BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3419—3420 (1975)

Phenolysis of 1,1- and 3,3-Dimethylallyl Chlorides. Rates and Product Distributions

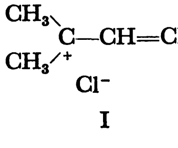
Ken'ichi Takeuchi, Yoshinobu Fujii, and Kunio Okamoto
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

(Received May 29, 1975)

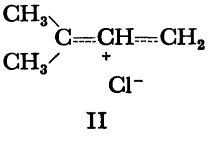
Synopsis. The phenolyses of 1,1- and 3,3-dimethylallyl chlorides were shown by kinetic studies to undergo S_N1 solvolysis. The distributions of the products, dimethylallyl phenyl ethers and (dimethylallyl)phenols, supported the mechanism that involves both localized ion-pairs and mesomeric ion-pairs.

Since the finding of the significance of ion-pair intermediates by Young, Winstein and Goering[1] for the solvolysis of 1,1-dimethylallyl chloride, various efforts have been made to characterize the intermediates involved in the solvolysis of allylic compounds.[2,3] Recent works by Sneen and his coworkers[4] and by Wiberg and Nakahira[5] on the solvolyses of allylic compounds appear to have provided clear-cut evidence for the presence of discrete unsymmetrical ion-pairs preceding the formation of a symmetrical mesomeric ion-pair.

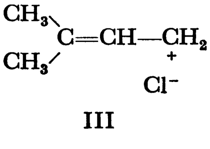
In the course of our study of solvolytic reactions in phenol,[6] the present authors have shown that phenol is characterized as a typical solvolytic solvent[7a] and that the phenolysis products provide useful information concerning the characteristics of the intermediates due to the ambident nature of the phenol molecule as a nucleophile.[7b] Consequently, the present study of the rates and products of the solvolysis of 1,1- and 3,3-dimethylallyl chlorides in binary mixtures of phenol with benzene was undertaken in the hope of distinguishing the intermediates I, II, and III which have occasionally been postulated in the solvolysis of the two isomeric chlorides.[1-4]



I

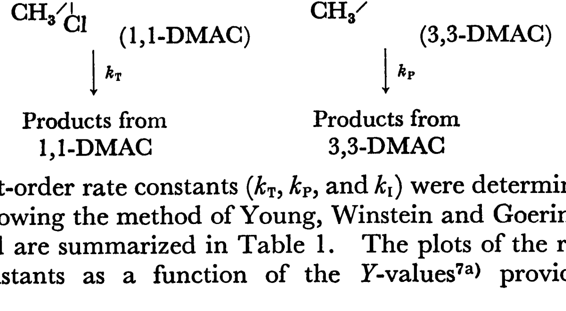


II



III

The rates of solvolysis were determined titrimetrically in phenol-benzene (1:9—3:7 by wt.) buffered with triethylamine. As expected from previous work,[1] the first-order plots for the solvolysis of 1,1-dimethylallyl chloride (1,1-DMAC) exhibited a downward drift as the reaction proceeded, showing concurrent rearrangement to 3,3-dimethylallyl chloride (3,3-DMAC). The



first-order rate constants (k_T, k_P, and k_I) were determined following the method of Young, Winstein and Goering[1] and are summarized in Table 1. The plots of the rate constants as a function of the Y-values[7a] provided

Table 1. Titrimetric phenolysis rates of 1,1- and 3,3-dimethylallyl chlorides in phenol–benzene at 25 °C[a)]

Solvent[b)]	Chloride M	Et_3N M	k_T	k_P $\times 10^5\ s^{-1}$	k_I
1,1-Dimethylallyl chloride					
10% PhOH	0.0440	0.0571	12.2	—	17.3
20% PhOH	0.0462	0.0555	110	—	180
30% PhOH	0.0486	0.0554	408	—	450
3,3-Dimethylallyl chloride					
10% PhOH	0.0458	0.0553	—	3.89	—
20% PhOH	0.0392	0.0554	—	33.9	—
30% PhOH	0.0482	0.0644	—	120	—

a) The temperature controlled at ±0.05°C. b) Percent by weight of phenol in phenol–benzene.

Grunwald-Winstein m-values[8] of 0.95, 0.96, and 0.91 for k_T, k_P, and k_I, respectively. The magnitude of the present m-values of approximately 1.0 provides an evidence for the S_N1 character of the phenolysis of 1,1- and 3,3-dimethylallyl chlorides.

The products, 1,1- and 3,3-dimethylallyl phenyl ethers and o- and p-(dimethylallyl)phenols, were isolated by tlc. Control experiments revealed that the phenyl ethers neither interchanged with each other, nor isomerized to alkenylphenols during the reaction and work-up. The isolated yields of the products were divided by the recovery percents which were determined from the control experiments. The corrected yields thus calculated are shown in the first column under the respective starting chlorides in Table 2. As pointed out above, 1,1-DMAC isomerizes to 3,3-DMAC during phenolysis. Therefore, the product in the solvolysis of 1,1-DMAC is actually a

Table 2. Product distribution in the phenolysis of 1,1- and 3,3-dimethylallyl chlorides in phenol–benzene (1: 4 by wt) at 25 °C

Product[a)]	1,1-DMAC		3,3-DMAC		1,1-DMAC (Estimated)	
	Yield %	Ratio[b)]	Yield %	Ratio[b)]	Yield %	Ratio[b)]
R_POPh	17.0	1.0	21.2	1.0	10.1	1.0
R_TOPh	38.6	2.3	31.0	1.5	51.0	5.0
o-R_PPhOH	12.8	1.0	20.0	1.0	10.1	1.0
p-R_PPhOH	13.6	1.1	12.9	0.65	14.7	1.5
o-R_TPhOH	≦0.25	~0	≦0.25	~0	≦0.25	~0
p-R_TPhOH	0.0	0.0	0.0	0.0	0.0	0.0
Total[c)]	82.2		85.3		86.1	

a) R_P=3,3-dimethylallyl, R_T=1,1-dimethylallyl b) Ratios based on R_POPh for the ethers and on o-R_PPhOH for the phenols. c) The rest is presumed to have been lost as hydrocarbon products.

blend of those from 1,1- and 3,3-DMAC. Thus the product distribution from 1,1-DMAC itself was estimated by utilizing the rate constants k_T, k_P, and k_I and the yields of the products from 3,3-DMAC alone. The results are shown in the fifth and sixth columns of Table 2. The ratio of the amount of tertiary alkenyl phenyl ether to that of the primary ether is 5.0 in the phenolysis of 1,1-DMAC, while it is 1.5 for 3,3-DMAC. Since kinetic studies showed that the phenolyses of the both chlorides are classified as S_N1-type solvolysis, the product spread[2a)] in the ether formation will be explained most reasonably by postulating that the localized ion-pairs I and III are first formed from the corresponding chlorides.

The finding that 1,1-DMAC gives a larger *para*: *ortho* product ratio in (3,3-dimethylallyl)phenol than 3,3-DMAC appears to require the presence of another intermediate which attacks the phenol nucleus with higher *para* selectivity than the intermediate III. The postulation of a mesomeric intermediate II, which is present in equilibrium with III, gives a plausible explanation, since it is presumed that the intermediate II exhibits a larger steric requirement than the localized ion-pair III in *ortho* substitution, which leads to higher *para* selectivity.

It should be pointed out that no *p*-(1,1-dimethylallyl)-phenol could be detected in the product to within experimental error, with the corresponding *ortho*-isomer produced being less than 0.25%, if at all present. The absence of (1,1-dimethylallyl)phenol in the products is in accord with the absence of the same product in the reaction of isoprene with phenol catalyzed by phosphoric acid.[9)] Presumably, the tertiary carbonium ion center is more sterically hindered to nucleophilic approach of the phenol nucleus than the primary carbonium ion center. A similar phenomenon has been observed in the trapping of intermediates with borohydride and in the *t*-butanolysis of 1,1- and 3,3-DMAC.[10)]

The present results support the presence of two localized ion-pairs (I and III) and one mesomeric ion-pair (II).

Experimental

Materials. The isomeric chlorides were prepared by the method reported by Sneen and Kay[4b)] and stored at −78 °C in the presence of small amounts of anhydrous potassium carbonate. The purity of each chloride was checked by glpc[10)] just prior to use; 1,1-DMAC, bp 33.9—34.2 °C/150 Torr, n_D^{20} 1.4190; 3,3-DMAC, bp 59—66 °C/160 Torr, n_D^{20} 1.4489. Other organic reagents employed were of analytical grade and were fractionated before use.

Kinetic Measurement. The pipetting technique[7a)] was employed and the first-order rate constants determined in the manner described in the literature.[1)]

Isolation of the Phenolysis Product. To 1,1-DMAC (525.7 mg, 5.02 mmol) was added 100 ml of phenol–benzene (1 : 4 by wt.) containing 0.055 M of triethylamine which had been previously equilibrated at 25 °C. After 4 h at this temperature, the solution poured into 200 ml of chilled ether. The ether solution was washed with chilled water and then with a chilled 10% sodium hydroxide solution, and dried over magnesium sulfate. After evaporation of the ether, the products were separated by tlc (silica gel) into three fractions, alkenyl phenyl ethers, *o*- and *p*-alkenylphenols. The isomer distribution in each fraction was determined by NMR. The phenolysis of 3,3-DMAC was carried out in the same manner except that the reaction was conducted for 16 h.

References

1) W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1958 (1951).

2) For reviews see a) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 794 (1956). b) P. B. D. de la Mare, "Molecular Rearrangements," Vol. 1, ed. by P. de Mayo, Interscience Publishers, New York, N. Y. (1963), Chapter 2.

3) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, **1954**, 2504.

4) a) R. A. Sneen and W. A. Bradley, *J. Amer. Chem. Soc.*, **94**, 6975 (1972). b) R. A. Sneen and P. S. Kay, *ibid.*, **94**, 6983 (1972). c) R. A. Sneen and J. V. Carter, *ibid.*, **94**, 6990 (1972).

5) K. B. Wiberg and T. Nakahira, *Tetrahedron Lett.*, **1974**, 1769, 1773.

6) K. Okamoto, T. Kinoshita, Y. Takemura, and H. Yoneda, *J. Chem. Soc. Perkin II*, **1975**, in press, and previous work cited therein.

7) a) K. Okamoto, K. Matsubara, and T. Kinoshita, This Bulletin, **45**, 1191 (1972). b) K. Okamoto and T. Kinoshita, *Chem. Lett.*, **1974**, 1037.

8) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948).

9) A. R. Bader and W. C. Bean, *ibid.*, **80**, 3073 (1958).

10) M. Eckert-Maksić, Z. Majerski, S. Borčić, and D. E. Sunko, *Tetrahedron*, **27**, 2119 (1971).