## Summary

The peroxide-induced condensation of saturated hydrocarbons (including propane, isobutane, *n*-pentane, cyclopentane, 2,2- and 2,3-dimethylbutane, cyclohexane, and methylcyclohexane) with *cis*- and *trans*-dichloroethylene, trichloroethylene, and tetrachloroethylene is a chain reaction which results in the chlorovinylation of the hydrocarbon, a chloroölefin containing one chlorine atom less than the chloroethylene used being formed. Thus, the reaction of propane with these chlorides yields, as principal isomer in each case, 1-chloro-, 1,1-dichloro- and 1,1,2-trichloro-3-methyl-1-butene, respectively.

The peroxide-induced reaction differs from that catalyzed by aluminum chloride in that both *n*- and isoparaffins give significant yields and the products are unsaturated chlorides instead of saturated chlorides. Furthermore, *cis*- and *trans*-dichloroethylene show little difference in reactivity.

The mechanism of the reaction is discussed.

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

# Allylic Rearrangements. XXVI. The Reaction of Butenyl Mesitoates and Chlorides with Phenylmagnesium Bromide

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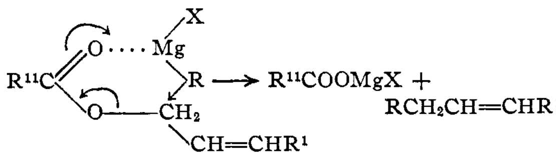
In 1941, Arnold, Bank and Liggett[1] suggested that the formation of allylbenzene from the reaction of allyl mesitoate with phenylmagnesium bromide involved the combination of an intermediate allyl carbonium ion with a phenyl carbanion from the Grignard reagent. In a later paper[2] this mechanism was modified since it was found that the reaction of crotyl mesitoate with phenylmagnesium bromide gave only crotylbenzene instead of the mixture of crotyl- and α-methylallylbenzenes expected from an intermediate butenyl carbonium ion. The exclusive formation of crotylbenzene was formulated as being the result of a concerted process involving a cyclic intermediate.

$$R^{11}COOCH_2CH{=}CHR^1 + RMgX \longrightarrow$$



The reaction of allyl and crotyl mesitoate with phenylmagnesium bromide is analogous to the coupling reactions between allyl halides and Grignard reagents, which with crotyl and α-methylallyl halides[3] and several Grignard reagents give almost exclusively *crotyl* derivatives. For this reason, we have made a comparative study of the reactions of crotyl and α-methylallyl mesitoates and chlorides with phenylmagnesium bromide.

## Results and Discussion

The compositions of the butenylbenzene mixtures isolated from the reaction of phenylmagnesium bromide with the butenyl chlorides and mesitoates were determined by fractional distillation and are given in Table I. With crotyl mesitoate only pure crotylbenzene was isolated, while in the other reactions, mixtures of butenylbenzenes were obtained.

TABLE I

PRODUCTS FROM THE REACTIONS OF PHENYLMAGNESIUM BROMIDE WITH BUTENYL MESITOATES AND CHLORIDES

| Butenyl derivative | Crotylbenzene, % | α-Methylallylbenzene, % |
|---|---|---|
| Crotyl mesitoate | 100 | 0 |
| α-Methylallyl mesitoate | 83 ± 6 | 17 ± 3 |
| Crotyl chloride | 77 ± 5 | 23 ± 3 |
| α-Methylallyl chloride | 72 ± 5 | 19 ± 2 |
| Butenyl chloride mixture[a] | 81 ± 3 | 19 ± 2 |

[a] 41% crotyl chloride, 59% α-methylallyl chloride.

The striking similarity among the product and compositions with α-methylallyl mesitoate, crotyl and α-methylallyl chlorides suggests that the same intermediate, a butenyl carbonium ion, is involved in each of these reactions. Formation of a carbonium ion intermediate is expected to be made possible in these processes by a weakening of the C–X or C–O bond of the chlorides or esters by preliminary coördination with the Grignard reagent. It is not considered that a free carbonium ion is produced but rather that an ion-pair is produced in which the butenyl cation is sufficiently free to effectively lose its identity as either a crotyl or α-methylallyl group. The small difference between the product compositions from the coupling reactions with the isomeric chlorides is typical of many reactions in the butenyl system involving carbonium ions.[4]

The importance of preliminary coördination by the Grignard reagent in producing the butenyl carbonium ion is shown by the fact the sodium derivative of allylbenzene, which is likely to react

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(1) Arnold, Bank and Liggett, THIS JOURNAL, **63**, 344 (1941).

(2) Arnold and Liggett, *ibid.*, **67**, 337 (1945).

(3) (a) Young, Roberts and Wax, *ibid.*, **67**, 841 (1945); (b) Henne, Chanan and Turk, *ibid.*, **63**, 3474 (1941); (c) Levy and Cope, *ibid.* **66**, 1684 (1944).

(4) (a) Meisenheimer and Link, *Ann.*, **479**, 211 (1930); (b) Young and Lane, THIS JOURNAL, **59**, 2051 (1939); (c) Roberts, Young and Winstein, *ibid.*, **64**, 2159 (1942); (d) Young and Andrews, *ibid.*, **66**, 421 (1944).

without preliminary coördination, couples with the crotyl and $\alpha$-methylallyl chlorides[5] without rearranging the butenyl system.

The reaction of phenylmagnesium bromide with crotyl mesitoate gives a single pure product and in this case it is likely that a cyclic mechanism may operate as suggested by Arnold and Liggett.[2] The differences in the course of the reactions of crotyl and $\alpha$-methylallyl mesitoate with phenylmagnesium bromide are similar to those observed in the reactions of the corresponding chlorides with diphenylguanidinium acetate in acetic acid.[4c] In the acetolysis reaction, the secondary chloride reacts exclusively by way of a carbonium intermediate to give much rearrangement, while the primary chloride reacts principally by a direct mechanism to give largely unrearranged product. Similar observations have been made by Pudovik and Arbusov.[6] The formulation of an ionic mechanism for the reaction of the allylic ester similar to that involved in the reaction of allylic halides is supported by work of Balfe and Kenyon,[7] who showed that loss of optical activity may occur in the methanolysis of optically active allylic esters.

## Experimental

**Crotyl and $\alpha$-Methylallyl Mesitoate.**—The esters were prepared from mesitoyl chloride and the pure alcohols in pyridine–chloroform solution using the procedure employed by Arnold and Liggett[8] for allyl 2-ethylcaproate. The yields were about 60%. The crotyl ester boiled at 122–123° (2 mm.), $n^{25}\text{D}$ 1.5101.

*Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.06; H, 8.26. Found: C, 76.75; H, 8.28.

$\alpha$-Methylallyl mesitoate distilled at 113° (2 mm.), $n^{25}\text{D}$ 1.5024.

*Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.06; H, 8.26. Found: C, 76.72; H, 8.24.

**Reactions of Esters with Phenylmagnesium Bromide.**—The ester (0.4 mole) was added with stirring to 0.4 mole of phenylmagnesium bromide in ether and the mixture was allowed to stand overnight. The reaction mixture, which contained a thick white precipitate, was decomposed by pouring onto iced ammonium chloride solution. The ether layer was removed, washed with 2 $N$ sodium hydroxide solution and dried over magnesium sulfate. After distillation of the ether, the products were analyzed by fractionation through a Podbielniak Hyper-Cal column at 50 mm. The compositions of the intermediate cuts were determined from their refractive indices.

From the reaction of the crotyl ester was obtained 47.2 g. (86%) of pure crotylbenzene. No $\alpha$-methylallylbenzene was detected.

Analysis of the distillation curve of the products from the reaction of $\alpha$-methylallyl mesitoate with phenylmagnesium bromide indicated 6 g. of $\alpha$-methylallylbenzene and 29 g. of crotylbenzene for a total yield of 76%.

The olefins were identified by hydrogenation to the saturated hydrocarbons, which were converted to the solid acetylated diaminoalkylbenzenes by the procedure of Ipatieff and Schmerling.[9]

Mesitoic acid was recovered from the alkaline aqueous residues in 85% yield.

**Reaction of Butenyl Chlorides with Phenylmagnesium Bromide.**—The chloride (0.36 mole) was added with stirring to 0.36 mole of phenylmagnesium chloride in ether and the mixture was allowed to stand overnight. The reaction mixture was treated with iced ammonium chloride and the ether layer separated, washed with water and dried over magnesium sulfate. After distillation of the ether, the products were analyzed as in the preceding experiments.

The distillation curve for the products from crotyl chloride indicated 6 g. of $\alpha$-methylallylbenzene and 20 g. of crotylbenzene for a total yield of 60%. From the reaction with $\alpha$-methylallyl chloride the yields were 7.5 g. and 19.6 g. of $\alpha$-methylallyl- and crotylbenzenes, respectively. The total yield was 72%.

The olefins were identified as described in the preceding experiments. A small amount of phenol in the low-boiling material made the preparation of pure derivatives very difficult but the hydrogen absorption was nearly quantitative and the refractive index was correct for $\alpha$-methylallylbenzene. Pure samples of $\alpha$-methylallyl- and crotylbenzene were obtained from a 1.06-mole run employing a mixture of butenyl chloride (41% crotyl chloride and 59% $\alpha$-methylallyl chloride). In this run the phenol was removed by washing with sodium hydroxide. The properties of the products so obtained were: crotylbenzene, b. p. 95° (50 mm.), $n^{20}\text{D}$ 1.5120; and $\alpha$-methylallylbenzene, b. p. 85° (50 mm.), $n^{20}\text{D}$ 1.5075. The diacetyldiaminoalkylbenzene derivatives prepared from these materials did not depress the melting points of the authentic samples.

## Summary

The reactions of crotyl and $\alpha$-methylallyl mesitoates and chlorides with phenylmagnesium bromide have been investigated. Crotyl mesitoate was found to give only crotylbenzene, while $\alpha$-methylallyl mesitoate, crotyl chloride and $\alpha$-methylallyl chlorides gave nearly identical mixtures of crotyl- and $\alpha$-methylallylbenzenes.

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[5] See Ref. 3c. The reported results have been confirmed by Mr. M. Kosmin of these laboratories.

[6] Pudovik and Arbusov, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 377 (1947); *C. A.*, **42**, 1556 (1948).

[7] Balfe and Kenyon, *Trans. Faraday Soc.*, **37**, 72 (1941).

[8] Arnold and Liggett, THIS JOURNAL, **64**, 2875 (1942).

[9] Ipatieff and Schmerling, *ibid.*, **59**, 1056 (1937).