chlorophenol and *p*-chlorophenol showed no depression in melting point. Efforts to isolate additional trinuclear material from the benzene mother liquor by additions of petroleum ether (b.p. 40–60°) yielded gummy, uncrystallizabl. materials.

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[CONTRIBUTION FROM THE PETRO-TEX DEPARTMENT, FOOD MACHINERY AND CHEMICAL CORPORATION CHEMICAL RESEARCH AND DEVELOPMENT CENTER]

The Autoxidation of Liquid Allylic Chlorides

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The autoxidation of allyl chloride, methallyl chloride, 1,4-dichlorobutene-2, and 3,4-dichlorobutene-1 forms chloro hydrins by attack at the double bonds. Analysis of the initial products from methallyl chloride indicates an epoxide precursor is involved. Oxidation rates for the dichlorobutenes were studied and show an unusual dependency on added anions.

Little is known about the autoxidation of liquid allylic halides.[1] This paper reports the oxidation of methallyl chloride, allyl chloride, 1,4-dichlorobutene-2 and 3,4-dichlorobutene-1 and describes the major products formed.

While a complex mixture of compounds was produced in each case, a single α-chlorocarbonyl compound and a chlorohydrin constituted a major portion of the products as shown in Table I. It was apparent from the nature of the compounds found that products arise not only from the decomposition of hydroperoxides, the primary intermediates usually postulated, but also from the addition of hydrogen chloride and carboxylic acids to a reactive epoxide. This epoxide could be identified and isolated in the oxidation of methallyl chloride and in fact constituted a major component in the very early stages of the reaction.

TABLE I

OXIDATION PRODUCTS OF ALLYLIC CHLORIDES

Compound, % Reacted	Product	% of Products[a]
Methallyl chloride	Chloroacetone	28
27% reacted	1,3-dichloro-2-methylpropanol-2	19
Allyl chloride	Chloroacetaldehyde	22
25% reacted	1,3-dichloropropanol-2	19
1,4-Dichlorobutene-2	1,3,4-trichlorobutanol-2	
3,4-Dichlorobutene-1		

[a] Analysis by gas chromatography.

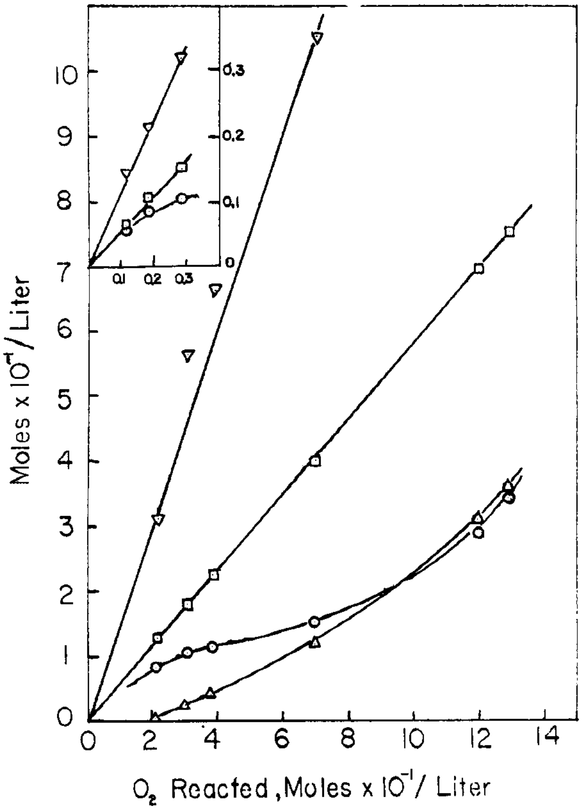

Fig. 1. The oxidation of methallyl chloride with insert showing products at less than 1% reacted

△ 1,3-dichloro-2-methylpropanol-2
○ 1,2-epoxy-2-methylpropane
□ chloroacetone
△ methallyl chloride reacted

The initial reaction of methallyl chloride with oxygen produces unexpectedly few products as shown by gas chromatographic analysis. Figure 1 shows that chloroacetaldehyde and 1,2-epoxy-3-chloro-2-methylpropane constituted nearly all the products when less than 1% of the allylic chloride had reacted. Only one other product, which must be considered minor, could be detected while products more volatile than methallyl chloride may have been obscured by impurities originally present. As the oxidation progressed, 1,3-dichloro-2-methylpropanol-2 appeared and formed in significant amount until it was present in the second largest concentration. The production of epoxide, however, became slower with time. Measurement of the oxygen consumed showed that for every mole of oxygen 1.5 moles of allylic chloride reacted.

As this was true even at the very advanced stages of the oxidation, where as many as seventeen prod-

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[1] D. J. Loder and A. McAlevey, U. S. Pat. 2,316,604 (1943) describing the production of glycerol from allyl chloride appears to be the only reference to this reaction.

ucts could be detected, it is apparent that most secondary products do not result from the oxidation of the initial products. The products found on extended oxidation included formic acid and some of its addition products with the epoxide. Distillation yielded high boiling fractions which appear to be mixtures of esters and hydroxyesters.

As the peroxide catalyzed dimerization of methallyl chloride and other allylic chlorides is known to occur readily,[2] it was expected that under the conditions of the oxidation extensive dimerization would occur. However, gas chromatography revealed that no dimer was formed during the oxidation. Reaction products containing unchanged methallyl chloride did form dimer on standing and during distillation. It is of interest to note that samples of methallyl chloride not stored under nitrogen were found to contain chloroacetone, epoxide, and dimer in addition to the 1-chloro-2-methyl-1-propene usually present as impurity.

The production of chloroacetone and formic acid can readily be explained by applying the now generally accepted olefin oxidation mechanisms calling for the formation and decomposition of an *alpha* hydroperoxide.

$$CH_2{=}C(CH_2Cl)CH_3 \xrightarrow{O_2} CH_2{=}C(CH_2Cl)CH_2OOH \longrightarrow CH_2{=}C(OH)CH_2Cl + CH_2O$$

Similarly, removal of hydrogen by attack on the other *alpha* position would result in the production of hydrogen chloride, a phenomenon which was readily detected in the case of the dichlorobutenes. By reaction at this position the isomeric hydroperoxide $ClCH{=}CRCH_2OOH$ may arise from the radical $CH_2{=}CR\dot{C}HCl \leftrightarrow \dot{C}H_2CR{=}CHCl$. This is in fact indicated by the products from allyl chloride.

The epoxide may arise as the first stable product of a free radical chain reaction[3] which assigns it an analogous role to hydroperoxide, and not by the secondary action of hydroperoxide on the olefinic double bond as has been proposed.[4] This hypothesis is supported by the appearance of the epoxide at a very low degree of oxidation and by independent experiments performed in our laboratories with 2,4,4-trimethylpentene-1. Rapid addition of hydrogen chloride to the epoxide then accounts for the formation of 1,3-dichloro-2-methylpropanol-2, which as the reaction approaches completion constitutes, along with chloroacetone, one of the two products produced in the largest amounts. The slower addition of formic acid to epoxide, epoxide rearrangement, displacement reactions of the allylic chloride, and esterification of the chlorohydrin all seem likely to occur to some extent and would account for the large number of minor products.

The autoxidation of allyl chloride was not intensively investigated as its low boiling point necessitated oxidation under pressure. The major products were identified as chloroacetaldehyde, 1,3-dichloropropanol-2, chloroacetic acid, and formic acid. An unidentified component with the same retention time as epichlorohydrin under the gas chromatographic conditions used in this work made it difficult to determine with certainty whether any epoxide existed in the final product.

The oxidation of either 1,4-dichlorobutene-2 or 3,4-dichlorobutene-1 gave the same trichlorobutanol in approximately 30% yield as demonstrated by the preparation of the same urethane derivative from either product. 1,3,4-Trichlorobutanol-2 was isolated as a mixture with its corresponding esters by fractional distillation. The pure chlorohydrin was obtained by methanolysis of the distillate. The formation of the same chlorohydrin from both allylic isomers is not surprising if one accepts the prior formation of epoxide since the addition of hydrogen chloride to either the 1,2 or 2,3 epoxide may be expected to favor the production of the same end product.[5] Unfortunately, this result does not contribute to the evidence for epoxide formation for the dichlorobutenes as in a single case, viz., the catalyzed incomplete oxidation of 3,4-dichlorobutene without a solvent, rearrangement of the allylic chloride was found to occur.

As the high boiling point of the dichlorobutenes allowed their convenient oxidation at atmospheric pressure, their catalytic and noncatalytic oxidation rates were studied in acetic acid as well as without a solvent. The results were extremely complex and not readily interpreted. In the absence of solvent, 1,4-dichlorobutene-2 was far more reactive than its isomer which represents the same relationship observed in this laboratory for the unchlorinated butene-2 and butene-1. In acetic acid with a soluble ionic cobalt catalyst added as cobaltous chloride both isomers oxidized much faster, as was expected. However, when cobaltous acetate was the catalyst, the oxidation of 1,4-dichlorobutene-2 slowed to a rate little different from that of its isomer, or from its rate without solvent. The behavior of 3,4-dichlorobutene-1 with cobalt acetate was also curious. A pronounced retardation followed by a second induction period and further rapid oxidation was observed at 30% or at 50% reacted using $0.1M$ or $0.05M$ acetate, respectively. The liberation of chloride by oxidation or displacement during the reaction may be involved, and the addition of hydrochloric acid or lithium chloride caused this phenomenon to occur strongly at 20% reacted. Sodium acetate, a strong base, eliminated it. In the absence of a solvent, the use of a soluble naph-

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(2) C. E. Frank and A. V. Blackham, *J. Am. Chem. Soc.* **72,** 3283 (1950).

(3) G. H. Twigg, *Chemical Engineering Science,* **3,** Special Supplement 11 (1954), "The Proceedings of the Conference on Oxidation Processes."

(4) E. Farmer and A. Sundralingam, *J. Chem. Soc.,* 121 (1942).

(5) S. Winstein and R. B. Henderson, *Heterocyclic Compounds,* Vol. 1, R. C. Elderfield, ed., Wiley, New York, 1950.

thenate catalyst or an initiator accelerated oxidation initially but resulted in eventual retardation of the reaction at a much earlier stage. It would appear that in addition to the usual complexities found in olefin oxidation, additional factors are introduced with allylic chlorides.

EXPERIMENTAL

Procedure. All allylic chlorides were purified by fractionation. Oxidations at atmospheric pressure were conducted in a magnetically stirred vessel using U.S.P. cylinder oxygen.[6] For pressure oxidations a stirred 1.4-l. 316 autoclave of stainless steel was used. Oxygen consumption was followed by means of a calibrated pressure reservoir which fed oxygen into the autoclave through a constant pressure regulator. Effective cooling was required.

Products from methallyl and allyl chlorides were analyzed by gas chromatography using a Perkin Elmer Model 154C Vapor Fractometer. Retention times reported here (after each compound) are for 130° using a 2-m. column of 25% diisodecyl phthalate on 60 to 100 mesh Celite (Perkin Elmer "A" Column) and a flow rate of 41 ml./min. of helium at 25 p.s.i. A column of Silicone grease on Celite at 200° proved useful in resolving the higher boiling components. The general procedure for identifying compounds which could not be isolated in pure form by distillation was to subject distillate enriched in the unknown component to gas chromatography and collect the separated sample in a 9.5-cm. evacuated Baird gas cell. The infrared spectrum so obtained was compared with the gas spectra of known compounds purified in the same manner.[7]

Methallyl chloride oxidation. Without a catalyst the oxidation at 60° was very slow. A maximum oxidation rate of 5.5×10^{-7} mole oxygen/mole olefin/sec. was reached in approximately 12 hr. After 44.7 hr., 0.064 mole of oxygen/mole olefin was consumed and the reaction was terminated. An attempt to prevent the formation of chlorohydrin from the epoxide by using 20 mole % of light magnesium oxide was unsuccessful, the distribution of products remaining approximately the same.

In order to obtain a higher conversion and allow isolation of products, 90.6 g. (1.0 mole) of methallyl chloride containing 1.8 g. (0.005 mole) of cobaltic acetylacetonate and 5.0 g. (0.02 mole) of cumene hydroperoxide was oxidized at 60°. for 46.3 hr. Consumption of oxygen at first accelerated but after 6 hr. showed a constant rate of 9.7×10^{-7} mole/mole olefin/sec. Total oxygen consumed was 0.22 mole. Distillation of an 89-g. aliquot of the liquid product through a 1-ft. Vigreux column gave: (1) 40.7 g., 35–37°/200 mm.; (2) 5.9 g., 78–79°/200 mm., (contained 1.6 m.eq./g. of epoxide by titration with hydrogen bromide); (3) 2.5 g., 55–75°/50 mm.; (4) 4.5 g., 66–90°/10 mm.

At 200 p.s.i., 487.1 g. (5.37 moles) of methallyl chloride containing 20 g. (0.5 mole) of light magnesium oxide and 4.8 g. (0.053 mole) of *tert*-butyl hydroperoxide was oxidized at 100° with an off gas of 0.2 l./min. A strongly exothermic reaction with a maximum rate of 3.9×10^{-5} mole oxygen/mole olefin/sec. occurred at approximately 50 min. The reaction slowed and was terminated at 375 min. after the consumption of 3.55 moles of oxygen. The solid product was separated, dissolved in water, washed with ether, and acidified to free the acids. Ether extraction yielded 9.8 g. of liquid which was nearly all formic acid with no chloroacetic acid. The liquid oxidation product, 510 g., gave a minimum of 15 separated peaks on gas chromatography. Chloroacetone and 1,3-dichloro-2-methylpropanol-2 constituted 24% and 11% of the products respectively.

Identification of products from methallyl chloride. Chloroacetone (distillate 42-49°/40 mm., retention time 4.8 min.) and 1,2-epoxy-3-chloro-2-methylpropane (distillate 78–79°/200 mm., retention time 6.0 min.) were identified from their infrared gas spectra. 1,3-Dichloro-2-methylpropanol-2 was purified by redistillation, b.p. 62.8°/14 mm.; n_D^{20} 1.4708; d_4^{20} 1.250. The bis-2-naphthyl ether derivative,[8] recrystallized from alcohol-water, melted at 146–148°. Reaction with an aqueous suspension of calcium hydroxide as described by Hearne[9] gave 1,2-epoxy-3-chloro-2-methylpropane. Acidification of the salts from reactions in the presence of magnesium oxide yielded nearly all formic acid (3.0 min.), a trace of acetic acid (3.45 min.) and no chloroacetic acid (43.2 min.). The retention times of the addition products of these acids with the epoxide were established and only the formate peak (54 min.) was found to be present in crude oxidate. The retention time for the formic acid addition product was close to that for methallyl chloride dimer (58 min.) using the usual diisodecyl phthalate column but these compounds separated well on a Silicone grease absorbent.

Attempts to titrate samples from various reaction stages for hydroperoxide iodometrically gave poor reproducibility and very low results probably due to the consumption of iodine by reaction products.

Oxidation of allyl chloride. The oxidation of 497.3 g. (6.5 moles) of allyl chloride containing 20 g. (0.5 mole) of light magnesium oxide at 100° and 200 p.s.i. for 440 min. required 76.8 g. (2.4 moles) of oxygen. Consumption of oxygen began in 120 min. and a constant maximum rate of 2.5×10^{-5} moles oxygen/mole olefin/sec. was reached in approximately 260 min.

Identification of products from allyl chloride. Chloroacetaldehyde (distillate 41–43°/50 mm., retention time 2.7 min.) was identified by its spectrum. Formic acid (3.4 min.) was also present in the distillate and may have been formed during the distillation. The spectra of the next peaks emerging (5.0 min. and 8.1 min.) were contaminated with some formic acid and treatment of the distillate (45–60°/50 mm.) with powdered potassium carbonate was required. Although it had the same retention time as epichlorohydrin (5.0 min.), the first of these peaks gave the spectrum of an unidentified carbonyl compound while the second was clearly a formate ester.

1,3-Dichloropropanol was isolated as a pure liquid by fractional distillation and identified from the melting point and mixed melting point of its phenyl urethane derivative,[10] m.p. 172–173°.

The acid components, 8.5 g., extracted from the acidified magnesium oxide residue contained approximately equal quantities of chloroacetic acid (43 min.) and formic acid (3.0 min.) with some acetic acid (3.4 min.). In addition, the crude liquid product contained approximately 4% of one or both of the latter two acids which were shown to have identical retention times (3.7 min.) in the presence of large quantities of allyl chloride. The infrared spectra of the high boiling distillates were characterized by strong hydroxyl and ester absorptions.

1,4-Dichlorobutene-2. The oxidation of 1,4-dichlorobutene-2 at 90° was terminated after the consumption of 0.74 mole of oxygen in 27 hr. at which time negligible reaction was observed. Several tenths of a gram of oxalic acid was filtered directly from the reaction product. The reaction solution had a *p*H of 2.4 and was found to contain 2.2 meq./g. of acid by potentiometric titration. The solution, 81 g., was taken up in chloroform, washed with water, and cold dilute sodium bicarbonate to remove acids and aldehyde, and dried over Drierite. Distillation gave 13 g. of unchanged 1,4-dichlorobutene-2. No 1,3-isomer was obtained or detected by infra-

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(6) W. F. Brill, *J. Org. Chem.*, **24**, 257 (1959).

(7) Infrared spectra were obtained on a Baird Model 4-55 by Mr. Herman Adelman and Miss Nadia Chikalo.

(8) G. M. Gibson, *et al.*, *J. Chem. Soc.*, 171 (1942).

(9) G. Hearne and H. W. deJong, *Ind. Eng. Chem.*, **33**, 940–943 (1941).

(10) T. B. Johnson, R. W. Langley, *Am. Chem. J.*, **44**, 357 (1910).

red examination. Trichlorobutanol, in 28% yield, was collected at 68–77°/1 mm.; n_D^{25} 1.4980; 14.8 g.; the material contained 56.8% chlorine as shown by analysis (calcd. 59.9) and was contaminated with a carbonyl compound which yielded an unstable 2,4-dinitrophenylhydrazone.

The oxidation of 2M 1,4-dichlorobutene-2 in acetic acid with 0.1M cobaltous chloride gave 0.19 mole of hydrochloric acid and 0.13 mole of carbon dioxide per mole of dichlorobutene. Distillation gave no separation of products: an 82% weight yield of liquid was collected between 73–160°/2 mm. which appeared to consist of impure esters contaminated with acids, olefinic and hydroxy compounds. When the oxidation product was first treated with cold sodium hydroxide a relatively pure acetate ester (80–100°/3 mm.) as shown by methanolysis and infrared spectra was obtained.

Titration of the crude oxidation mixture for hydroperoxide was unsuccessful since it was found that the dichlorobutenes are able to quantitatively liberate iodine from potassium iodide.

3,4-Dichlorobutene-1. Oxidation at 90°, with 0.5% cobalt naphthenate consumed only 0.16 mole of oxygen in 24 hr. Removal of acids and distillation as described above gave 35 g. of starting dichloride and 7.6 g. of 1,4-dichlorobutene-2. The product, 9.6 g., was collected at 76°/2 mm.; n_D^{25} 1.5079. No isomer was recovered for reaction in the absence of catalyst.

The combined products from the oxidation of 2M 3,4-dichlorobutene-1 in acetic acid, representing 225 g. of starting material, were distilled. The acetic acid forerun, 99–110°/760 mm., 29 g., yielded an unstable 2,4-dinitrophenylhydrazone melting at about 125°. From the 18.5 g. fraction boiling at 54–66°/4 mm., 4.5 g. of crystals were obtained which on recrystallization from ligroin melted at 62–63° and showed no melting point depression with chloroacetic acid. The *p*-bromophenacyl ester melted at 97–99°. The ester fraction, b.p. 72–81/4 mm., 14.5 g., on hydrolysis with 1% sulfuric acid and steam distillation yielded acetic acid, identified by its *p*-bromophenacyl ester, and a liquid from which white platelets of 1,2,3,4-tetrachlorobutane, identified by its spectrum and melting point 73°,[10] precipitated. The liquid remaining was mostly trichlorobutanol and gave a urethane derivative, m.p. 132–133°. The next highest boiling distillate, 81–127°/1 mm., 8.6 g., appeared to be mixed esters with no free hydroxyl present. The last fraction, 17 g. at 127°/1.1 mm. precipitated a small quantity of crystals, m.p. 76–77°, on standing. The pot residue was 40.8 g.

1,3,4-Trichlorobutanol-2. The pure alcohol was obtained by refluxing either the impure chlorohydrin or the ester fraction from the oxidation of either isomeric dichlorobutene with five times its weight of N methanolic hydrogen chloride. By using a high efficiency concentric tube column, methyl acetate could be removed as it was formed. The solution was neutralized with solid barium carbonate, filtered and distilled. The product was collected at 80°/1 mm.; n_D^{25} 1.5022; contained 9.8% free hydroxyl (calcd. 9.6%).

The preparation of 1,3,4-trichlorobutanol-2 by the chlorination of 1-chloro-3-buten-2-ol was reported by Bessinger[11] who characterized it only by a distillation range of 86–93° (mostly 93°)/4 mm.; n_D^{20} 1.5047. With base it yielded an epoxide distilling at 96–100°/45 mm.; n_D^{20} 1.4749.

A phenylurethane was prepared by heating the chloroalcohol with phenyl isocyanate at 100° for 20 min. and extracting with hot ligroin. Recrystallization from ligroin or carbon tetrachloride did not improve the melting point, 132–133°. The residue from the extraction melted slightly less sharply at 132°. Admixtures of derivatives from the chloro alcohols from both isomeric dichlorobutenes did not show a depressed melting point.

Anal. Calcd. for $C_{11}H_{12}O_2Cl_3N$: C, 44.54; H, 4.08; Cl, 35.87; Found: C, 44.72; H, 4.51; Cl, 35.00.

Reaction of the chlorohydrin with 20% sodium hydroxide gave an 80% yield of the dichloroepoxybutane distilling at 73–75°/10 mm.; n_D^{20} 1.4767; oxirane oxygen by titration with hydrogen bromide, 11.1% (Calcd. for $C_4H_6Cl_2O$: 11.3%). The rate of basic hydrolysis of 0.1N chlorohydrin using 0.26N sodium hydroxide in 50% ethanol was determined at 0°. Its second order rate constant, $k_2 = 1.4$ appears to be appropriate for a primary chlorohydrin,[5] being only slightly less than that for 1,3-dichloropropanol-2, $k_2 = 1.7$, whose rate was determined for comparison purposes.

Oxidation rates of dichlorobutenes. A plot of oxygen consumed against time generally produced typical *sigma* shaped curves. The greatest slope was taken as the maximum rate in every case and is reported in moles of oxygen consumed/mole of initial dichlorobutene/min. Given in order below after each isomer, solvent and temperature are the concentration of dichlorobutene, concentration of catalyst, added salt or acid and the rate $\times 10^4$.

3,4-Dichlorobutene-1, acetic acid, 90°—2M, 0.1M CoAc, 10; 1M, 0.1M CoAc, 7.6; 2M, 0.05M CoAc, 7.8; 2M, 0.05M CoAc, 0.015M hydrochloric acid, 5.5; 2M, 0.05M CoAc, 0.1M sodium acetate, 5.5; 2M, 0.05M CoAc 0.2M lithium chloride, 3.2; 2M, 0.05M CoCl, 11. 3,4-Dichlorobutene, no solvent, 90°—no catalyst, 1.0, 0.5 mole % cobalt as cobalt naphthenate, 3.2; 15 mole % potassium carbonate, no reaction. CoAc and CoCl represent cobaltous acetate tetrahydrate and cobaltous chloride hexahydrate, respectively.

1,4-Dichlorobutene-2, acetic acid, 90°—2M, 0.1M CoAc, 13; 2M, 0.1M CoAc, 0.4M lead acetate, 26; 2M, 0.1 CoCl, 30. 100°—2M, 0.1M CoCl, 23. 80°—2M, 0.1 CoCl, 21; 2M, 0.1M CoCl, 1% 2-azobisisobutyronitrile, 20. 70°—2M, 0.1M CoCl, 8. 1,4-Dichlorobutene-2, no solvent, 90°—no catalyst, 10; 0.5 mole % cobalt as cobalt naphthenate, 6.8 no catalyst, 1% 2-azobisisobutyronitrile, 10. 80°—0.5% cobalt as cobalt naphthenate, 20% light magnesium oxide, 11; no catalyst, 20% light magnesium oxide, 13. 1,4-Dichlorobutene-2, *tert*-butyl alcohol, 90°—0.4M, negligible reaction.

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(11) W. E. Bessinger *et al.*, *J. Am. Chem. Soc.*, 69, 2955 (1947).