Phenolysis of *gem*-Dichlorocyclopropanes

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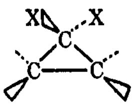
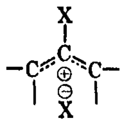
Since Doering's and Hoffmann's discovery of a simple general synthesis of *gem*-dihalocyclopropanes,[1] these compounds have been used in the synthesis of many otherwise difficultly accessible molecules.[2] Solvolysis of *gem*-dihalocyclopropanes, in principle a generally useful synthetic procedure, has had limited application because of their low reactivity under the usual solvolytic conditions. Special structures, notably 6,6-dihalobicyclo[3.1.0]hexanes[3] and alkoxy-substituted *gem*-dihalocyclopropanes,[4] are especially reactive and have shown useful solvolytic reactivity. The minimum structural change observed during these solvolyses was similar to the acetolytic conversion of cyclopropyl tosylate to allyl acetate observed by Roberts and Chambers.[5] The bond opposite the *gem*-dihalo group was broken with probable initial generation of an allylic ion-pair moiety. A substantial change in molecular geometry[6] is required for this transformation which is probably related to the low solvolytic reactivity of cyclopropyl halides and tosylates. Depending on substituents and reaction conditions, the intermediate allylic halide ion pair may be partly or completely converted to β-haloallylic halide,[7] to solvolysis products,[6] or by proton elimination to 2-halo-1,3-diene.[3b]

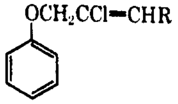




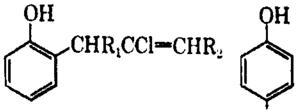
Recently high-temperature acetolysis of typically unreactive cyclopropyl halides[8] and tosylates[6,9] has been studied. The products, where isolated, fit the previously observed structural pattern. The variation of acetolysis rate with structure is consistent with the Woodward–Hoffman[10,11] rules for electrocyclic reactions as applied to incipient cyclopropyl cations isomerizing to allylic cations. This lends theoretical support to the expectation based on experience with especially reactive species that cyclopropyl halides generally will solvolyze with initial isomerization to allylic ion-pair intermediates.

We have found that phenol solutions of *gem*-dichlorocyclopropanes rapidly solvolyze at 150–178°, conditions under which the neat materials are usually indefinitely stable. In view of the possible utility of phenol as a solvent for kinetic studies of *gem*-dichlorocyclopropane reactivity (phenolysis)[12] and of the probable novelty of the reaction products, a detailed study was made of the phenolysis products from representative *gem*-dichlorocyclopropanes. The product studies were carried out in phenol containing excess sodium phenolate to suppress possible hydrogen chloride catalysis of side reactions. Phenolysis products from 2,3-dichloropropene (isomeric with 1,1-dichlorocyclopropane) were also studied. To the extent that β-chloroallylic chlorides or derived ion-pair species are intermediates in the phenolysis of *gem*-dichlorocyclopropanes related products should be obtained.

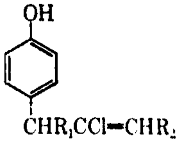
Phenolysis of 2,3-dichloropropene under the standard conditions (0.10 *M*, 175°, 0.22 *M* sodium phenoxide in phenol) gave two major phenolic products along with a major and a minor neutral product. The major neutral (Claisen's alkali insoluble) product was shown to be β-chloroallyl phenyl ether (IA) while the most abundant phenolic product proved to be *o*-β-chloroallylphenol (IIA), previously reported by Hurd and Webb[13] from Claisen rearrangement of IA. Because of a discrepancy between the observed and reported refractive index of IIA, it was reduced to the alkyl phenol which was identical by vpc with authentic *o*-*n*-propylphenol. This together with the 11.3-μ terminal methylene infrared band in the spectrum of IIA, established the structure. The second phenolic product, IIIA, gave the proper elemental analysis for a β-chloroallylphenol and was from its infrared spectrum a *para*-disubstituted benzene with an unhindered phenolic hydroxyl group. This and a terminal methylene infrared band at 11.3 μ showed the substance to be *p*-β-chloroallylphenol. The minor neutral product was not obtained pure and was not characterized.



IA, R = H
B, R = n-C_4H_9



II
A, $R_1 = R_2 = H$
B, $R_1 = H$; $R_2 = n$-C_4H_9
C, $R_1 = CH_3$ or C_2H_5; $R_2 = C_2H_5$ or CH_3
D, $R_1 = R_2 = (CH_2)_3$
E, $R_1 = R_2 = (CH_2)_4$



III

Phenolysis of 1,1-dichloro-2-*n*-butylcyclopropane gave three major products, one neutral and two phenolic, together with two minor neutral products. The most abundant phenolic product, IIB, was from its infrared and nmr spectra an *ortho*-substituted phenol. The elemental analysis of the phenoxyacetate of IIB required the substituent to be $C_7H_{12}Cl$. The presence

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[1] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[2] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 172–174.

[3] See, among others, (a) J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962); (b) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956); (c) C. W. Jefford, *Proc. Chem. Soc.*, 64 (1963); (d) L. Ghosez and P. Laroche, *ibid.*, 90 (1963).

[4] See, among others, (a) J. C. Anderson, D. G. Lindsay, and C. B. Reese, *Tetrahedron*, **20**, 2091 (1964); (b) W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Am. Chem. Soc.*, **83**, 603 (1961); (c) A. J. Birch and J. M. H. Graves, *Proc. Chem. Soc.*, 282 (1962); (d) M. F. Dull and P. G. Abend, *J. Am. Chem. Soc.*, **81**, 2588 (1959); (e) W. E. Parham, R. W. Soeder, and R. M. Dodson, *ibid.*, **84**, 1755 (1962).

[5] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

[6] C. H. DePuy, L. G. Schack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966).

[7] L. Gatlin, R. E. Glick, and P. S. Skell, *Tetrahedron*, **21**, 1315 (1965).

[8] S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Am. Chem. Soc.*, **87**, 4007 (1965).

[9] P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2868 (1966).

[10] R. B. Woodward and R. H. Hoffmann, *ibid.*, **87**, 395 (1965).

[11] H. C. Longuet-Higgins and E. W. Agrahmson, *ibid.*, **87**, 2045 (1965).

[12] Although phenol has not been studied as a solvent for solvolysis of simple alkyl halides, it does have a reasonable dielectric constant (9.78 compared with 6.6 for acetic acid) and is acidic, suggesting efficient anion solvation. The high boiling point of phenol (180°) is advantageous for study of unreactive halides.

[13] C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, **58**, 2190 (1936).

of a trisubstituted double bond was suggested by an infrared band at 11.92 μ and confirmed by the observation of a single vinyl proton in the nmr at 5.52 ppm. A two-proton singlet at 3.64 ppm shows the double bond to be one carbon atom removed from the aromatic ring with no hydrogen atom attached to the β-carbon. The presence of two allylic protons, four methylene protons, and a methyl group doublet shows the side chain structure is $CH_3CH_2CH_2CH_2CH{=}CClCH_2{-}$. A conceivable alternative structure $CH_3CH_2CH_2CH_2C({=}CHCl)CH_2{-}$, is ruled out since the vinyl proton triplet shows first-order coupling ($J = 7$ cps) to an adjacent methylene group.

The second phenolic product, IIIB, could not be induced to crystallize and alternate methods of purification failed; so a satisfactory elemental analysis was not obtained. A reasonably pure (90% by vpc) sample contaminated chiefly with IIB was examined by nmr and gave a pattern in the aliphatic and vinyl proton region very similar to IIB establishing the side-chain structure. The four-proton aromatic proton pattern was a pair of doublets characteristic of *para* disubstitution and the phenolic proton absorption was shifted to 6.28 from 5.29 ppm in IIB and broadened, indicating an unhindered hydroxyl group. From this evidence IIIB is *p*-(2-chlorohept-2-en-1-yl)phenol.

The neutral product, IB, was not obtained analytically pure on fractional distillation and partial decomposition occurred during preparative vpc separation. The aliphatic and vinyl proton pattern was, however, essentially the same as in IIB and IIIB, establishing the structure of the side chain. The presence of five aromatic protons and the absence of a phenolic proton showed IB to be 2-chlorohept-2-en-1-yl phenyl ether.

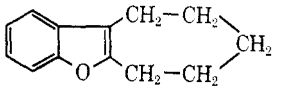
It is noteworthy that none of the allylicly isomeric 2-chlorohept-2-en-3-yl side chain was found among any of the reaction products although it would have been easily detected in the infrared and nmr spectra. The stereochemistry about the double bond was not established in these compounds although they appeared to consist of single isomers. The structure of the minor neutral products was not established although the ultraviolet spectrum of a mixture of the two was characteristic for a benzofuran[14] and the analysis was consistent with this hypothesis.

Phenolysis of mixed *cis*- and *trans*-1,1-dichloro-2-ethyl-3-methylcyclopropanes yielded two phenolic products together with two minor neutral components which were not investigated. The separated phenolic materials had generally similar nmr spectra in the nonaromatic proton region with the more volatile material, IIC, having a complex aromatic four-proton pattern characteristic for an *ortho*-disubstituted phenol while the less volatile material, IIIC, gave the pattern of a *para*-substituted phenol. The nmr spectra showed that IIC and IIIC were each mixtures of two isomeric products even though neither vpc nor distillation resolved the mixtures. Two well-separated methyl doublets were noted in IIC at 1.40 ($J = 6$ cps) and 1.67 ppm ($J = 7$ cps) and in IIIC at 1.36 ($J = 8.5$ cps) and 1.69 ppm ($J = 7$ cps) assignable to a methyl group at the benzylic carbon atom and to an allylic methyl group, respectively. Relative intensities showed the presence of comparable amounts of α-methyl-γ-ethylallyl and α-ethyl-γ-methylallyl isomers in each mixture, with the former predominating in the *ortho*-substitution product mixture and the latter predominating in the *para*-substitution product mixture.

Phenolysis of 6,6-dichlorobicyclo[3.1.0]hexane gave an unidentified minor neutral product and two phenolic products. The lowest boiling phenolic product, IID, gave a crystalline phenoxyacetate whose analysis required the substituent to be C_6H_8Cl. Reduction of IID gave *o*-cyclohexylphenol, demonstrating the presence of an *ortho* six-membered ring. The presence of one benzylic proton and a single vinyl proton triplet ($J = 3.5$ cps) further split by second-order coupling to doublets ($J = 1.2$ cps) is consistent only with a 2-chlorocyclohex-2-en-1-yl substituent. The four-aromatic proton pattern was characteristic for *ortho* substitution as was the hindered phenolic hydroxyl band in the infrared spectrum, showing IID to be (2-chlorocyclohex-2-en-1-yl)phenol.

The higher boiling phenol, IIID, from its analysis and infrared spectrum was identified as *p*-(2-chlorocyclohex-2-en-1-yl)phenol. Formation of *p*-cyclohexylphenol on reduction further confirmed the structure.

Phenolysis of 7,7-dichlorobicyclo[4.1.0]heptane gave two phenolic products and one neutral product. The neutral product, IV, $C_{13}H_{14}O$, showed the very characteristic three maximum ultraviolet spectra of a benzofuran[14] as well as the aromatic four-proton nmr pattern of an *ortho*-disubstituted benzene. The absence of methyl group absorption in the nmr spectrum together with the elemental analysis shows the aliphatic portion of the molecule to be $(CH_2)_5$. This requires 2,3 substitution of the benzofuran ring, which is confirmed by the presence of two distinct α-methylene nmr peaks and six aliphatic methylene protons. The neutral product is, therefore, 2,3-pentamethylenobenzofuran.



IV

The lowest boiling phenolic product, IIE, was isolated by distillation but proved unstable on standing, yielding IV with evolution of hydrogen chloride. By analogy with previous runs IIE is considered to be *o*-(2-chlorocyclohept-2-en-1-yl)phenol which can cyclize to IV, as was observed.

The least volatile phenol, IIIE, was *para* substituted from its aromatic four-proton pattern in the nmr. The elemental analysis requires the *para* substituent to be $C_7H_{10}Cl$. The absence of methyl group absorption in the nmr together with the presence of one benzylic proton and a vinyl one-proton triplet ($J = 6.5$ cps) requires formulation of IIIE as *p*-(2-chlorocyclohept-2-en-1-yl)phenol.

The relative amounts of the various products as determined by vpc analysis are summarized in Table I. The unknown minor neutral products are listed as benzofurans although only 2,3-pentamethylenobenzofuran was conclusively identified. Hurd and Webb found 3-methylbenzofuran among the products of Claisen rearrangement of β-chloroallyl phenyl ether,[13] and cyclization of the *o*-β-chloroallylphenolic products

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[14] J. Entel, C. H. Ruof, and H. C. Howard, *J. Am. Chem. Soc.*, **73**, 4152 (1951).

TABLE I

PHENOLYSIS PRODUCTS OF *gem*-DICHLOROCYCLOPROPANES

gem-Dichlorocyclopropane	Yield, %	Benzofuran, %	Allyl ether, %	Allylphenol, % *ortho*	Allylphenol, % *para*
Allyl chloride[a]	100		23	37	40
2,3-Dichloropropene	90	3[b]	52	24	14
1,1-Dichloro-2-*n*-butylcyclopropane	42	4[b]	17	17	4
1,1-Dichloro-2-ethyl-3-methylcyclopropane[b]		11		64	25
6,6-Dichlorobicyclo-[3.1.0]hexane	75	5[b]		56	14
7,7-Dichlorobicyclo-[4.1.0]heptane	60	29		14	17

[a] N. Kornblum, P. J. Berrigan, and W. J. Le Noble, *J. Am. Chem. Soc.*, **85**, 1141 (1963). Data at 43°. [b] Area % data only.

affords a reasonable route for formation of benzofurans in all our reaction mixtures.

The phenolysis products shown several gross features. They all contain phenol bonded at oxygen or at the *ortho–para* positions to a carbon chain derived from the *gem*-dichlorocyclopropane reactant by cyclopropane ring cleavage opposite the *gem*-dichloro group. Except for the benzofurans, which appear to be secondary products, the substituents all have a β-chloroallyl partial structure. These structural features are consistent with an initial solvolytic isomerization of the *gem*-dichlorocyclopropane to a β-chloroallylic chloride ion pair. The available data do not reveal the detailed route by which phenol (or sodium phenolate) subsequently becomes bonded to the β-chloroallylic system. The products from phenolysis of 2,3-dichloropropene are, however, identical in structural type and similar in relative abundance with those from 1,1-dichloro-2-*n*-butylcyclopropane.

More subtle features of the product distribution are predominance of *ortho* over *para* substitution and absence of O-alkylation products from phenolysis of 2,3-disubstituted *gem*-dichlorocyclopropanes. The latter observation may reflect only the facility with which α-alkylallyl phenyl ethers undergo Claisen rearrangement. Rhoads, *et al.*,[15] found α-ethylallyl phenyl ether to rearrange to *o*-γ-ethylallylphenol at 120°, much below our standard 175° reaction temperature. To the extent that O-allylation and subsequent Claisen rearrangement occurs extra *ortho* product will be formed. Predominance of *ortho* over *para* substitution is, however, observed even in phenolysis of 2,3-dichloropropene where Claisen rearrangement should not occur.

Finally, it should be noted that, although minor products suggested to be benzofurans are formed in all reactions, 2,3-pentamethylenobenzofuran (IV) is a major product in phenolysis of 7,7-dichlorobicyclo-[4.1.0]heptane and the product of *ortho* substitution, IIE, is quite unstable, cyclizing to IV after isolation. This suggests that mild conditions would, in general, suffice for cyclization of *o*-β-chloroallylphenols to benzofurans, offering an easy route from *gem*-dichlorocyclopropanes to unusual benzofurans.

Experimental Section[16]

Material.—*gem*-Dichlorocyclopropanes were prepared by dichlorocyclopropanation of the appropriate olefin with chloroform and sodium hydroxide in tetraglyme with final purification by distillation (18-in. spinning-band column).[17] 7,7-Dichlorobicyclo[4.1.0]heptane was identical (by vpc) with material prepared by the method of Wagner and co-workers.[18] 6,6-Dichlorobicyclo-[3.1.0]hexane (bp 82–83° (40 mm), lit.[19] bp 69° (20 mm)) showed no double-bond absorption in its infrared spectrum. 1,1-Dichloro-2-*n*-butylcyclopropane (bp 83–84° (40 mm), lit.[1] 75–76° (25 mm)) gave a single vpc peak and the correct elemental analysis. The product from dichlorocyclopropanation of mixed *cis*- and *trans*-pentene-2 was a mixture of two compounds by vpc. Authentic *cis*-1,1-dichloro-2-ethyl-3-methylcyclopropane (bp 69–70° (50 mm), lit.[20] 64–68°, 49 mm) was identical by vpc with one of the compounds, and the second was assumed to be *trans*-1,1-dichloro-2-ethyl-3-methylcyclopropane.

Sodium phenolate solutions in phenol (0.22 mole/100 g) were prepared as needed by cautious addition of sodium to molten phenol or by distilling a solution of sodium hydroxide in phenol until the distillate temperature was 176°. Sodium, sodium hydroxide, and phenol were commercial materials used without purification, as was 2,3-dichloropropene.

Phenolysis of 2,3-Dichloropropene.—To a stirred solution of sodium phenoxide in phenol (0.22 mole/100 g) kept at 165–170° under nitrogen was added 2,3-dichloropropene (11.66 g, 0.108 mole) as rapidly as the heat of reaction permitted. The mixture was heated an additional hour and, after cooling, phenolic materials were extracted with aqueous sodium hydroxide. The neutrals (9.79 g) consisted largely of β-chloroallyl phenyl ether (bp 94–96° (10 mm), $n^{21}\text{D}$ 1.5350; lit.[13] bp 89–91° (12 mm), $n^{20}\text{D}$ 1.5329) having no hydroxyl bands in its infrared spectrum. A small forerun (3% of the neutrals, bp 74–80° (10 mm)) contained both β-chloroallyl phenyl ether and an unidentified second component. The sodium hydroxide extracts were acidified and extracted with ether, and the ether and phenol were stripped from the extract by distillation (20-mm) (Vigreaux column). The residual oil, on careful fractionation (18-in. spinning-band column), gave *o*-β-chloroallylphenol (bp 101–103° (4 mm), $n^{20}\text{D}$ 1.5614; lit.[13] bp 130–134° (12 mm), $n^{20}\text{D}$ 1.5779):[21] infrared spectrum (10 wt % in chloroform) 2.80 (strong nonbonded hydroxyl with a weak shoulder indicating slight hydrogen bonding) and 11.3 μ (terminal methylene). Reduction under the conditions of Brown and Brown[22] gave 2-*n*-propylphenol (vpc identification).

Extraction of the distillation residues with boiling *n*-heptane yielded *p*-β-chloroallylphenol, a new compound, (white solid, mp 55.5–57°): infrared spectrum (10 wt % in chloroform) 2.8 (nonbonded hydroxyl), 3.0 (strong hydrogen-bonded hydroxyl), and 11.3 μ (terminal methylene).

Anal. Calcd for C_9H_9OCl: C, 64.10; H, 5.38; Cl, 21.03. Found: C, 64.24, 64.31; H, 5.40, 5.52; Cl, 20.5.

Phenolysis of 1,1-Dichloro-2-*n*-butylcyclopropane.—A stirred solution of sodium phenolate in phenol (0.22 mole/100 g) was heated under a nitrogen atmosphere at 135° and 1,1-dichloro-2-*n*-butylcyclopropane (16.7 g, 0.10 mole) was added. The temperature was raised gradually to 158° and then rose spontaneously to 176° where it was kept for 80 min. Sodium chloride (4.4 g, 0.075 mmole) was separated by filtration and washed with methanol. The acidified filtrate was taken up in ether and stripped of phenol at 40 mm, leaving 19.4 g of crude product. Vpc examination indicated a complex mixture with three products predominating. Fractional distillation gave first a mixture of two minor products (bp 75–78° (0.13 mm)): ultraviolet (hexane) λ_{max} 251 mμ (log ε 3.82), 278 (3.25), and 286 (3.25); infrared bands (chloroform) 5.21, 5.31, 5.52, 5.66, and 13.45 μ (*ortho*-

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(15) S. J. Rhoads, R. Raulins, and R. D. Reynolds, *J. Am. Chem. Soc.*, **76**, 3456 (1954).

(16) Melting points and boiling points are uncorrected. The standard vpc column was 15 ft by 0.25 in. packed with SE 30 on Chromosorb W NMR shifts are in parts per million relative to internal tetramethylsilane with coupling constants in cycles per sec (Varian A-60 spectrometer). Vpc analysis used pure components for instrument response calibration unless otherwise specified.

(17) G. C. Robinson, *Tetrahedron Letters*, 1749 (1965).

(18) W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. Trav. Chim.*, **80**, 740 (1961).

(19) E. Bergman, *J. Org. Chem.*, **28**, 2210 (1963).

(20) W. v. E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, **80**, 5274 (1958).

(21) The discrepancy in refractive index suggests the *o*-β-chloroallylphenol of Hurd and Webb was contaminated with *o*-2-chloropropenylphenol. The pair γ-chloroallylphenyl ether and *o*-γ-chloroallylphenol gave $n^{20}\text{D}$ 1.5421 and $n^{23}\text{D}$ 1.5638, consistent with our observations on the isomeric β-chloroallyl materials $n^{21}\text{D}$ 1.5350 and $n^{21}\text{D}$ 1.5614, respectively.

(22) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 2829 (1962).

disubstituted benzene). The spectra suggest that both components are benzofurans.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.79, 83.25; H, 8.89, 8.63.

Next was collected 2-chlorohept-2-en-1-yl phenyl ether (new compound, bp 94–97° (0.17 mm)): infrared bands (chloroform) 5.02, 5.20, 5.45, 5.66, 13.30 and 14.52 (monosubstituted benzene), and 6.25 μ (trisubstituted olefin). Minor decomposition during distillation and preparative vpc purification prevented satisfactory elemental analysis. Structure was established by the nmr spectral shifts, multiplicities, and integrated intensities (deuteriochloroform): 0.87 (three protons, methyl group), 1.3 (four protons, aliphatic methylenes), 2.2 (two protons, allylic methylene), 4.53 (two-proton singlet, allylic methylene bonded to oxygen and adjacent to the chlorovinyl group), 5.86 (one-proton triplet, $J = 7$ cps, vinylic proton), and 6.8–7.5 ppm (five aromatic protons).

Next was obtained *o*-(2-chlorohept-2-en-1-yl)phenol (new compound, bp 110–112° (0.23 mm)): infrared bands (chloroform) 2.87 (hindered hydroxyl), 6.02 and 11.92 (trisubstituted olefin), and 13.28 μ (*ortho*-disubstituted benzene); nmr (deuteriochloroform) 0.88 (three protons, aliphatic methyl group), 1.3 (four protons, aliphatic methylenes), 2.2 (two protons, allylic methylene), 3.64 (two-proton singlet, benzylic methylene adjacent to chlorovinyl group), 5.52 (one-proton triplet $J = 7$ cps, vinylic proton), and 6.7–7.3 ppm (four aromatic protons). The phenoxyacetate (mp 129–130°, 50% aqueous ethanol) was prepared by a standard method.[23]

Anal. Calcd for $C_{15}H_{19}O_3Cl$: C, 63.71; H, 6.77; Cl, 12.54: neut equiv, 283. Found: C, 63.82, 63.81; H, 6.94, 6.92; Cl, 12.7; neut equiv, 289.

Finally *p*-(2-chlorohept-2-en-1-yl)phenol (new compound, bp 113° (0.2 mm)) was obtained but it was not analytically pure. Identification depended on the nmr spectrum which was substantially the same as for the *ortho* isomer except the pair of aromatic proton doublets clearly indicated *para* disubstitution: 0.92 (three protons, aliphatic methyl group), 1.3 (four protons, aliphatic methylenes), 2.2 (two protons, allylic methylene), 3.50 (two protons, benzylic methylene adjacent to a chlorovinyl group), 5.50 (one-proton triplet, $J = 6.5$ cps, vinylic proton), 6.28 (one-proton singlet, hydroxyl), and 6.7–7.2 ppm (four aromatic protons, two doublets).

Phenolysis of 7,7-Dichlorobicyclo[4.1.0]heptane.—To a solution of sodium phenolate in phenol (0.22 mole/100 g) at 188° (bath) was added 7,7-dichlorobicyclo[4.1.0]heptane (16.5 g, 0.10 mole). After an initial vigorous reaction the mixture was kept at 170–188° for 55 min, quenched with water, and extracted with ether. The crude phenolysis products were isolated by stripping ether and phenol (Claisen head, 40 mm of Hg). The 30.2-g residual material contained three products (vpc, programmed 100–225° at 15°/min). Careful fractionation (18-in. spinning-band column) gave first 2,3-pentamethylenobenzofuran (new compound, insoluble in Claisen's alkali, bp 104–106° (0.25 mm), mp 14°) whose ultraviolet spectrum (*n*-hexane) was characteristic of a benzofuran:[14] λ 253 mμ (log ϵ 3.93), 280 (3.37), and 287 (3.36); nmr spectrum (deuteriochloroform) 1.52 (six protons, multiplet, aliphatic methylenes), 2.42 (two protons, methylene at 3 position), 2.72 (two protons, methylene at 2 position), 6.9–7.5 (multiplet, four aromatic protons).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: C, 83.66, 83.82; H, 7.63, 7.70.

The second fraction, tentatively identified as *o*-(2-chlorocyclohept-2-en-1-yl)phenol was unstable, evolving hydrogen chloride and forming 2,3-pentamethylenobenzofuran (identified by insolubility in Claisen's alkali and superposition with authentic material on vpc examination).

The least volatile product (bp 150–170° (0.1 mm)) was *p*-(2-chlorocyclohept-2-en-1-yl)phenol (new compound, mp 86–87° from *n*-heptane): infrared bands (chloroform) at 2.80 (hydroxyl), 2.99 (hydrogen-bonded hydroxyl), 6.08 (trisubstituted olefin), 7.99 (COH deformation), 8.54 (COH stretch), and 5.31, 5.66, and 12.07 μ (*para*-disubstituted benzene); nmr spectrum 1.6 (four-proton multiplet, aliphatic methylenes), 2.1 (four-proton multiplet, superposition of allylic methylene and methylene group nearest the benzene ring), 3.82 (tertiary benzylic proton triplet), 5.6 (hydroxyl proton), 6.18 (vinyl CH triplet $J = 6.5$ cps), and 6.72, 6.87, 7.07, and 7.22 ppm (*para*-disubstituted benzene, four-proton pair of doublets).

Anal. Calcd for $C_{13}H_{15}ClO$: C, 70.10; H, 6.79; Cl, 15.92. Found: C, 69.7, 70.0; H, 6.85, 6.69; Cl, 15.9.

Phenolysis of 6,6-Dichlorobicyclo[3.1.0]hexane.—6,6-Dichlorobicyclo[3.1.0]hexane (15.1 g, 0.10 mole) was added dropwise during 20 min to a stirred solution of sodium phenolate in phenol (0.22 mole/100 g) initially at 152°, rising to 175° where it was kept 1 hr. The cooled reaction mixture was acidified (30 ml of acetic acid), washed with water, and stripped of unreacted phenol, leaving 17.9 g of crude product. Examination by vpc (215°) revealed three products (area ratio 21:60:19). Careful distillation (18-in. spinning-band column) gave pure major product, *o*-(2-chlorocyclohex-2-en-1-yl)phenol (new compound, bp 113–114° (0.12 mm)): infrared bands (chloroform) at 2.82 (nonbonded hydroxyl), 5.25, 5.58, 5.85 (*ortho*-disubstituted benzene), and 6.05 μ (unconjugated trisubstituted olefin); nmr proton absorption (deuteriochloroform) 1.34–2.33 (six-proton multiplet, aliphatic and allylic methylenes), 3.97 (tertiary benzylic proton), 5.20 (hydroxyl proton), 6.13 (vinyl proton triplet, $J = 3.5$ cps, with further second-order splitting, $J = 1.2$ cps), and 6.5–7.3 (four aromatic proton multiplet, *ortho* substitution). The phenoxyacetate (mp 196–200°, ethanol–water) was prepared and analyzed.[20]

Anal. Calcd for $C_{14}H_{15}O_3Cl$: C, 63.04; H, 5.67. Found: 62.7, 62.9; H, 5.74, 5.79.

Extraction of the pot residues with *n*-hexane yielded *p*-(2-chlorocyclohex-2-en-1-yl)phenol (new compound, mp 108–110° from *n*-hexane): infrared bands (chloroform) at 5.29 and 5.88 (*para*-disubstituted benzene), 6.06 (trisubstituted olefin), and 2.99 μ (bonded hydroxyl).

Anal. Calcd for $C_{12}H_{13}OCl$: C, 69.06; H, 6.28. Found: C, 68.8, 69.1; H, 6.31, 6.39.

The distillation foreruns on extraction with Claisen's alkali yielded an unidentified neutral material: infrared bands at 5.18, 5.29, 5.41, 5.56, and 5.65 μ (*ortho*-disubstituted benzene). Reduction of a mixture of the phenolic products under the conditions of Brown and Brown[22] gave *o*-cyclohexylphenol (mp 55–56°, authentic sample mp 52–56°, mmp 52–56°, superposing on vpc comparison) and *p*-cyclohexylphenol (mp 128.5–131.5°, lit.[24] mp 130°).

Phenolysis of *cis*- and *trans*-1,1-Dichloro-2-ethyl-3-methylcyclopropanes.—Phenol (100 g, 1.03 mole) and sodium (5 g, 0.22 g-atom) were heated to 152° under nitrogen and *cis*- and *trans*-1,1-dichloro-2-ethyl-3-methylcyclopropanes (15.3 g, 0.10 mole, roughly 1:1 mixture) was added slowly. The reaction temperature rose rapidly to 175° and was kept at 175–169° for 1 hr. The hot mixture was filtered ("C" porosity filter), and the solids were washed with methanol and dried, giving 6.8 g (0.116 mole) of sodium chloride. Examination (vpc programmed from 75 to 225° at 7.9°/min) of the crude reaction mixture revealed two unidentified minor neutral components (insoluble in Claisen's alkali) and two major phenolic products. Removal of phenol left 19.1 g of crude product which was distilled through an 18-in. spinning-band column. The most volatile phenol (bp 98–101° (0.08–0.14 mm)) gave a single symmetrical peak on gas–liquid partition chromatography. However, the nmr spectrum indicated a mixture of *o*-(4-chlorohex-3-en-5-yl)phenol and *o*-(3-chlorohex-2-en-4-yl)phenol (62:38): 1.40 (doublet, $J = 6$ cps, methyl group adjacent to tertiary aliphatic proton) and 1.67 ppm (doublet, $J = 7$ cps, allylic methyl group split by one adjacent vinyl proton). The methyl and methylene absorptions of the ethyl group in the two isomers are also reasonably well resolved. The aromatic proton absorptions are complex as expected for an *ortho*-disubstituted benzene. The less volatile *para* isomers (bp 114–115° (0.17 mm)) also gave a single symmetrical vpc peak, but the nmr spectrum showed the product to be a mixture of *p*-(4-chlorohex-3-en-5-yl)phenol and *p*-(3-chlorohex-2-en-4-yl)phenol (44:56). Doublets at 1.36 ($J = 8.5$ cps) and 1.69 ppm ($J = 7$ cps) were assigned to the methyl group adjacent to the tertiary proton and the allylic methyl group respectively. The aromatic proton absorption pattern was to a first approximation a pair of doublets, as expected for a *para*-disubstituted benzene.

Registry No.—IIB, 13396-29-7; IIC, 13283-41-5; IID, 13283-40-4; IIIA, 13283-34-6; IIIB, 13283-42-6;

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[23] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 201.

[24] W. Schrauth and K. Görig, *Ber.*, **56**, 1900 (1923).

IIIC, 13283-36-8; IIID, 13283-35-7; IIIE, 13283-37-9; IV, 5010-79-7; 2-chlorohept-2-en-1-yl phenyl ether, 13283-39-1.

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Photochemistry of Cycloalkenes. IV. Comparison with Crotonic Acid[1]

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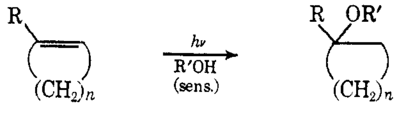
Recent studies have revealed that either direct or photosensitized irradiation of cycloalkenes (I, R = H or alkyl) in alcoholic or aqueous solvents results in addition of the alcohol or water in Markovnikov fashion to give the corresponding ether or alcohol (II).[2,3] The reaction was found to be limited to six- or seven-membered cyclic olefins; larger ring and acyclic systems, which are capable of easily undergoing instead the well-established *cis–trans* photoisomerization,[4] showed no evidence of adduct formation.[2,5,6]



I II

The similarity of this reaction of cycloalkenes to that of various examples of light-initiated, Michael-type addition of alcohols, water, or acetic acid to the β positions of cyclohexenones,[7] cyclooctenone,[8] and thymines and uracils[9] suggests the possibility of parallel mechanistic features in some, or perhaps even all, of these cases. However, in contradiction to this possibility is the long-standing report of Stoermer and Stockmann that irradiation of crotonic acid (**1a**) in methanol results in formation of the β-methoxy derivative **4a**.[10] Since, to the best of our knowledge, this is the only claim of a light-initiated, Michael-type addition to an *acyclic* α,β-unsaturated carbonyl system, it was deemed worthy of reinvestigation.

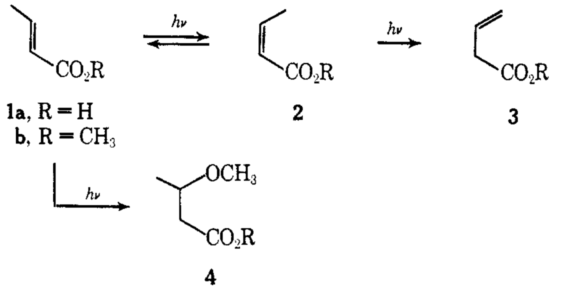
When methanolic solutions of crotonic acid (**1a**) were irradiated and aliquots were removed periodically, esterified with diazomethane, and analyzed by gas chromatography, there was observed a rapid establishment of the *cis–trans* equilibrium **1** $\rightleftarrows$ **2** followed by a slower formation of the deconjugated isomer **3** (Table I). On extended irradiation **3** became the principal component of the reaction mixture. Identical results were obtained by similar irradiation of methyl crotonate (**1b**) in methanol with or without the addition of xylene as a photosensitizer, although the reaction proceeded more slowly in the latter case. *In no instance was there any detectable formation of the adduct* **4**, despite the fact that a specimen of **4b** independently prepared by base-catalyzed addition of methanol to **1b** was found to be adequately stable under the irradiation conditions.

TABLE I

IRRADIATION OF CROTONIC ACID AND METHY CROTONATE[a]

Starting material	Time, hr	Yield, % 1	2	3	4
1a	4	24	17	59	. . .[b]
1b	4	20	19	39	. . .[b]
4b	4	. . .	. . .	. . .	56
1b[c]	1	79	17	3	. . .[b]
	4	50	28	8	. . .[b]
	8	35	29	16	. . .[b]
4b[c]	8	. . .	. . .	. . .	88

[a] See Experimental Section for details. [b] None detectable. [c] Contained 2% xylene.



The migration of the double bond to the β,γ position, which probably occurs in the *cis* isomer **2**,[11] is a familiar process which has been previously documented for a number of α,β-unsaturated esters, including **1b**.[12] Although it is not as well documented, similar behavior in the corresponding carboxylic acid series is not surprising.[13] Unfortunately, occurrence of the migration process competes with any potential addition of methanol across the double bond of the crotonic system. Nonetheless, there was still a considerable amount of the conjugated esters **1b** and **2b** remaining in the xylene-sensitized irradiation under conditions in which the cyclic analog **5**[14] incorporated a substantial amount of

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(1) Part III: P. J. Kropp and H. J. Krauss, *J. Am. Chem. Soc.*, **89**, 5199 (1967).

(2) (a) P. J. Kropp, *ibid.*, **88**, 4091 (1966); (b) P. J. Kropp and H. J. Krauss, unpublished data.

(3) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

(4) See, for example, the summary by R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964).

(5) Smaller ring systems undergo hydrogen abstraction rather than protonation; see P. J. Kropp, *J. Am. Chem. Soc.*, **89**, 3650 (1967).

(6) It is not yet clear whether the protonation of cyclohexenes and -heptenes involves the orthogonally oriented triplet species or a highly strained ground-state *trans*-cycloalkene intermediate.

(7) O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., **88**, 161 *ibid.*, (1966); T. Matsuura and K. Ogura, *ibid.*, **88**, 2602 (1966).

(8) T. K. Hall, Ph.D. Dissertation, Iowa State University of Science and Technology, Ames, Iowa, 1965; *Dissertation Abstr.*, **26**, 5034 (1966).

(9) See S. Y. Wang, *Federation Proc.*, **24**, Suppl. 15, 71 (1965), and references cited therein.

(10) R. Stoermer and H. Stockmann, *Chem. Ber.*, **74**, 1786 (1914).

(11) See N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).

(12) M. J. Jorgenson, *Chem. Commun.*, 137 (1965).

(13) For one precedent, involving sorbic acid, see K. J. Crowley, *J. Am. Chem. Soc.*, **85**, 1210 (1963).

(14) Prepared as described by W. J. Bailey and R. A. Baylouny, *ibid.*, **81**, 2126 (1959).