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.

SOUTH MIAMI 43, FLORIDA

[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

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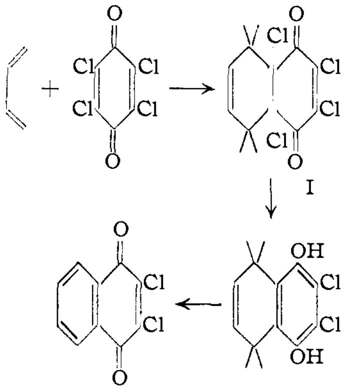
Chloranil or 2,5-dichloroquinone and simple dienes form crystalline 1:1 adducts, which contain both angular and "vinyl" halogen atoms. Removal of the angular groups by reducing agents with concomitant aromatization of the potentially quinoid ring followed by oxidation of the 5,8-dihydro- or 5,6,7,8-tetrahydronaphthohydroquinones 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.



III II

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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).

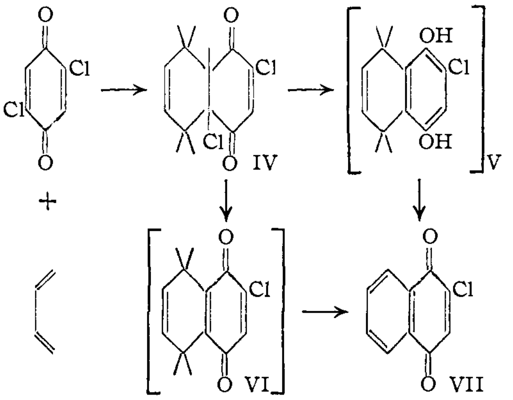
[5] Aromatization of these adducts with retention of the desired 2,3-dichloronaphthoquinone structure presented a special problem. Adducts with exclusively angular chlorines have been converted to aromatic compounds by sodium acetate, alkalies, amines, oxidizing agents, or heat in specific cases.[1] 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.

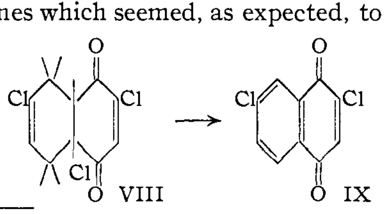
[6] The reaction recalls the conversion of a 2,2-dichloro-3,5-cyclohexadienone type to a 2-chlorophenol type with this reagent by L. F. Fieser and J. T. Dunn, THIS JOURNAL, **59**, 1024 (1937).

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

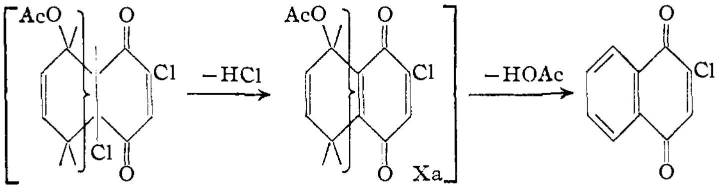
The mechanism of the rapid reduction is probably not simple dehalogenation of a 1,2-dihalide since the angular chlorines are doubtless *cis* in these adducts; presumably the reaction is to be viewed as reduction of an α-haloketone[8] with the formation of the aromatic hydroquinone the driving force.

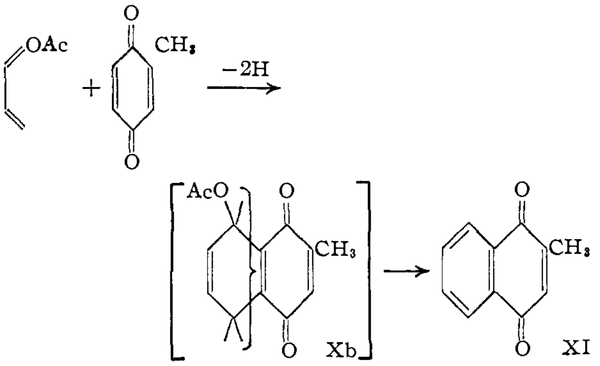
By analogy with the reactions with chloranil it seemed that 2,5-dichloroquinone should react with dienes to give adducts in which one chlorine would be angular and the other "vinyl." This possibility was realized, although the instability to light of the crystalline adducts from cyclopentadiene, chloroprene and 2,3-dimethylbutadiene prevented satisfactory characterization. However, the solutions of the adducts in benzene were rather stable and gave rise to 2-chloro-5,8-dihydro-1,4-naphthohydroquinones (*e.g.*, V) when treated with zinc in acetic acid. Oxidation *in situ* afforded the corresponding quinones VII.[9] Alternatively *sym*-collidine dehydrohalogenated IV to the 5,8-dihydroquinone VI which was oxidized to VII. These methods were applied also to solutions of adducts from the unsymmetrical dienes, 2-methylpentadiene and isoprene. However, in both cases only one of the two possible isomeric naphthoquinones could be obtained in pure form; their structures were not established nor could a ratio of isomers be estimated. In the case of chloroprene the pure major adduct was VIII since it was converted to 2,7-dichloro-1,4-naphthoquinone (IX). The use of 2,6-dichloroquinone afforded mixtures of naphthoquinones which seemed, as expected, to be principally isomeric with those derived from the 2,5-isomer; similar difficulties were encountered in the separations.



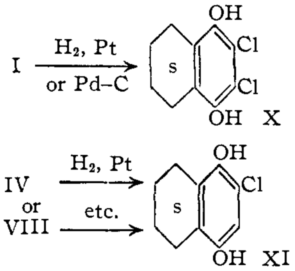


When 1-acetoxybutadiene was added to 2,5-dichloroquinone, and the product dehydrohalogenated with collidine and oxidized, the acetoxyl group was lost. The similar loss of acetoxyl from the acetoxybutadiene–chloranil adduct upon treatment with zinc in acetic acid and the fact that attempted dehydrogenation of the adduct mixture from acetoxybutadiene and toluquinone produced only 2-methyl-1,4-naphthoquinone (XI), suggests that elimination of the acetoxyl group from 5-acetoxy-5,8-dihydronaphthohydroquinones (*e.g.*, Xa and Xb) is nearly independent of the experimental conditions and probably promoted by the resulting aromatization.[10]





Removal of the angular chlorines from the derivatives of both chloranil I and 2,5-dichloroquinone (IV) was accomplished also by catalytic low-pressure hydrogenation[8] over palladium-on-charcoal or platinum oxide. The latter also effected saturation of the isolated double bond. The nature of the products (X and XI) was indicated in the case of the butadiene derivatives by the identity of the corresponding quinones with samples prepared by usual methods. Although palladium-on-charcoal also catalyzed in part conversion of I to X, both the chloranil–2,3-dimethylbutadiene and –isoprene adducts escaped



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[8] Reductive removal of halogen α to a carbonyl group has been accomplished by various reagents including stannous chloride,[6] Grignard reagents (C. H. Fisher, T. S. Oakwood and R. C. Fuson, THIS JOURNAL, **52**, 5036 (1930)), catalytic hydrogenation (J. S. Buck and W. S. Ide, *ibid.*, **54**, 4359 (1932)) and zinc in acetic acid (W. R. Nes and H. L. Mason, *ibid.*, **73**, 4765 (1951), and other references therein). The latter reaction, accomplished under reflux, is not spontaneous as in the present case.

[9] Fieser and Dunn[6] obtained phenanthraquinones, etc., by direct oxidation of diene derivatives of 3-bromo-1,2-naphthoquinone and related compounds with chromic acid. However, this method converted IV to tar from which no trace of a quinone could be isolated.

[10] R. Adams and J. D. Edwards, Jr., *ibid.*, **74**, 2605 (1952), observed elimination of the acetoxyl group from the acetoxybutadiene–*p*-quinone monobenzenesulfonimide adduct by hydrobromic acid.

saturation over this catalyst, *i.e.*, 5,8-dihydrohydroquinones were obtained. In subsequent runs platinum effectively saturated all chloranil and dichloroquinone adducts studied. The chlorine in the 7-position of the chloroprene–2,5-dichloroquinone adduct VIII was removed during hydrogenation, giving a product identical with that from butadiene XI.

In the Experimental part the specific products of these reactions are tabulated. The study of certain similar reactions continues.

Acknowledgments.—The author is indebted to Mr. Donald Stoltz and Mrs. Winifred Harden for the microanalyses. He is grateful to Drs. William S. Emerson, W. Scott Worrall, Bernard S. Wildi and Erhard J. Prill for discussions and encouragement during this work.

Experimental Part[11]

Addition of Dienes to Chloranil (Procedure A).—A mixture of 0.1 mole of chloranil, usually a 10% excess of diene and 80 ml. of reagent benzene was rocked and heated in a 300-ml. bomb under the conditions listed in Table I, cooled slightly and emptied with rinsing with benzene. Pressures were not recorded, and there was no indication of an exothermic reaction in any case. In most runs unchanged chloranil separated from the colored solution (light brown to black). Tetrachlorohydroquinone, mixed with the black quinhydrone (which gave only chloranil when oxidized with chromic acid), often formed an adherent cake in the bomb; all insoluble material was calculated as chloranil in the reports of yields and conversions.

The charcoal-treated solution was concentrated by distillation and the benzene replaced with methanol (with removal of more chloranil), concentrated again, and the rather pure crude nearly colorless to tan adduct allowed to crystallize. For analysis the crystals could be recrystallized from methanol, followed by sublimation below 100° at 1 mm.

Some entries in Table I are based on charges of 0.05–0.3 mole of chloranil. Results of a few experiments in boiling benzene are included; however, only methylpentadiene and isoprene reacted at a practical rate. Difficulties with bumping do not recommend this procedure in general.

When catalytic amounts of trichloroacetic acid were added to a run with isoprene in refluxing benzene (24 hours), hydrogen chloride was evolved and only tetrachlorohydroquinone (76%) was isolated. Sorbic acid had not reacted in boiling benzene after 70 hours. Chloroprene after 96 hours had polymerized, chloranil being recovered; at 120° in the bomb tetrachlorohydroquinone was isolated. At 110° in the presence of trimethylamine and *t*-butylcatechol a tarry polymer was formed. Attempted condensations also failed with hexachlorocyclopentadiene, hexachlorobutadiene, 2-lauroxybutadiene, 1,3-dichloro-2,4-pentadiene, 1,4-diphenylbutadiene and 2,5-dimethylfuran. Attempts to condense octachlorodiphenoquinone with 2,3-dimethylbutadiene (110°, benzene, 48 hours) or butadiene (90°, benzene, 40 hours) gave octachlorodihydroxybiphenyl as the only product isolated.

Reduction–Aromatization of Adducts (Procedure B).—To a solution or suspension of the adduct in about tenfold its weight of glacial acetic acid was added at once an excess (at least 10%) of zinc dust. The reaction was spontaneous and exothermic, the temperature rising to 60–90°. When the reaction began to subside, the mixture was swirled and heated briefly on the hot plate. The excess zinc was removed by filtration of the hot solution and rinsed with hot acetic acid. Since 2,3-dichloro-5,8-dihydro-1,4-naphthohydroquinones are darkened and destroyed by air and light,[7] the solution was oxidized by addition of excess chromic acid in the minimum amount of water at 60–80°. The crude 2,3-dichloro-1,4-naphthoquinones (Table II) obtained by dilution with water were rather pure and were prepared for analysis by recrystallization from methanol, alone or replacing chloroform by distillation, followed by sublimation *in vacuo* at 100–130°.

TABLE I

CHLORANIL ADDUCTS (PROCEDURE A)

°C.	Hr.	Percentage Yield	(conv.)	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Butadiene								
100	48	86	(35)	74.5–76.5	40.04	2.01	40.32	2.46
110	65	98	(73)					
Isoprene								
80[a]	72	77	(42)	96.5–98	42.07	2.57	42.19	2.68
90	90	87	(81)					
100	20	30.5[b]	(25)					
2-Methyl-1,3-pentadiene								
80[a]	24	86[c]	(86)	50.5–52.5	43.93	3.07	44.25	3.42
90	72	76	(76)					
1-Acetoxybutadiene								
100	48	45	(32)	95.5–96.5	40.25	2.25	40.31	2.66
2,3-Dimethylbutadiene								
110	38	96	(96)	96.5–98.5	43.93	3.07	44.23	3.34
120	48	74	(74)					
140[d]	90	..	..					
Cyclopentadiene[e]								
70	48	62	(62)	143–145[4]				
50	65	88	(88)	145–147[4]				

[a] In boiling benzene at atmospheric pressure. [b] Hydrogen chloride was evolved, no chloranil was recovered, and the hydroquinone separated. A contaminant (rust?) in the bomb may have been responsible; when the bomb was cleaned with dilute hydrochloric acid before use no difficulty was experienced. [c] Isolated as a viscous red distillate, b.p. 117–137° (0.2 mm.), which slowly crystallized. [d] Using 0.15 mole of diene to 0.05 mole of chloranil, the product was black and intractable. [e] With 1 ml. of trimethylamine in methanol as catalyst.[4]

When 6.0 g. of the 1-acetoxybutadiene–chloranil adduct was reduced as usual and oxidized, only 2,3-dichloro-1,4-naphthoquinone (m.p. 187–192°, 3.65 g., 96%) was obtained.

TABLE II

2,3-DICHLORO-1,4-NAPHTHOQUINONES (PROCEDURE B)

Subst.	Yield	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
....	71	191–193	...			
6-Methyl	51	149–150	54.80	2.51	54.82	2.90
5,7-Dimethyl	64	158–159	56.50	3.16	56.98	3.51
6,7-Dimethyl[a]	65	219–220	56.50	3.16	56.45	3.24
5,8-Dihydro- 5,8-methano	85	145–146	54.80	2.51	54.96 54.93	2.83 2.60

[a] During reduction of the adduct, white needles precipitated and were removed by filtration; purified by rapid recrystallization from acetone–methanol, they darkened in air. The color was removed by charcoal but reappeared rapidly in the filtrate. However, the red crystals of impure 2,3-dichloro-5,8-dihydro-6,7-dimethyl-1,4-naphthohydroquinone, m.p. 221–223°, had the expected composition. *Anal.* Calcd. for $C_{12}H_{12}O_2Cl_2$: C, 55.62; H, 4.67. Found: C, 55.70; H, 4.58.

A brief study of variations of the reduction–aromatization revealed that, although zinc in boiling toluene did not attack the butadiene–chloranil adduct, use of boiling ethanol gave after 2 hours, followed by dilution with acetic acid and oxidation, the dichloronaphthoquinone (69% yield). A single run using iron-by-hydrogen in acetic acid proved it superior (84% yield) to zinc. Magnesium in commercial anhydrous ethanol, heated under reflux with the butadiene–chloranil adduct for 30 minutes, then diluted with acetic

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[11] Melting points are corrected; boiling points are not. Statements of identity are based upon the failure of mixture melting points with authentic samples to show depression, unless other evidence is specifically mentioned. The generalized procedures are presented to conserve space; the tabulated results occasionally were obtained with minor variations, which have been mentioned in footnotes if they seem consequential.

acid and oxidized, yielded 38% of 2-chloro-3-ethoxy-1,4-naphthoquinone,[12] m.p. 95.5–97.5°, identical with a sample prepared by adding rapidly a solution of 22.7 g. of 2,3-dichloro-1,4-naphthoquinone in 100 ml. of benzene to a solution of 5 g. of sodium in 50 ml. of anhydrous ethanol; dilution and extraction with ether gave 15.9 g. (67%).

The chloranil-2-methylpentadiene adduct, with excess sodium acetate in acetic acid, heated under reflux 12 hours, afforded only a trace of 2,3-dichloro-5,7-dimethyl-1,4-naphthoquinone. *sym*-Collidine with this adduct in boiling benzene gave only water-soluble and tarry products.

When 5 g. of the chloranil–isoprene adduct in 50 ml. of acetic acid was treated with 18 g. of stannous chloride dihydrate in 18 ml. of concd. hydrochloric acid, and the mixture warmed to 90° briefly and diluted with water, white 2,3-dichlorodihydro-6-methyl-1,4-naphthohydroquinone (3.35 g., 85%) separated. Surprisingly it darkened only slightly during recrystallization from carbon tetrachloride and drying *in vacuo*, but the analysis showed poor agreement [*Anal.* Calcd. for $C_{11}H_{10}O_2Cl_2$: C, 53.90; H, 4.11. Found: C, 53.26; H, 4.44]; m.p. 118–120°. It was probably not the 5,8-dihydro isomer but may be a 5,6-dihydro compound since oxidation with chromic acid converted it quantitatively to 2,3-dichloro-6-methyl-1,4-naphthoquinone. The chloranil–isoprene adduct (3.12 g.) also was converted to this quinone (78% yield) by heating under reflux with 69 g. of old Raney nickel catalyst sludge and 150 ml. of ethanol for 30 minutes; the mixture was cooled, filtered, concentrated by distillation and diluted with water. The tan precipitate did not melt on a heated spatula, left a residue on burning and was oxidized directly with chromic acid.

Chlorination of 5,7-Dimethyl-1,4-naphthoquinone.[13]—A solution of 9.3 g. of the quinone in 50 ml. of acetic acid containing 0.5 g. of iodine was saturated with chlorine without heating; 9 g. of anhydrous sodium acetate and 75 ml. of acetic acid were added, and the mixture was heated under reflux with stirring as chlorine was allowed to bubble through the solution for 2 hours. Dilution with water and careful recrystallization from 1:1 chloroform–methanol gave 0.4 g. of 2,3-dichloro-5,7-dimethyl-1,4-naphthoquinone, m.p. 158–160°, identical with the product derived from chloranil. The remaining product was a mixture, m.p. 102–122°.

Addition of Dienes to Dichloroquinones (Procedure C).—Usually 0.1 mole of 2,5-dichloroquinone and a 10% excess of diene in 100 ml. of reagent benzene were heated under reflux 48 hours. Isolation of the adduct was accomplished by aspiration of the solvent below 40°. Some darkening of the crystalline adducts always occurred, most markedly in bright light. They decomposed slowly when dry with evolution of hydrogen chloride. Solutions in benzene were stable unless more concentrated than those described above, even after being heated for several days, although no better yields were noted after longer heating periods. The adducts could be recrystallized (with some loss due to decomposition) from methanol with a minimum period of heating. A satisfactory analysis could be obtained only with the butadiene derivative.

Anal. Calcd. for $C_{10}H_8O_2Cl_2$: C, 51.98; H, 3.49. Found: C, 52.42; H, 3.80.

The other compounds either decomposed too rapidly for recrystallization and analysis or could not be freed completely from contaminating yellow impurities, probably quinones. The yields listed below refer to crude products which are essentially pure; melting points are the best noted during attempted purification for analysis. No attempt was made to isolate adducts from unsymmetrical dienes; the separation of the higher-melting adduct from chloroprene occurred spontaneously when the solution, which had been diluted to 125 ml. with benzene, was allowed to stand at ordinary temperatures. The mixture remaining in the benzene was obtained by replacing the solvent with methanol, by distillation and allowing crystallization to take place; it could not be more completely separated.

Diene	Yield, %	M.p., °C.
Cyclopentadiene	93	113.5–115.5
Butadiene	83	84–86
Chloroprene	37	145–147
	39	111–121
2,3-Dimethylbutadiene	80	102.5–104.5

2-Chloro-1,4-naphthoquinones from 2,5- and 2,6-Dichloroquinones (Procedures Dc and Dz).—Early in the work collidine was used as the dehydrohalogenating agent for adducts. Although it later became apparent that the reduction with zinc was more convenient and of comparable efficiency, both procedures are presented. It was not feasible to repeat all preparations with zinc.

Dc.—With collidine, the adducts were formed in benzene as usual and to the cooled solution was added the theoretical amount of 2,4,6-collidine; the mixture was swirled and usually placed in cool water to prevent a rise in temperature. After several days at room temperature in a stoppered flask, the cake of collidine hydrochloride which had separated was removed by filtration and washed with benzene. The washings and mother liquors were combined and washed with dilute hydrochloric acid, diluted with an equal volume of acetic acid and oxidized with chromic acid as in procedure B. The quinone was isolated from the benzene layer after dilution, or more easily, the benzene was removed by distillation with steam, whereupon the quinone separated from the cooled aqueous solution.

Dz.—With zinc, either the crystalline adduct could be treated according to procedure B or its solution in benzene was diluted with an equal volume of acetic acid and processed similarly. The filtered solution was oxidized directly in all cases, without isolation of the presumably unstable 2-chloro-5,8-dihydro-1,4-naphthohydroquinones. The 2-chloro-1,4-naphthoquinones in Table III were recrystallized from methanol and sublimed *in vacuo* for analysis. It was not possible in any case to separate completely isomers obtained from an unsymmetrical diene. Only one isomer could be isolated in a state of reasonable purity.

Attempts to aromatize the cyclopentadiene adduct by either procedure yielded only gummy intractable materials. Condensations with 1-phenylbutadiene, 1-4-diphenylbutadiene or sorbic acid failed, as judged by attempts to aromatize the mixture. Use of pyridine in place of collidine in the dehydrohalogenation of 0.02 mole of the chloroprene adduct mixture in benzene afforded, after oxidation, 5.4 g. of orange acetone-insoluble plates, m.p. 265–267°, which were not identified.

Anal. Found: C, 56.33; H, 3.36.

Oxidation of a solution in benzene–acetic acid of 0.025 mole of the butadiene–2,5-dichloroquinone adduct with excess chromic acid at 50° gave water-soluble black materials but no detectable 2-chloro-1,4-naphthoquinone.

Use of 2,6-Dichloroquinone.—When this quinone was employed in place of the 2,5-isomer, in reactions with isoprene and chloroprene according to procedures C and Dc or Dz, the products seemed to be predominantly isomeric with those of the earlier reactions. The results summarized in Table IV do not justify a conclusive statement in this connection because of unresolved difficulties encountered in the separation of mixtures of products.

When 17.7 g. of the quinone and 12.3 g. of 2-methylpentadiene were mixed without a solvent, a vigorous reaction occurred with evolution of hydrogen chloride. After being cooled and aspirated, the viscous residue was oxidized. The orange needles (6.6 g.), m.p. 132–133°, were not identified.

Anal. Found: C, 62.03; H, 4.09; Cl, 20.72.

Similarly 6.5 g. of the quinone and 3.5 g. of cyclopentadiene in 50 ml. of benzene at room temperature 4 days, by aspiration and addition of methanol, afforded 2.35 g. of white crystals, m.p. 138–140° dec., which darkened and evolved hydrogen chloride in a few hours. When 2.3 g. of the partially decomposed adduct was aromatized (Dz), 0.9 g. of a colorless mixture was obtained and separated by recrystallization from chloroform–methanol. Neither component was identified. The less soluble plates melted at 262–263° (dec., bath preheated to 248°).

Anal. Found: C, 86.80; H, 7.70.

The prisms melted at 188.5–190.5°. *Anal.* Found: C, 72.55; H, 6.28.

Hydrogenation of Haloquinone–Diene Adducts (Procedure E).—The crystalline adduct in a volume of acetic acid

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[12] L. F. Fieser, This Journal, **48**, 2922 (1926).

[13] The quinone described by H. v. Euler and H. Hasselquist, *Arkiv. Kemi*, **2**, 367 (1950); *C. A.*, **45**, 1989*b* (1951), was prepared from quinone and 2-methylpentadiene in 89% yield by the general procedure of Fieser.[7]

TABLE III

2-CHLORO-1,4-NAPHTHOQUINONES FROM 2,5-DICHLOROQUINONE (PROCEDURE D)

Subst.	Yield, %	M.p., °C.	Proc.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
5,7- (or 6,8-) Dimethyl[b]	25	123–125	[a]	65.31	4.11	65.33	4.25
					Cl, 16.07		Cl, 16.28
[c,d]	22	72.5–75.5	Dc				
6,7-Dimethyl	86	145–147	Dc	65.31	4.11	65.63	4.32
7-Chloro	40	187.5–188.5	Dc	52.90	1.78	53.15	2.10
6-Chloro[c]	14	136–140[e]		52.90	1.78	53.24	2.00
6- and 7-Chloro[c]	59	117–142	Dz				
7-Chloro[f]	73	185.5–187.5	Dz				
......	71	109.5–111.5	Dz				
......	100	109.5–112.5	Dc				
......[g]	43	113.5–114.5	Dc	62.36	2.62	62.75	2.95
7- or 6-Methyl	47	125–126	Dc	63.97	3.42	64.01	3.55
6- or 7-Methyl[c]	23	102–117					

[a] Braces associate fractions from the same run. [b] Identical with the product of chlorination of 5,7-dimethyl-1,4-naphthoquinone as described above but without the addition of iodine; yield 29%. The analysis was performed on this purified material, m.p. 126–127°. [c] Not obtained isomerically pure. [d] From the reaction with methylpentadiene was isolated 0.7 g. of a methanol-insoluble compound, m.p. 189.5–190.5°, with the composition of a tetrahydrotetramethylanthraquinone. *Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.49; H, 7.82. [e] Pure 2,6-dichloro-1,4-naphthoquinone melts at 148–149° (A. Claus and P. F. Müller, *Ber.*, 18, 3073 (1885)). [f] From the adduct melting at 145–147°. [g] The diene was 1-acetoxybutadiene; the product was identical with that from butadiene.

TABLE IV

2-CHLORO-1,4-NAPHTHOQUINONES FROM 2,6-DICHLOROQUINONE

Subst.	Yield, %	M.p., °C.	Proc.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
6- or 7-Methyl[a]	38	140.5–142.5 [c]	Dc	63.97	3.42	64.25	3.58
7- or 6-Methyl[a,b]	14	109.5–114.5					
6- and 7-Chloro[b]	30	122	Dc	52.90	1.78	53.13	2.49
7-Chloro[b]	15	163–171	Dz				
6- and 7-Chloro[b]	53	96.5–116.5					

[a] Mixtures with corresponding derivatives of 2,5-dichloroquinone were at least measurably depressed. [b] Not obtained isomerically pure; chloroform–methanol was the solvent for all recrystallizations. [c] Braces associate fractions from the same run.

TABLE V

5,6,7,8-TETRAHYDRO-1,4-NAPHTHOHYDROQUINONES (PROCEDURE E)

Subst.	Adduct, g.	Yield, %	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2,3-Dichloro[a]	9.0	84	123–125[b]	51.53	4.32	51.62	4.88
2,3-Dichloro-6-methyl	12.6	81	119–120	53.46	4.90	53.85	5.19
2,3-Dichloro-5,7-dimethyl	5.0	99	81.5–86.5[c]	55.19	5.40	55.94	5.46
2,3-Dichloro-6,7-dimethyl	10.0	75	115–142[f]	55.19	5.40	55.73	5.76
2,3-Dichloro-5,8-methano	12.5	98	139–141	53.90	4.11	54.02	4.40
2-Chloro	7.0	65	141–142	60.46	5.58	60.16	5.62
2-Chloro[e]	6.0	68	139–141	...			
2-Chloro-6,7-dimethyl	10.0	6.2[d]	101.5–102.5	63.57	6.67	63.84	6.76

[a] Catalyst: 10% palladium-on-charcoal. [b] Recrystallized from aqueous acetic acid. [c] This mixture could not be purified; recrystallization gave finally only a trace of 2,3-dichloro-5,7-dimethyl-1,4-naphthoquinone, m.p. 155–157°. [d] When the filtered diluted mixture was refrigerated overnight, these colorless plates separated from the black oil which was oxidized directly with ferric chloride. Extraction with ether, etc., gave 5.7 g. of a red oil which corresponded approximately in composition to the expected quinone plus hydrogen chloride. The presence of excess sodium acetate did not alter the course of hydrogenation. *Anal.* Calcd. for $C_{12}H_{14}Cl_2O_2$: C, 55.19; H, 5.40. Found: C, 56.90; H, 5.18. [e] The starting material was the high-melting chloroprene–2,5-dichloroquinone adduct. [f] This mixture could not be separated and may consist of *dl-* and *meso-*isomers.

equal to tenfold the weight of adduct with 0.1–0.5 g. of platinum oxide was exposed to less than 50 p.s.i. of hydrogen pressure at room temperature in a low-pressure hydrogenation apparatus with provision for shaking. The larger fraction of the calculated decrease in pressure (2 moles of hydrogen per mole of a chloranil adduct or 1 for a 2,5-dichloroquinone derivative) usually was absorbed within 10–15 minutes, corresponding to the removal of the angular chlorine atoms, and the white 5,8-dihydro-1,4-naphthohydroquinone occasionally precipitated. As another mole of hydrogen was absorbed with the saturation of the double bond, any precipitate usually dissolved and the reaction was complete within 1 hour. The catalyst was removed by warming to dissolve precipitates and filtering; dilution with ten volumes of water precipitated the tetrahydronaphthohydroquinone. The presence of a small amount of an oil with a sweet odor often suggested that more extensive hydrogenation had occurred. The products were purified for analysis by repeated recrystallization from carbon tetrachloride. The white needles darkened slightly in air if wet with solvent or during drying *in vacuo;* the results are summarized in Table V.

As noted in the table, 10% palladium-on-charcoal was a catalyst for saturation of the butadiene–chloranil adduct.

TABLE VI

5,6,7,8-TETRAHYDRO-1,4-NAPHTHOQUINONES

Subst.	Yield, %	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2,3-Dichloro	86[a]	147–149	[b]			
2,3-Dichloro-6-methyl	95	119–120	53.90	4.11	53.97	4.30
2,3-Dichloro-5,7-dimethyl	94	Red oil[c]	55.62	4.67	56.83	4.75
2,3-Dichloro-6,7-dimethyl	100	70.5–71.5[f]	55.62	4.67	56.09	4.77
2,3-Dichloro-5,8-methano	94	138.5–140.5	54.35	3.32	54.67	3.18
2-Chloro	100	54–58	[d]			
2-Chloro-5,8-methano	77	Red oil[e]	63.32	4.35	63.76	5.18

[a] This yield was obtained by hydrogenation of the adduct followed by oxidation directly. Using chromic acid, the yield was 71% from the hydroquinone. [b] Identical with material prepared by the method of A. Skita and W. Rohrmann, *Ber.*, **63B**, 1473 (1930); m.p. 151–153°. The reported melting point was 145–147°. [c] This oily quinone could not be purified although 0.3 g. of 2,3-dichloro-5,7-dimethyl-1,4-naphthoquinone separated from its solution in ether; it is probably a mixture of stereoisomers. [d] As in (*b*); m.p. 63–64°. [e] The hydroquinone was an intractable gum which was oxidized directly with ferric chloride. [f] The crude quinone had a wide melting range, 74–94°; no other pure material could be separated.

On the contrary, both the isoprene and 2,3-dimethylbutadiene derivatives were converted to 5,8-dihydro compounds. Thus a mixture of 9.6 g. of the chloranil–isoprene adduct with 0.5 g. of catalyst in 50 ml. of methanol was hydrogenated as usual; absorption ceased after 2.05 moles of hydrogen/mole of adduct had been taken up, to give an homogeneous solution. Dilution precipitated 6.8 g. (90%) of white matted needles, m.p. 144–146° dec., which were too sensitive to air and light for analysis, but were oxidized (6.0 g.) with chromic acid to 2,3-dichloro-6-methyl-1,4-naphthoquinone (72% yield); m.p. 152–153°. The difference between the dihydro compound and that obtained by reduction with stannous chloride may be isomerism of the double bond. Similarly, 5.75 g. of the chloranil-2,3-dimethylbutadiene adduct absorbed 1.93 moles of hydrogen/mole of adduct in 40 ml. of acetic acid with 0.4 g. of catalyst. A total of 3.8 g. (83%) of 2,3-dichloro-5,8-dihydro-6,7-dimethyl-1,4-naphthohydroquinone (m.p. 224–226°), identical with the product obtained with zinc in acetic acid, was isolated.

Oxidation of the hydroquinone in acetic acid was effected by either chromic acid as usual or at room temperature with a solution of ferric chloride hexahydrate (1 g./ml.) in excess. Dilution with water precipitated the quinone; if an oil it was isolated by extraction with ether, the extracts being treated with charcoal before drying and evaporation left the red oily quinone. Crystalline yellow quinones were purified as were the aromatic analogs.

2,3-Dichloro-1,4-naphthoquinone Adducts.—When 11.4 g. of the quinone, 8.3 g. of 2-methylpentadiene and 100 ml. of benzene were heated under reflux 24 hours, another 15 ml. of the diene added and heating continued a like period, a total of 4.85 g. (31% conversion, 48% yield) of an adduct was isolated and purified by recrystallization from methanol and sublimation at 90° (0.5 mm.), m.p. 97.5–99.5°.

Anal. Calcd. for $C_{16}H_{14}Cl_2O_2$: C, 62.15; H, 4.56. Found: C, 62.65; H, 4.86.

In the bomb at 90° for 48 hours only a 24% yield was obtained.

The adduct (3.0 g.) was treated with 0.6 g. of iron-by-hydrogen in 50 ml. of acetic acid. No reaction occurred at 25° but a light-colored solid separated after heating under reflux 10 minutes. After oxidation with chromic acid, 0.55 g. (24%) of 1,3-dimethyl-9,10-anthraquinone[14] was isolated and purified by recrystallization from ethanol; m.p. 159–161°.

An adduct of the quinone (11.5 g.) with cyclopentadiene (5 g.) was formed at room temperature (65 hours) in 50 ml. of benzene, followed by 48 hours at 65°. A total of 6.0 g. (41% conversion, 69% yield) of brown crystals separated from methanol; m.p. 146–148°. They could not be purified by recrystallization; when sublimation was attempted at 110° (0.5 mm.), only dichloronaphthoquinone was obtained by reversal of the addition.

Attempts to aromatize or hydrogenate by the methods of this paper the 3,4-dichloro-1,2-naphthoquinone-2,3-dimethylpentadiene adduct[15] produced gums or oils of undetermined constitution. Similar results were obtained upon hydrogenation of the 2,3-dichloro-1,4-naphthoquinone-2-methylpentadiene adduct.

Condensation of 1-Acetoxybutadiene and Toluquinone.—A mixture of 11 g. of the diene and 11.2 g. of toluquinone in 200 ml. of benzene was heated under reflux for 72 hours. After 250 ml. of xylene and 49 g. of chloranil had been added, the benzene was removed by distillation until the temperature of the solution reached 135°; heating was continued for 4 hours. The cooled mixture was filtered to remove 35 g. of chloranil and tetrachlorohydroquinone. The xylene layer was washed with sodium carbonate solution and dilute alkali and dried over calcium chloride. A total of 6.45 g. (37%) of 2-methyl-1,4-naphthoquinone[16] was isolated. Before its identity was apparent, recrystallization and sublimation gave yellow needles, m.p. 106–107°.

Anal. Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 77.04; H, 4.97.

DAYTON, OHIO

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[14] O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

[15] L. F. Fieser and J. T. Dunn, THIS JOURNAL, **59**, 1016 (1937).

[16] *Cf.* F. Radt, "Elsevier's Encyclopedia of Organic Chemistry" Vol. 12B, Elsevier Publishing Co., New York, N. Y., 1952, p. 2823.