI).—In a cylindrical glass vessel equipped with an efficient multipaddled stirrer was placed a mixture of 425 g. of HNO_3 (66% strength, sp. gr. 1.395), 625 g. of fuming H_2SO_4 (30% SO_3) and 300 g. of II previously pulverized to sufficient fineness to pass through a 125-mesh sieve. The suspension was vigorously stirred and kept at a temperature of 90–97° for 3 hours. During the heating period, the suspension of white solid gradually turned a pale yellow. It was noted that the fineness of II influenced the nitration rate considerably. Completion of nitration was determined by infrared spectrophotometry. After three hours of heating and stirring, the mixture was cooled and filtered with suction through a sintered glass filter. The light yellow crystalline material thus collected was washed with water and dried at 110°. The product melted at 209–211°; yield 317 g. (99%). Recrystallization from heptane raised the melting point to 222–223°.

Anal. Calcd. for $C_{20}H_7Cl_{12}NO_2$: Cl, 59.2; N, 2.0. Found: Cl, 59.0, 59.5; N, 2.0.

No dinitration product was isolated. However, it appeared that on using 95% fuming HNO_3 and heating at 120° for 24 hours some dinitration (*ca.* 15%) occurred. Studies of polynitration are still in progress.

Preparation of 1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene-10-sulfonic Acid (XX).—Twenty-five grams of IV was triturated to a "thin" suspension with 250 g. of fuming sulfuric acid (30% SO_3). While maintaining a temperature of 60° the suspension was stirred vigorously for 16 hours. At the end of this interval the reaction mixture was cooled and slowly poured onto 300 g. of ice. An off-white, amorphous, gelatinous ppt. was collected by filtration and dried in an oven at 100°. The crude sulfonated product melted, when heated rapidly, at 220–225°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 40–50°) gave rosettes melting at 245–248°. The XX formed "gels" with water and with 10% NaOH soln. Work on this material is still in progress.

Thermal Dissociation of Adducts. Batch Method A.—A 500-ml., 3-necked, round-bottomed flask equipped with a thermometer nearly touching the bottom was charged with approximately 300 g. of reacted adduct.

The flask was connected by a Claisen arm adapter, an air condenser for downward distillation, receiver and NaOH trap to a vacuum pump. A vacuum of 0.5 to 15 mm. was applied and the flask and contents were then heated to an appropriate temperature (220–290°) by means of an electric mantle. The dissociation products consisting of hexachlorocyclopentadiene and naphthalenic compounds were collected by subsequent fractional distillation, solvent extraction and/or crystallization.

Prolonged heating of VI produced considerable coking and on one occasion led to a violent decomposition in the distillation flask. The other adducts described herein underwent little coking during batch cracking.

Continuous Method B.—It was found that coking was largely avoided and dissociation of the adducts proceeded smoothly by passing toluene, xylene or carbon tetrachloride solutions of the adducts through a tube preheated to 360–400° and at a rate so that contact time with the heated surface was restricted to a few seconds. The effluent vapors are condensed and stripped of solvent. A continuous cracker developed for pilot plant work is described in the paper by Chirtel, *et al.*[11] For laboratory scale operations, batch cracking is more convenient than the continuous cracking method.

Preparation of VII. Method A.—Three hundred grams (0.42 mole) of VI was placed in the batch cracking apparatus previously described. Vacuum (1 mm.) was applied and the pot contents heated to a temperature of 220 to 270°. The distilled material, boiling at 60–110° (1 mm.), weighed 274.0 g. (91.4% of the charge). Twenty-six grams of a coke-like residue, that became friable when heated to 290–300°, remained in the distilling flask. Analysis of the distillate by infrared spectroscopy indicated the presence of 24.7% β-nitronaphthalene and 73.5% hexachlorocyclopentadiene (theory, 24.1 and 75.9%, respectively). The infrared spectroscopic method of analysis is described elsewhere.[11] The distillate was fractionated carefully *in vacuo* (1.0 mm. abs.) to separate the hexachlorocyclopentadiene and naphthalene from VII; the C_5Cl_6 was collected at 79–84°. The residue in the distilling flask crystallized on cooling, and was taken up in ethanol and treated with decolorizing charcoal. After separation of the charcoal on a filter, the ethanol solution was diluted with water and slowly cooled, causing yellow crystals of 2-nitronaphthalene to separate. One additional recrystallization from aqeuous ethanol gave a product melting at 78–79°, whose mixture with an authentic sample of β-nitronaphthalene, m.p. 78–79° showed no depression of m.p.

Anal. Calcd. for $C_{10}H_7NO_2$: C, 69.4; H, 4.2. Found: C, 69.2; H, 4.1.

The product obtained by the foregoing method also was reduced to the corresponding amine and the acetyl and benzoyl derivatives of the amine were prepared. The amine thus obtained, and its two derivatives, were compared with an authentic sample of β-naphthylamine and its corresponding derivatives by mixed melting points and infrared spectroscopy and found to be identical. The product was thus unambiguously identified as β-nitronaphthalene.

Method B.—A solution containing 200 g. of VI dissolved in 500 g. of xylene was pumped, at the rate of 48 ml. per minute, through a 0.5″ i.d. nickel tube heated over an eight-inch length to a temperature of 325–375°. The effluent vapors from the cracking tube were condensed and stripped of the xylene. Analysis by infrared spectroscopy of the liquid residue remaining after the xylene had been removed indicated that it contained 23.0% of β-nitronaphthalene (theory, 24.1%). The β-nitronaphthalene was isolated by the method described in method A above.

Note: By using the continuous cracker described by Chirtel, *et al.*,[11] a cracking conversion of 98% to β-nitronaphthalene was obtained.

Preparation of IV.—A mixture of 50 g. (0.28 mole) of anthracene (m.p. 213–214°) and 155 g. (0.57 mole) of hexachlorocyclopentadiene was heated in a flask at 150–160° for 20 hours. The mixture formed a clear solution in two hours. At the end of the heating period, the flask contents were cooled to 100° and poured, with rapid stirring, into three volumes of hot isopropyl alcohol. The resulting grayish crystalline precipitate of adduct IV was collected by suction filtration and dried, m.p. 230–235°; yield 70 g. (35%). Recrystallization of the adduct from heptane raised the m.p. to 241–242°. Some 9,10-dichloroanthracene is formed as a by-product in this reaction.

Anal. Calcd. for $C_{24}H_{10}Cl_{12}$: Cl, 58.8; mol. wt., 724. Found: Cl, 59.1; mol. wt., 766 (cryoscopic, benzene).

Preparation of III.—The isopropyl alcohol filtrate referred to in the preceding paragraph was stripped of solvent by distillation under water aspirator pressure (11 mm.) and then most of the hexachlorocyclopentadiene was removed under 0.5 mm. pressure. Care was taken not to exceed pot temperature of 150° during removal of solvent and hexachlorocyclopentadiene. The pot residue was dissolved in heptane and the heptane solution decolorized with charcoal. Fractional crystallization from the heptane solution yielded 10 g. of the white crystalline adduct III, m.p. 147–148°.

Anal. Calcd. for $C_{19}H_{10}Cl_6$: Cl, 47.1. Found: Cl, 47.2.

A higher yield of adduct III can be attained by using 1:2 mole ratios of hexachlorocyclopentadiene to anthracene.

Preparation of V.—A mixture of 50 g. (0.28 mole) of anthracene and 100 g. (0.38 mole) of hexachlorocyclopentadiene was heated in a flask at 150–160° for 1 week. The dark mixture was cooled to 80° and then an equal volume of acetone was added cautiously and with stirring. Most of the flask contents dissolved. The acetone suspension was filtered with suction. A greenish precipitate weighing 10 g. wet was collected. The precipitate was washed in ethanol in which it appears insoluble and then it was dissolved in boiling toluene. The toluene solution was charcoaled, filtered and concentrated to 30 ml. On cooling, a mustard-yellow precipitate (7.5 g.) of 9,10-dichloroanthracene was collected by filtration. The toluene filtrate resulting from the removal of the dichloroanthracene was diluted with an equal volume of ethanol. A precipitate golden yellow in color was collected, wet wt. 1.5 g. Recrystallization from heptane in which it appears quite soluble yielded 0.43 g. of golden yellow flakes (V) melting above 295°.

Anal. Calcd. for $C_{34}H_{10}Cl_{24}$: Cl, 64.1. Found: Cl, 63.9.

Preparation of 1,2,3,4,5,6,7,8,9,10,11,12,13,13,14,14-Hexadecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (XIV).—The chlorination of II was performed in a three-necked, round-bottomed flask fitted with a reflux condenser, an efficient stirrer, a thermometer and a 5 mm. gas inlet tube inserted through a stopper in a neck of the flask. The inlet tube extended close to the bottom of the flask and was provided with a small bulb with fine perforations to break up the gas stream into small bubbles; the tube was connected to a cylinder of chlorine through a bubble counter consisting of a 500-cc. wash bottle which contained about 200 cc. of concentrated sulfuric acid. The HCl formed was disposed through the condenser, the outlet of which was protected against atmospheric moisture by a tube of anhydrous calcium chloride. Into the reaction flask was placed a mixture of 100 g. of II, 0.5 g. each of iron powder and anhydrous $FeCl_3$ and 175 ml. of *sym*-tetrachloroethane. The flask contents were stirred and heated to 100° at which time all the II dissolved. A stream of chlorine gas was passed through the solution while maintaining its temperature at 95–105°. A considerable amount of XIV precipitate was formed toward the end of the chlorination period. The flask contents were cooled and filtered. The solid material was purified by charcoaling a solution of the product in hot toluene, filtering and diluting the filtrate with an equal volume of methanol. The white precipitate obtained on dilution with methanol melted at 232–234°, yield 103 g. (85%).

Anal. Calcd. for $C_{20}H_4Cl_{16}$: Cl, 69.91. Found: Cl, 69.74.

Preparation of XV.—Fifty grams of XIV was thermally dissociated by pyrolysis in a vacuum distillation apparatus at a pressure of less than 1 mm. The pyrolysis proceeded cleanly leaving no coke. The tetrachloronaphthalene sublimed as a solid in the condenser while most of the hexachlorocyclopentadiene distillate was collected in the receiver. The sublimate of tetrachloronaphthalene was recrystallized twice from benzene–methanol, to give a white crystalline material, yield 16 g. (97%, based on XIV), m.p. 199–200°. The literature m.p. 198°[21] and 196°.[22]

Anal. Calcd. for $C_{10}H_4Cl_4$: Cl, 53.33. Found: Cl, 53.06.

Preparation of 10,11-Dibromo-1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (XII).—One hundred grams of II, 200 ml. of tetrachloroethane and 0.5 g. of iron powder (reduced by hydrogen) were placed in a flask fitted with a reflux condenser and a dropping funnel. The mixture was heated to reflux (by which time the II had dissolved in the tetrachloroethane) and 30 ml. of bromine (twice theory, to compensate for bromine lost by entrainment) dissolved in 30 ml. of tetrachloroethane, was added dropwise over a period of an hour. Refluxing was continued for an additional two hours. The bromine and $FeBr_3$ which formed were removed by shaking the warm solution with aqueous sodium bisulfite and subsequently washing it with water. The solution was then dried and treated with a decolorizing charcoal. The warm solution, obtained after filtration, was then diluted with about 400 ml. of methanol. A crystalline solid separated which melted between 220–222°; yield 100 g. (81%).

Anal. Calcd. for $C_{20}H_6Cl_{12}Br_2$: C, 28.8; H, 0.72. Found: C, 28.5; H, 0.75.

Preparation of XIII.—Two hundred twenty grams of XII was introduced into a 200-ml. flask by melting it as it was introduced. When all the material was molten, the flask was mounted with a Claisen head, a condenser and a receiver and the distillation system was evacuated carefully to an absolute pressure of 70–100 mm. The flask contents were heated at a pot temperature of 220°; hexachlorocyclopentadiene distilled over. Distillation was continued until the production of hexachlorocyclopentadiene became very slow and small amounts of solid appeared in the material distilling over. The dark residue left in the flask, while still hot and fluid, was poured into benzene and heated with decolorizing charcoal. The solution remaining after the removal of the charcoal was diluted with methanol; a crude brown crystalline solid was deposited by this solution. This crude solid was recrystallized from heptane; there was thus obtained a light brown product which crystallized in flakes and melted between 139–140°; literature m.p. 140°.[23]

Preparation of 10-Bromo-1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4,5,8-dimethanotriphenylene (X).—In a 5-liter flask equipped with stirrer, dropping funnel and an upright Friedrichs-type condenser was placed 1 kg. of II (1.48 moles), 2 liters of CCl_4, 5 g. of iodine and 2.5 g. of iron powder. Ice-water was circulated through the condenser. A solution of 240 g. (1.5 moles) of bromine in 150 ml. of CCl_4 was placed in the dropping funnel.

The bromine solution was added to the stirred, refluxing solution in 5-ml. portions over a period of 2 hours. After all the bromine had been introduced into the reaction flask, stirring and refluxing was continued for an additional 20 hours.

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(21) J. V. Braun, *Ber.*, **56**, 2332 (1923).

(22) E. G. Turner and W. P. Wynne, *J. Chem. Soc.*, 243 (1941).

(23) W. P Wynne, *Proc. Chem. Soc.*, **30**, 204 (1914); J. Kenner, W. H. Ritchie and R. L. Wain, *J. Chem. Soc.*, 1526 (1937).

The reaction solution was filtered, and washed successively with a liter of 5% $NaHSO_3$ solution and two 500-ml. portions of water. The CCl_4 solution was then almost completely stripped of solvent and the oily residue crystallized twice from charcoaled solutions of hot toluene. A white crystalline product was obtained, m.p. 181–183°, wt. 1030 g. (yield 93%). This product yielded, on pyrolysis, 2-bromonaphthalene and hexachlorocyclopentadiene.

The mother liquors contained a viscous oily by-product which resisted further attempts at crystallization.

Preparation of XI.—One hundred grams of X was thermally dissociated in a vacuum distillation assembly at 1 mm. vacuum. The pot contents were melted and heated continuously to attain a gradually increasing temperature in the range, 230–270°. Ninety-five grams of yellow liquid distillate was collected. The distillate was fractionally distilled to give a forerun of hexachlorocyclopentadiene (b.p. 70–90° (<1 mm.)) and 23 g. of 2-bromonaphthalene, b.p. range 100–110° (<1 mm.); yield 23 g. (84%).

Recrystallization of the β-bromonaphthalene from 90% ethanol gave plates, m.p. 59–60°. Identity was established definitely by comparison by infrared spectroscopy with an authentic purified sample of 2-bromonaphthalene (Eastman Kodak Co.). The melting points for 2-bromonaphthalene reported in the literature range from 59°[24] to 62°.[25]

Preparation of 1-Chloro-3-nitronaphthalene (IX).—A refluxing solution of 20 g. of VI in 150 ml. of *sym*-tetrachloroethane was chlorinated for 8 hours. Approximately 0.5 g. of anhydrous $FeCl_3$ was used as a catalyst. Precautions were taken to carry out the chlorination under anhydrous conditions.

After the chlorination was stopped, the flask contents were filtered and the filtrate washed with dilute sodium hydroxide solution, then water and dried over anhydrous Na_2SO_4. The solvent was removed under water aspirator pressure. The resulting modified adduct presumably was 11-nitro-1,2,3,4,5,6,7,8,12,13,13,14,14-tridecachloro-1,4,4a,-4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (VIII). The residue was thermally cracked under high vacuum less than 1 mm. pressure. A short-path distillation was necessary for collecting the cracking-overhead product because the 1-chloro-3-nitronaphthalene distils with difficulty.

The overhead was fractionated by vacuum distillation. After discarding the C_5Cl_6 forerun, 5.8 g. of a viscous oil was collected at 160–180° (1 mm.). The oil was crystallized by dissolving it in 20 ml. of boiling ethanol, charcoaling and cooling; yield 4.3 g. (74%, based on VI). Lemon-yellow needles were collected which had a m.p. 123–125°.

Two recrystallizations from ethanol raised the m.p. to 128–129°. The m.p. reported in the literature for 2-nitro-3-chloronaphthalene is 129.5°.[26] Our product is presumed to be 1-chloro-3-nitronaphthalene, based on the powerful *meta*-directing influence of a nitro group.

Preparation of 1,2,3,4-Tetrachlorocyclopentadiene-1,3.—In a round-bottomed flask equipped with an efficient stirrer and a thermometer was placed 273 g. (1 mole) of hexachlorocyclopentadiene and 450 ml. of glacial acetic acid. Stirring was started and 150 g. (2.3 moles) of zinc dust was added portionwise over a period of 0.5 hour. The reaction with zinc is extremely exothermic. The temperature of the reactants was kept below 75° by external cooling with a CO_2–acetone-bath. Stirring was continued for 15 minutes after addition of all the Zn dust. The reaction mixture was filtered free of excess zinc dust and the filtrate poured into 1.5 liters of water. The resulting oily phase solidified in two hours. The supernatant liquid was decanted and the solid layer was then dissolved at room temperature in 500 ml. of pentane. The pentane was dried over anhydrous $CaCl_2$, filtered, evaporatively concentrated to 90 ml. and chilled to −20°. A crop of white tetrachlorocyclopentadiene crystals was obtained, m.p. 60°.

Anal. Calcd. for $C_5H_2Cl_4$: Cl, 69.58. Found: Cl, 69.35.

Octachlorocyclopentene, a normal impurity in commercial grade hexachlorocyclopentadiene, was found also to be readily reduced by the above procedure to 1,2,3,4-tetrachlorocyclopentadiene-1,3.

Preparation of 2-Nitronaphthalenemonosulfonic Acids.—Twenty grams of 2-nitronaphthalene was added to 100 g. of 10% fuming sulfuric acid in a round-bottomed flask which was equipped with an efficient stirrer and immersed in a 60° oil-bath. Monosulfonation was complete after stirring for about 15 hours. (Concentrated sulfuric acid may be used instead of 10% oleum in which case the reaction is continued for about 24 hours.) Completion of sulfonation was determined by diluting a sample approximately fivefold with water and then making the solution basic with caustic soda; lack of turbidity indicated completion of sulfonation. The mixture was then poured over 185 g. of ice with stirring. The iced mixture was treated with gaseous ammonia until it became slightly alkaline. An ice-bath was used to keep the mixture cold during the introduction of ammonia. Occasional agitation helped to keep the mass fluid and to facilitate absorption of the ammonia. The mixture, which had become thick with solids, was filtered through a large fast filter to remove the precipitated ammonium salt of 2-nitronaphthalenemonosulfonic acids. It was discovered that boiling and recooling to room temperature would produce harder, faster filtering crystals in those cases where the ammoniated mixture filtered with difficulty. The filter cake contained 29.15 g. of monosulfonic acids (theoretical 29.22 g.). The 2-nitronaphthalenesulfonic acids were determined from the naphthalene carbon content[27] or titration of nitro group with titanium trichloride.[28] The filter cake, which will contain varying amounts of ammonium sulfate depending on the efficiency of filtration, can be used as such for conversion to XVIII.

Preparation of 2-Naphthylaminemonosulfonic Acids.—The wet or dried filter cake of 2-nitronaphthalenemonosulfonic acid was reduced with iron according to the method described by Fierz-David.[29] The reduction products were isolated by the method described by Green and Vakil,[30] and analyzed for XVIII by the diazotization–bromination procedure described by Fierz-David for XIX[31] or by the gravimetric procedure of Green and Vakil.[30] A 94–96% conversion to the naphthylaminesulfonic acid was obtained readily on reduction and 90% of the product was found to be the 2-amino-5-sulfonic acid and the remaining 10% to be the 2-amino-8-sulfonic acid.

Preparation of 2-Nitronaphthalene-5,7-disulfonic Acid (XVII).—Twenty grams of 2-nitronaphthalene was added to 100 g. of 30% oleum which already had been heated to 60° in a two-neck, round-bottomed flask. The flask fitted with a stirrer was immersed in an oil-bath to maintain the temperature. Agitation was started as soon as all the 2-nitronaphthalene had been added to the acid. Sulfonation was continued for 24 hours. The mixture was poured over approximately 200 g. of ice, then diluted to approximately 1 l. with water. Barium carbonate or hydroxide was then added to the boiling solution with stirring until precipitation of barium sulfate ceased and the solution was just slightly alkaline. The precipitate was filtered off hot and leached four times by boiling with 750-ml. portions of water, filtering after each leaching. The filtration of barium sulfate and subsequent leaching had to be performed carefully to avoid loss of product in the filter cake. The combined filtrate and leachings was titrated with dilute sulfuric acid until precipitation of barium sulfate ceased. The precipitate was then filtered off and washed with water. The combined filtrate and washings were concentrated by evaporation to a thick solution which set to a wet cake on cooling to room temperature. Final drying was accomplished at 120° in a vacuum oven; the yield was 37.6 g. (97.7%). The product contained 95.1% of XVII. The impurity was 2-nitronaphthalene-6,8-disulfonic acid. The product is very hygroscopic.

The degree of sulfonation and the number of sulfonic acid groups per naphthalene ring or nitro group can be determined by the method of Calcott, *et al.*[27] The percentage

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[24] K. Gasiorowsky and A. F. Waijss, *Ber.*, **18**, 1936 (1885).

[25] Ch. Courtot and Paivar, *Chimie & Industrie*, **45**, 80 (1943); *C. A.*, **37**, 2366 (1943).

[26] H. H. Hodgson and R. L. Elliott, *J. Chem. Soc.*, 1850 (1935).

[27] W. S. Calcott, F. L. English and F. B. Downing, *Ind. Eng. Chem., Anal. Ed.*, **6**, 1199 (1924).

[28] E. Knecht and E. Hibbert, *Ber.*, **38**, 3318 (1905); "Estimation of Organic Compounds," F. Wild, Cambridge University Press, Cambridge, 1953, pp. 184–187.

[29] H. E. Fierz-David and L. Blangey, "Fundamental Processes of Dye Chemistry," Interscience Publishers, Inc., New York N. Y., 1949, p. 186.

[30] A. G. Green and K. H. Vakil, *J. Chem. Soc.*, **113**, 35 (1918).

[31] Fierz-David and Blangey, ref. 29, pp. 383–393.

of XVII in the product is determined by reduction to the 2-naphthylaminedisulfonic acids and the quantitative estimation of XIX according to the method described by Fierz-David, *et al.*[31]

Acknowledgment.—The authors are indebted to Dr. Julius Hyman for suggesting this project, and for constant encouragement and discussion during the course of the work.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Reactivities of Carbonyl-activated Angular and "Vinyl" Chlorine Substituents in Adducts from Dienes and Chloroquinones. Syntheses of Chloronaphthoquinones

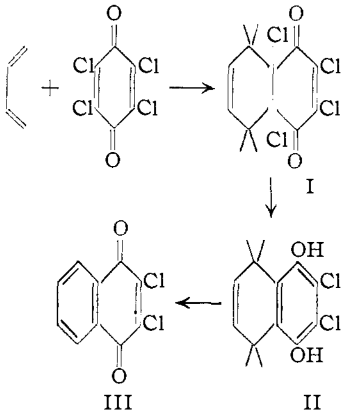
BY RUSSELL GAERTNER

RECEIVED JUNE 1, 1954

Chloranil or 2,5-dichloroquinone and simple dienes form crystalline 1:1 adducts, which contain both angular and "vinyl" halogen atoms. Removal of the angular groups by reducing agents with concomitant aromatization of the potentially quinoid ring followed by oxidation of the 5,8-dihydro- or 5,6,7,8-tetrahydronaphthohydroquinones constitutes a new and useful synthesis of the corresponding naphthoquinones. Adducts derived from 1-acetoxybutadiene lose the acetoxyl group during aromatization. Dichloroquinone adducts are dehydrochlorinated by collidine.

Interaction of simple dienes and polyhalobenzoquinones to give adducts possessing both angular and vinyl halogens in the potentially quinonoid ring appears to be virtually unknown.[1] The single possible example[2] is the chloranil–cyclopentadiene 1:1 adduct[3] of Albrecht[4]—"of unknown structure."[1] In the present work it has been found that stable crystalline adducts can be prepared from chloranil and simple dienes and more labile products from 2,5-dichloroquinone. This discovery prompted a study of the structures and reactions of these systems, resulting in the elucidation of methods for the selective removal of the angular chlorines and new syntheses for chloronaphthoquinones.

When chloranil and dienes are heated in benzene at 80–120° for one to three days colorless 1:1 adducts are obtained in good yield. They are not affected by sublimation *in vacuo* at 100°, but some decomposition seems to occur during distillation at 1 mm. The reactive 2-methylpentadiene and isoprene add slowly at the temperature of refluxing benzene; most of the experiments were conducted in a rocking bomb. Butadiene, 2,3-dimethylbutadiene and 1-acetoxybutadiene react similarly; a number of less reactive compounds, including chloroprene, did not form adducts. In some reaction mixtures, and especially at higher temperatures, the presence of tetrachlorohydroquinone indicated that dehydrogenation was competitive.



These adducts—as well as Albrecht's cyclopentadiene derivative—have structures of type I. The structures are apparent from their conversion by reducing agents to 2,3-dichloro-5,8-dihydro-1,4-naphthohydroquinones (II).[5] When zinc dust was added to a solution of the adducts in acetic acid a rapid exothermic reaction occurred; iron-by-hydrogen in acetic acid, stannous chloride in hydrochloric and acetic acids,[6] and zinc or Raney nickel in ethanol also brought about the transformation in specific instances. Zinc in toluene did not affect the butadiene adduct; magnesium in ethanol gave, after oxidation, 2-chloro-3-ethoxy-1,4-naphthoquinone. In most cases the dihydronaphthohydroquinones obtained routinely by the action of zinc in acetic acid were oxidized in solution (they are sensitive to light[7]) to the corresponding naphthoquinones (III) by chromic acid. The 1-acetoxybutadiene adduct lost the acetoxyl group when treated in this manner, giving 2,3-dichloronaphthoquinone.

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(1) However, adducts derived from mono- and dihalonaphthoquinones, etc., and having angular halogens, are well known; for a review, see L. W. Butz and A. W. Rytina in R. Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 136–192. Also, products obtained from chloranil and diene analogs (anthracene, 10-methylene-9-anthrone) presumably proceed through adducts with angular halogens.

(2) L. W. Butz, A. M. Gaddis and E. W. J. Butz, THIS JOURNAL, **69**, 924 (1947), described an adduct of chloranil with 2,5-dimethyl-1,5-hexadien-3-yne, but suggested no structure.

(3) Modern authors have formulated this reaction as a normal diene condensation; W. Rubin and A. Wassermann, *J. Chem. Soc.*, 2205 (1950), concluded from a study of kinetics that it did not differ qualitatively from the usual addition of dienes to quinones.

(4) W. Albrecht, *Ann.*, **348**, 31 (1906).

(5) Aromatization of these adducts with retention of the desired 2,3-dichloronaphthoquinone structure presented a special problem. Adducts with exclusively angular chlorines have been converted to aromatic compounds by sodium acetate, alkalies, amines, oxidizing agents, or heat in specific cases.[1] The first reagent gave only a trace of 5,7-dimethyl-2,3-dichloro-1,4-naphthoquinone from the 2-methylpentadiene derivative, which was unaffected by chromic acid. More alkaline conditions were obviously inapplicable because of the ease with which one chlorine of a 2,3-dichloroquinone is displaced by nucleophilic reagents.

(6) The reaction recalls the conversion of a 2,2-dichloro-3,5-cyclohexadienone type to a 2-chlorophenol type with this reagent by L. F. Fieser and J. T. Dunn, THIS JOURNAL, **59**, 1024 (1937).

(7) *Cf.* L. F. Fieser, *ibid.*, **70**, 3165 (1948), who discusses the properties of compounds of this type obtained from dienes and benzoquinones.