TABLE VI

*p*-TOLUENE SULFONYL ESTERS OF *p*-*t*-ALKYLPHENOLS

| Compound | M. or b.p., °C. (3 mm.) | Formula | Sulfur, % Calcd. | Sulfur, % Found |
|---|---|---|---|---|
| *p*-*t*-Butylphenol | M 109–110 | $C_{17}H_{20}O_3S$ | 10.52 | 10.44 |
| *p*-*t*-Amylphenol | M 54–55 | $C_{18}H_{22}O_3S$ | 10.06 | 9.93 |
| Di-Me-*n*-Pr-*p*-OH-Ph-methane | B 194–195 | $C_{19}H_{24}O_3S$ | 9.64 | 9.72 |
| Di-Me-*i*-Pr-*p*-OH-Ph-methane | B 187–188 | $C_{19}H_{24}O_3S$ | 9.64 | 9.57 |
| Di-Et-Me-*p*-OH-Ph-methane | B 188–189 | $C_{19}H_{24}O_3S$ | 9.64 | 9.60 |

suspension from a dropping funnel the delivery tube of which had been drawn to a capillary. The diazotized solution was then warmed on a water-bath and steam distilled. The tabulated esters were prepared by the pyridine method.[13]

## Summary

1. Aliphatic tertiary alcohols condense with phenol in the presence of aluminum chloride to give good yields of *p*-tertiary-alkyl phenols.

2. The benzoyl, benzene sulfonyl and *p*-toluene sulfonyl esters of five phenols were prepared.

3. Aliphatic secondary and tertiary alcohols condense with benzene to give the corresponding alkylbenzenes. The tertiary alcohols react much more readily and give higher yields than the secondary alcohols.

4. Aliphatic primary alcohols do not condense with either phenol or benzene in the presence of aluminum chloride, under the given experimental conditions.

EAST LANSING, MICH.

RECEIVED OCTOBER 28, 1935

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[13] Einhorn and Holland, *Ann.*, **301**, 95 (1898).

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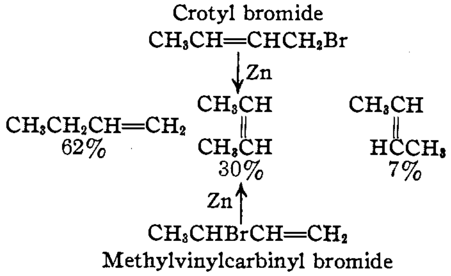
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# Allylic Rearrangements. III. The Action of Zinc on Crotyl and Methylvinylcarbinyl Bromides[1]

BY WILLIAM G. YOUNG AND SAUL WINSTEIN

A previous communication from this Laboratory[2] mentioned the possibility of allylic rearrangement during the preparation of butenes from mixtures of crotyl and methylvinylcarbinyl bromides by the formation and hydrolysis of the Grignard reagents of these bromides or by treatment of the bromides with zinc in alcohol. Recently we were able to show that rearrangement to an equilibrium took place during the preparation and hydrolysis of the Grignard reagents of these bromides.[3] It is the purpose of this paper to present evidence that an allylic rearrangement to a different equilibrium takes place in the analogous process of reducing the bromides with zinc, as shown below.



We have treated various mixtures of crotyl and methylvinylcarbinyl bromides with zinc in alcohol and have analyzed the resulting butene mixtures by the dibromobutane reaction rate method.[4] The same butene mixture was obtained from all of the bromide mixtures.

## Experimental Part

The preparation of mixtures of crotyl and methylvinylcarbinyl bromides was carried out as previously described.[5] None of the products used in this work contained butyl bromide. Carius analyses gave values within 0.15 of the calculated value of 59.20% Br. The refractive indices of the bromide mixtures and the corresponding compositions are given in the Table of Results.

The conversion of the bromides to butenes was carried out in the same apparatus used for the preparation of the Grignard reagents.[6] The bromides were dropped into zinc dust in boiling aqueous alcohol, the evolved butene

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[1] This work was accomplished with the aid of a grant from the Board of Research of the University of California.

[2] Young and Prater, THIS JOURNAL, **54**, 404 (1932).

[3] Young, Winstein and Prater, *ibid.*, **58**, 289 (1936).

[4] (a) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930); (b) Young and Winstein, *ibid.*, **58**, 102 (1936).

[5] Winstein and Young, *ibid.*, **58**, 104 (1936).

[6] Young, Prater and Winstein, *ibid.*, **55**, 4908 (1933).

TABLE OF RESULTS

| Run Number | 1 | 2 | 3 | 4 | 5 | 6 | Mean butene composition |
|---|---|---|---|---|---|---|---|
| $n^{23}D$ of bromide mixture | 1.4780 | 1.4778 | 1.4758 | 1.4743 | 1.4743 | 1.4679 | |
| % crotyl bromide | 87.0 | 86.0 | 75.7 | 67.9 | 67.9 | 34.7 | |
| % $\alpha$-methylallyl bromide | 13.0 | 14.0 | 24.3 | 32.1 | 32.1 | 65.3 | |
| $n^{25}D$ of dibromobutane mixture | 1.5123 | 1.5122 | 1.5122 | 1.5120 | 1.5122 | 1.5123 | |
| Reaction rate, $K_2$, of dibromobutane mixture | 0.0606 | 0.0604 | 0.0603 | 0.0600 | 0.0610 | 0.0611 | |
| $d^{25}_4$ of dibromobutane mixture | 1.7853 | 1.7849 | 1.7849 | 1.7845 | 1.7852 | 1.7855 | |
| % 1,2-dibromobutane (1-butene) | 63.2 | 61.2 | 61.0 | 58.4 | 63.6 | 65.2 | 62.1 ± 1.9 |
| % *dl*-2,3-dibromobutane (*cis*-2-butene) | 31.6 | 30.0 | 30.4 | 29.6 | 30.4 | 31.0 | 30.5 ± 0.5 |
| % meso-2,3-dibromobutane (*trans*-2-butene) | 5.0 | 8.8 | 8.8 | 12.2 | 6.2 | 3.8 | 7.5 ± 2.4 |

being purified and brominated as in the previous work.[3] The reaction to form butene was almost instantaneous. Three moles of C. P. zinc dust, 135 ml. of 95% ethyl alcohol, and 30 ml. of water were used for each mole of bromide mixture. The yields were 85–90%. Purification of the dibromobutane mixtures was carried out as before[3] except that it was not necessary to heat the crude dibromobutanes at reduced pressure to remove low density impurities. The boiling ranges of the dibromobutane mixtures at 50 mm. were all approximately 77.7–79.4°. Carius analyses agreed to within 0.15 with the theoretical value of 74.03% Br.

The analyses of the dibromobutane mixtures and thus of the original butenes resulting from the various bromide mixtures were carried out as was done previously in the Grignard investigations.[3] The reaction rate constants, densities and refractive indices of the dibromobutane samples and the calculated compositions appear in the Table of Results. The refractive indices of the samples and the refractive indices calculated from the analytical data based on the density and reaction rate measurements were compared as a further confirmation of the analyses and found to agree within 0.0001.

## Discussion of Results

An allylic rearrangement occurs when mixtures of crotyl and methylvinylcarbinyl bromides are treated with zinc. This is shown by the fact that the compositions of the butenes obtained do not correspond to the compositions of the original bromides used. The butene mixtures varied, in general, from a mean value only by amounts to be expected from the procedure of purifying and analyzing the dibromobutane mixtures, indicating that an allylic equilibrium is involved. These equilibrium mixtures consisted of 62.1 ± 1.9% 1-butene, 30.5 ± 0.5% *cis*-2-butene and 7.5 ± 2.4% *trans*-2-butene. Although there is a general similarity, nevertheless this composition is distinctly different from the composition of the butene mixture obtained from the preparation and hydrolysis of the Grignard reagents of crotyl and methylvinylcarbinyl bromides,[3] namely, 56.4% 1-, 26.5% *cis*-2- and 17.2% *trans*-2-butenes.

The formation of definite equilibrium mixtures of butenes when different mixtures of crotyl and methylvinylcarbinyl bromides are allowed to react with metals such as zinc and magnesium must be explained in one of the following ways: (1) the establishment and maintenance of equilibrium between the primary and secondary bromides, these bromides then reacting at different rates with the metal; (2) the formation of the same mixture of alkenyl metallic bromides from any bromide mixture at the instant the bromide reacts with the metal due to resonance between the primary and secondary forms of the intermediate positive ion, $CH_3CH{=}CHCH_2^+$ and $CH_3{}^+CHCH{=}CH_2$; (3) the establishment of equilibrium between the primary and secondary alkenyl metallic bromides after the bromide has reacted with the metal; (4) rearrangement to equilibrium during hydrolysis of the alkenyl metallic bromides; and (5) rearrangement of the butenes after they have been liberated.

Number 5 may be eliminated since the butene mixtures obtained do not agree with the few facts known about butene equilibria[7] and since the butenes are known to be stable under the conditions of the experiments.[3,4b] Number 1 may also be ruled out since the bromides react long before equilibrium could possibly be established at room temperature when magnesium is the metal, or even at 75–80°, when zinc is used.[5] Number 4 is also unlikely since it would not be possible qualitatively to interpret[3] the coupling reactions of crotyl bromide with metals if rearrangement occurs at the hydrolysis step. Quantitative experiments on the coupling reaction are now being performed which should definitely settle this point. This leaves numbers 2 and 3 as possibilities. The latter seems unlikely, unless it is assumed that the two alkenyl zinc bromides rearrange into each

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[7] (a) Hurd and Goldsby, THIS JOURNAL, **56**, 1812 (1934); (b) Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441–9 (1933).

other instantaneously, for they are decomposed as soon as formed. If they do rearrange instantaneously, there would be no essential difference between numbers 2 and 3. In any event, the rearrangement takes place during or after the formation of the alkenyl metallic bromides, but before hydrolysis takes place.

Although the mechanisms of the transformations of crotyl and methylvinylcarbinyl bromides to butenes by the Grignard procedure and zinc in alcohol treatment need not necessarily be the same, nevertheless, the similarity in results by the two procedures indicates that this may be the case. The differences in results between the zinc and magnesium methods which are observed might well be due to differences in solvents, metals, and temperature. For example, the higher temperature of the zinc method yields a larger quantity of the *cis* compound than does the lower temperature of the Grignard method, as might be expected from the effect of temperature on *cis–trans* equilibria. The reactions of crotyl and methylvinylcarbinyl bromides with other metals are now being studied in several solvents.

It should be noted that the very reactions carried out in this investigation were reported by Charon[8] in 1899. Not realizing that he was actually working with a mixture of bromides, Charon treated so-called crotyl bromide with zinc in alcohol and reported a butene which gave a dibromobutane boiling at 158°. It happens that 158° is the exact boiling point of meso-2,3-dibromobutane, obtained from *trans*-2-butene. In fact, one of us, on the basis of Charon's report, at one time[2] attempted to synthesize pure *trans*-2-butene by this method. It is evident that Charon, not anticipating any rearrangements to give mixtures, neglected to mention the small boiling range which his dibromobutane must undoubtedly have had.

## Summary

An allylic rearrangement to an equilibrium has been shown to occur when different mixtures of crotyl and methylvinylcarbinyl bromides are decomposed with zinc in alcohol to form butenes. The composition of the butene mixture obtained is 62.1 ± 1.9% 1-butene, 30.5 ± 0.5% *cis*-2-butene and 7.5 ± 2.4% *trans*-2-butene.

[8] Charon, *Ann. chim. phys.*, [7] **17**, 197 (1899).

LOS ANGELES, CALIF. RECEIVED DECEMBER 12, 1935

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# The Photochemical Decomposition of Oxalyl Chloride Vapor

BY K. B. KRAUSKOPF AND G. K. ROLLEFSON

The existence of the intermediate COCl and its usefulness in explaining the mechanisms of various photochemical reactions involving phosgene have been amply demonstrated by previous investigations in this Laboratory.[1] Since the oxalyl chloride molecule consists of two COCl radicals joined through a C–C bond, its reaction should be related to those of phosgene, and it was hoped that a study of this substance would lead to further information concerning COCl. The first reaction selected for investigation was the photochemical decomposition of the vapor, which is reported in the present paper.

### Apparatus and Materials

Oxalyl chloride was prepared by fractional distillation from a mixture of anhydrous oxalic acid and phosphorus pentachloride which had been allowed to stand for several days. The fraction distilling between 61 and 65° was placed in a liquid air trap and further purified by vacuum distillation, only about half the original quantity of material being kept.

Other gases used in these experiments, chlorine. phosgene, carbon monoxide and carbon dioxide, were prepared by orthodox methods.

The corrosive properties of oxalyl chloride necessitated special precautions for its handling and its preservation. No stopcock lubricant could be found immune to attack by its vapor. All ordinary greases, including Shell Apiezon, developed leaks after a few seconds' exposure. Phosphoric acid is useless because of its water content. The only material which proved at all satisfactory was a mixture of glycerol, mannitol and dextrin in the ratio 24:4:15 parts by weight. Even this mixture was slowly attacked, resulting in a gradual "freezing" of the stopcock; but it seldom developed leaks, and by frequent replacement could be made to serve fairly well. To protect the stopcock attached directly to the oxalyl chloride reservoir, the material was kept in a trap surrounded at all times by liquid air.

The photochemical decomposition of oxalyl chloride vapor results in an increase of pressure, so that the most

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[1] See Montgomery and Rollefson [THIS JOURNAL, **56**, 1089 (1934)] for bibliography.