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COMPETITIVE REACTIONS OF NUCLEOPHILES—II[1a]

SOLVOLYSIS OF α,α,- AND γ,γ-DIMETHYLALLYL CHLORIDES

M. ECKERT-MAKSIĆ[1b], Z. MAJERSKI, S. BORČIĆ[1c] and D. E. SUNKO
Rudjer Bošković Institute, Zagreb, Yugoslavia

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Abstract—α,α-Dimethylallyl (1T) and γ,γ-dimethylallyl (1P) chlorides were solvolyzed in water, absolute and aqueous ethanol in the presence of an excess of base ($CaCO_3$, NaOEt or $NaBH_4$). The reaction products were isolated and analyzed by glc. Both primary (P) and tertiary (T) products were obtained in all cases. The P/T product ratio from both chlorides increases with increase of nucleophilicity of attacking reagent, but this increase is considerably faster with the primary chloride (1P) indicating an S_N2 reaction of 1P with stronger nucleophiles. Under the same conditions the S_n2' reaction seems to be unimportant. The results indicate that stronger nucleophiles attack intimate ion pairs and the undissociated primary substrate rather than dissociated solvated cations. The composition of the solvolysis product mixture depends, therefore, upon both the charge distribution in the cationic part of the ion pair (favoring tertiary products) and on reactivity relationships characteristic for direct displacement reactions (favoring primary products). t-Butanol and borohydride yield almost exclusively primary products under solvolytic condition indicating the importance of steric factors. The difference in behaviour between the solvated cation and an ion pair should be considered whenever experimental results are interpreted in terms of structure of solvolysis intermediates.

SOLVOLYSIS of tertiary α,α-dimethylallyl derivatives yields a considerable amount of rearranged primary products.[2] Thus, hydrolysis and ethanolysis of α,α-dimethylallyl chloride (1T) gives rise to 15 and 30% of primary products,[2] respectively, while in acetolysis the amount of the primary product is even higher (55%).[2] Similar behavior has been observed in the solvolysis and deamination of cyclopropylcarbinyl and cyclobutyl derivatives.[3] Careful studies of these latter reactions in the presence of external nucleophiles[1a] indicated that: (a) the composition of the product mixture depends upon the structure of the starting derivative (cyclopropylcarbinyl or cyclobutyl methanesulfonate) favoring the formation of unrearranged material; (b) a direct displacement reaction on the undissociated substrate is practically unimportant and; (c) increasing the nucleophilicity of the attacking reagent increases the relative amount of primary alkyl products. These observations are in accord with preferential attack of the nucleophile at the ion pair stage rather than attack on the dissociated solvated carbonium ions.[4–6] An ion pair exhibits behavior between that of a covalently bound substrate and a free solvated carbonium ion. Hence, if in a reaction intermediate the positive charge is delocalized, then the balance of the following two main factors will determine the course of the product forming step: (1) the charge distribution at different carbon atoms in the cationic part of the ion pair favoring the attack on the most substituted site, (2) reactivity and selectivity similar to that in S_N2 reactions since the reaction of a nucleophile with the tight ion pair resembles a direct displacement reaction. Therefore, the attack on the least substituted site should be favored.

The course of the product forming step and the structure of the intermediate ion pairs was further investigated using isomeric dimethylallyl chlorides 1T and 1P as substrates. The results of these studies are presented here

RESULTS AND DISCUSSION

The isomeric dimethylallyl chlorides 1T and 1P were isolated by preparative GLC from the mixture of products obtained by introducing gaseous HCl into isoprene and γ,γ-dimethylallyl alcohol, respectively. The purity of 1T and 1P as determined by GLC was better than 99%. Both chlorides were solvolyzed in either water, anhydrous ethanol or 66·7% aqueous ethanol in the presence of an excess of $CaCO_3$, NaOEt or $NaBH_4$ at 45°. Products were isolated after three or more half-lives* and analyzed by GLC.

A rearrangement subsequent to the formation of solvolysis products seems improbable since an excess of base was always present. Internal return 1T → 1P is known to be unimportant in absolute ethanol[8] although it takes place in aqueous ethanol[8] and acetic acid.[9] The composition of the mixture of hydrocarbons resulting from the reaction in the presence of $NaBH_4$ remained unchanged upon prolongation of the reaction time. Therefore, it can be assumed that low boiling hydrocarbons, i.e. 3-methyl-1-butene and 2-methyl-2-butene (b.p. 20·4 and 38·5°)[10] were isolated quantitatively as they were formed.

The composition of the product mixtures depends upon both the attacking nucleophile and the starting chloride. Products of unrearranged structure are formed preferentially. A very small product spread of the alcohols (3·1%) indicates that 1T and 1P hydrolyze *via* the same or very similar cationic intermediates. A direct displacement reaction of 1P with water is insignificant. The P/T products ratio with both chlorides 1T and 1P increases with increasing nucleophilicities of the attacking reagent $EtO^- \gg EtOH > H_2O$. This increase is faster with the primary chloride (1P) which indicates that stronger nucleophiles react with the primary substrate also *via* a direct displacement reaction. This is particularly true in the case of the ethoxide ion. The tertiary chloride (1T) behaves quite differently. Here ethoxide, a much stronger nucleophile than ethanol, gives only a slightly higher P/T product ratio than pure ethanol. Although 1T may react with ethoxide to a small extent by an S_N2' reaction, this path should be practically unimportant with ethanol or water.

The amount of primary products in hydrolysis and ethanolysis of 1T is relatively high and parallels the increase of nucleophilicity ($EtOH > H_2O$). Similar phenomena were observed previously with cyclopropylcarbinyl and cyclobutyl methanesulfonates and were taken as an indication that the nucleophile attacks ion pairs rather than dissociated solvated carbonium ions.[1a] The results described in this paper and obtained with isomeric dimethylallyl chlorides can be interpreted similarly (see the Scheme).

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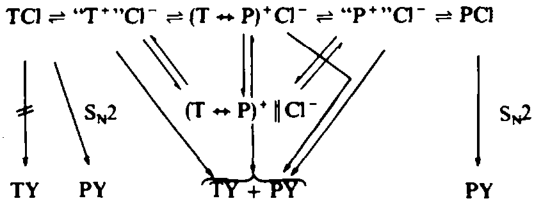
* The reported rates of ethanolysis of 1T and 1P at 44·6° are 1.84×10^{-4} sec^{-1} and 9.02×10^{-4} sec^{-1}, respectively.[7]

TABLE. COMPOSITION OF PRODUCT MIXTURES IN SOLVOLYSIS OF α,α-DIMETHYLALLYL (1T) AND γ,γ-DIMETHYLALLYL (1P) CHLORIDES AT 45°

Exp	Chloride[a]	Solvent	Added Salt mole/l	Products in %[b] T-X	P-X	X	P/T
1	1T	H_2O	$CaCO_3$	85·5	14·5	OH	0·17
2	1P	H_2O	$CaCO_3$	82·4	17·6	OH	0·21
3	1T	abs EtOH	$CaCO_3$	61·0	39·0	OEt	0·64
4	1P	abs EtOH	$CaCO_3$	51·9	48·1	OEt	0·93
5	1T	abs EtOH	1·0 NaOEt	50·5	49·5	OEt	0·98
6	1P	abs EtOH	1·0 NaOEt	3·0	97·0	OEt	32·4
7	1T	abs EtOH	0·5 $NaBH_4$	13·8	86·2	H	6·25
8	1T	abs EtOH	1·0 $NaBH_4$	12·5	87·5	H	7·00
9	1P	abs EtOH	0·5 $NaBH_4$	7·7	92·3	H	12·00
10	1P	abs EtOH	1·0 $NaBH_4$	6·1	93·9	H	15·4
11	1T	66·7% aq EtOH	1·0 $NaBH_4$	23·0	77·0	H	3·35
12	1P	66·7% aq EtOH	1·0 $NaBH_4$	15·1	84·9	H	5·62
13	1T	abs t-BuOH	$CaCO_3$	6·5	93·5	t-BuO	14·4

[a] 2·5 mmole in 10 ml of solvent;

[b] T = tertiary, P = primary; average values of 2-3 independent experiments with 3–4 GLC analysis of each product mixture; the reproducibility was better than ± 0·2% (± 0·4% in solvolysis with added NaOEt or $NaBH_4$)



Y = H, OH, OEt, t-BuO

SCHEME

The structure of the two intimate ion pairs formed in the rate determining step, "T^+"Cl^- and "P^+"Cl^-, can be considered as being between the structures of the starting chlorides and that of the solvent separated ion pair (T ↔ P)$^+$‖Cl^-. Therefore, the intimate ion pairs "T^+"Cl^- and "P^+"Cl^- are slightly different,[2b] the anionic part (anionoid)[4] being closer and probably more strongly bound to the original carbon atom than in the solvent separated ion pair. Ion pair type intermediates in the solvolysis of allylic compounds have been reported previously by several authors.[2b, 5, 6] In some cases asymmetrical ion pairs intermediates are involved.[6] Products can be formed from the primary chloride at each of the following stages: (1) by an S_N2 reaction on the unionized substrate; (2) from the "asymmetrical" intimate ion pairs; (3) the "common" intimate ion pair $(T \leftrightarrow P)^+Cl^-$; and/or (4) the solvent separated ion pair.* Stronger nucleophiles attack at the intimate ion pair stage. Therefore, the course of the product forming step depends not only upon the charge distribution in the cationic part of the ion pair (cationoid)[4] but also upon reactivity relationship and steric factors similar to those observed in direct displacement reactions. This path favors primary products. A product spread can be expected because the intimate ion pairs formed in the rate determining step of the solvolysis of 1T and 1P are not identical. An increase of the polarity of the solvent facilitates ionization and dissociation and the amount of the primary products can therefore be expected to decrease. This was actually observed with borohydride when the solvent was changed from anhydrous ethanol to 66·7% aqueous ethanol (experiments 8, 10–12, see Table). A possible internal return of 1T to 1P would increase the amount of primary product.

The borohydride anion, as a strong nucleophile, attacks the intimate ion pairs in accord with the Scheme. The hydrocarbon product spread (Table, exps. 7–10) is relatively small, "primary" hydrocarbon being the main volatile product of both chlorides 1T and 1P. The direct displacement reactions (S_N2 and S_N2') appear to be unimportant since a change in $NaBH_4$ concentration makes very little change in the hydrocarbon product compositions. This indicates that there should be an additional factor affecting the course of the product forming step. The exact structure of the attacking agent (i.e. borohydride anion) in EtOH is not known but, in any case, it is solvated and quite bulky in this form. The preferential attack of the borohydride on the primary carbon can be, therefore, rationalized on stereochemical grounds. This is supported by the results of t-butanolysis of 1T which yields almost exclusively the primary ether (Table, exp. 13). tBuOH, a bulky molecule, attacks almost exclusively the primary carbon atom.

In a recent paper[12] a preferred formation of primary products in solvolysis of strained cyclic allyl 3,5-dinitrobenzoates of the general formula $(CH_2)_nC{=}CH{-}CH_2X$ was reported and explained as being caused by constrictions of the endocyclic tertiary CCC angle. Distortions could, in principle, occur also from repulsions of gem-dimethyl groups in 1P and disturb the pi-electron density at the tertiary carbon. Since no detailed studies of products obtained under different reaction conditions were reported it is not possible from these data to evaluate the importance of sigma framework distortions vs. steric and ion pairing effects in solvolyses of allyl derivatives.

Ion pairing phenomena reflect upon the product forming step of a solvolytic reaction even with substrates which can form stable, tertiary and resonance stabilized intermediates (allyl cations) in solvents having a high dielectric constant. The analogous observation was made in our previous work[1a] on substrates that solvolyze via bridged, charge-delocalized nonclassical intermediates. It is to be expected that ion pairing will be even more important in cases where the substrate and/or the solvent are not favorable for promoting ionization. Therefore, the difference in behavior between a carbonium ion and an ion pair has to be taken into account when experimental results are being interpreted in terms of the structure of solvolysis reaction intermediates.

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* This scheme differs from the original picture formulated by Winstein[11] in two important points: (1) products can also be formed by attack on the intimate ion pair, and (2) the S_N2 reaction is included

EXPERIMENTAL

GLC analysis and purifications were carried out on an Aerograph Autoprep A-700 chromatograph using a pen type recorder and Disc Integrator 201B: H_2 was used as the carrier gas. NMR spectra were recorded on a Varian A-60A spectrometer, TMS as reference.

α,α-Dimethylallyl chloride (1T) *and γ,γ-dimethylallyl chloride* (1P). Two procedures were used both leading to mixtures of chlorides 1T and 1P but in different ratios. Introduction of gaseous HCl (5·1 g, 0·14 moles) into an isoprene–ether mixture (2·6 g, 0·2 moles; 2 ml of ether) at −80° gave predominantly 1T (80–90%).[13] Bubbling of gaseous HCl (1·86 g, 51 mmoles) through γ,γ-dimethyllyl alcohol[14] (4·4 g, 51 mmoles) at 0° afforded 4·7 g (87·6%) of a mixture of chlorides containing about 75% of 1P.[15] The chlorides were separated by preparative GLC on 300 × 0·6 cm 15% SE-30 on Chromosorb AW 30/60 column at 25°. At higher temperatures the chlorides isomerized on the column. The purities of 1T and 1P were greater than 99% (by GLC). The separated chlorides were identified by NMR.

Product studies. The structures of all solvolysis products were determined from the NMR spectra of the pure compounds isolated by preparative GLC from the solvolysis mixtures. The quantitative analysis of the solvolysis product mixtures were carried out by GLC under the following conditions. Alcohols and ethers (ethyl and t-butyl): 600 × 0·6 cm 20% Carbowax on Chromosorb P 60/80 at 140 and 95°, respectively; hydrocarbons: 600 × 0·6 cm 15% SE-30 on Chromosorb P 45/60 at 45°. Data given in the Table represent average values of 2–3 independent experiments with 3–4 GLC analysis of each product mixture. The reproducibility was better than ±0·2% (±0·4% in solvolysis with added NaOEt or $NaBH_4$).

Hydrolysis. Dimethylallyl chloride (1T or 1P; 0·25 g, 2·5 mmoles) was added to a vigorously stirred suspension of $CaCO_3$ (0·15 g, 1·5 mmoles) in water (10 ml) and the stirring continued at 45° for 6 and 12 hours, respectively. After cooling and filtering, the alcohols were continuously extracted with ether; the extracts were dried over $CaSO_4$ and the solvent was removed by distillation through a Vigreaux column. The residue was analyzed by GLC as described above.

Alcoholysis. The procedure was analogous to that described for hydrolysis (2·5 mmoles of chloride, 0·15 g of $CaCO_3$, 10 ml of anhydrous alcohol, 45°). The reaction times were 210 min (1T) and 420 min (1P), respectively. $CaCO_3$ was omitted in ethynolysis with added NaOEt. After cooling and filtering, 50 ml of pentane was added and the mixture washed 8 times with 100 ml of water. The pentane soln was dried over a mixture of $CaCl_2$ and $CaSO_4$. Pentane was removed by distillation through a Vigreaux column and the residue analyzed by GLC.

Solvolysis of 1T *and* 1P *in the presence of* $NaBH_4$. To a stirred soln of $NaBH_4$ (see the Table) in 10 ml of anhydrous or 66·7% aqueous ethanol at 45°, 0·25 g (2·5 mmoles) of the corresponding chloride was added. In anhydrous EtOH stirring was continued at the same temperature for 150 min in the case of 1T and 300 min with 1P; 0·5 and 30 min with 1T and 30 min with 1P in aqueous EtOH. The volatile products were flushed with N_2 through (45°) aqueous soln of $CaCl_2$ (45°) into a trap cooled with liquid air. Before the GLC analysis, the hydrocarbon product mixtures were distilled under high vacuum. There was no detectable difference in the composition of the hydrocarbon mixtures resulting from 1T in solvolysis (66·7% aqueous EtOH) after 30 sec and after 30 min.

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