All of the acids listed were sent to us from the Organic Chemistry Division, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland, by Dr. L. A. Kaplan and Dr. M. J. Kamlet.

It may be noted that the successive replacement of the three methyl groups of *t*-butyl by nitro groups brings about a fairly steady increase in σ_{para}. The σ_{para} and the σ^* values listed for the trinitromethyl group appear to be the largest that have been measured for any electrically neutral group.[3,4]

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(3) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(4) R. W. Taft, Jr., in M. S. Newman's *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, chap. 13.

An Example of Ester Cleavage by Mechanism $B_{Al}2$

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In the course of an investigation into the solvolytic behavior of some isomeric allylic esters we have uncovered an interesting example of the rarely observed $B_{Al}2$ mechanism[1] of ester cleavage: base-catalyzed, bimolecular attack with alkyl-oxygen cleavage. The evidence for this reaction forms the subject matter of this communication.

In particular the methanolysis of α-methyl-γ-phenylallyl *p*-nitrobenzoate had been under study[2] and it had been shown that in the absence of added bases this ester reacts in methanol by an S_N1-type ionization process to furnish *p*-nitrobenzoic acid and both possible isomeric methyl ethers with a first order rate constant at 65° of $k_1 = 1.50 \pm 0.03 \times 10^{-5}$ sec.$^{-1}$ In an attempt to prevent the rather rapid acid-catalyzed equilibration of the initially formed allylic ethers, sodium phenoxide was added as a buffering agent to a methanolic solution of the ester. Interestingly, the rate of production of acid (consumption of base) under these conditions proved to be less than the rate of normal solvolysis of this ester. Furthermore, the reaction appeared to be heading for completion by an essentially second order process, first order in the stoichiometric base concentration. The kinetic data for this run are summarized in Table I. We interpreted these results to mean that the allyl *p*-nitrobenzoate was being consumed by a rapid process to furnish nonacidic products which subsequently underwent a slow base-catalyzed acid-producing reaction, presumably the rate determining step of the reaction.

TABLE I

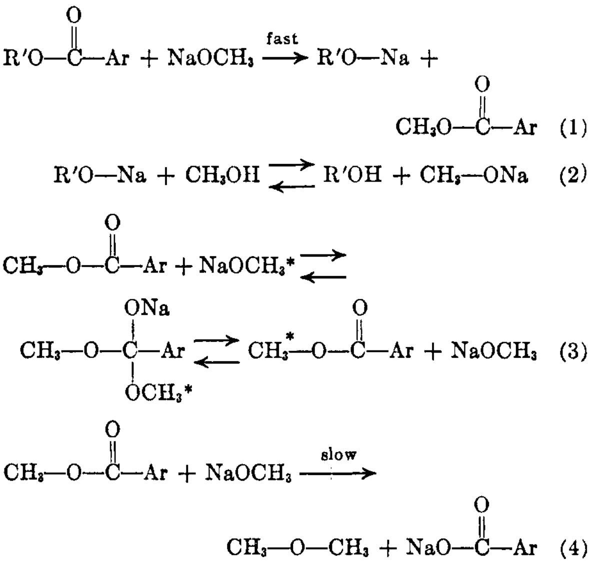
RATE OF REACTION OF α-METHYL-γ-PHENYLALLYL *p*-NITROBENZOATE WITH SODIUM PHENOXIDE IN METHANOL AT 65.0°

$[\mathrm{Ester}]_{\mathrm{initial}} = 0.0184M$
$[\mathrm{NaOC_6H_5}]_{\mathrm{initial}} = 0.0220M$
Titrant = 0.0209*M* aqueous hydrochloric acid
Quench = 10 ml. acetone
Aliquot = 5 ml.

% Reaction	$\dfrac{-d[\mathrm{NaOC_6H_5}]/dt \times 10^4}{[\mathrm{NaOC_6H_5}][\mathrm{R'X}]}$, L. Mole^{-1} Sec.$^{-1}$[a]
12.6	2.39
18.0	2.36
26.0	2.46
37.8	2.34
43.5	2.31
47.2	2.32
	Av. 2.36 ± 0.04

[a] Derivative obtained by taking tangents to a plot of time *vs.* ml. of titrant.

One sequence of reactions which appeared consistent with these facts is reproduced below (for simplicity in representation the scheme has been modified by assuming base to be present only in the form of sodium methoxide, even though it was introduced in the form of sodium phenoxide):



$$\mathrm{R'O{-}\overset{O}{\overset{\|}{C}}{-}Ar + NaOCH_3 \xrightarrow{fast} R'O{-}Na + CH_3O{-}\overset{O}{\overset{\|}{C}}{-}Ar} \quad (1)$$

$$\mathrm{R'O{-}Na + CH_3OH \rightleftarrows R'OH + CH_3{-}ONa} \quad (2)$$

$$\mathrm{CH_3{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar + NaOCH_3^* \rightleftarrows CH_3{-}O{-}\underset{OCH_3^*}{\overset{ONa}{C}}{-}Ar \rightleftarrows CH_3^*{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar + NaOCH_3} \quad (3)$$

$$\mathrm{CH_3{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar + NaOCH_3 \xrightarrow{slow} CH_3{-}O{-}CH_3 + NaO{-}\overset{O}{\overset{\|}{C}}{-}Ar} \quad (4)$$

R′ = α-methyl-γ-phenylallyl

The first step of this scheme, ester interchange, is presumed to be very fast as required by the observation that the rate of reaction is slower than ordinary solvolysis. (Methyl *p*-nitrobenzoate should, of course, be stable to ionization.) Step 3 is also an ester interchange reaction of mechanism $B_{Ac}2$[1] whose rate is probably very rapid but whose incurrence has no effect on the overall reaction since the products are identical with starting materials. The slow step of the reaction is step 4, the so-called $B_{Al}2$[1] reaction whose presence in most systems is masked by the faster $B_{Ac}2$ reaction. Step 4 is essentially an S_N2 reaction,

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(1) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., pp. 765 *et seq.*, 1953.

(2) R. A. Sneen and A. M. Rosenberg, *J. Am. Chem. Soc.*, **83**, 895 (1961).

TABLE II

COMPARISON OF RATES OF REACTION OF METHYL AND α-METHYL-γ-PHENYLALLYL p-NITROBENZOATE ESTERS WITH SODIUM METHOXIDE IN METHANOL AT 65.0°

[Methyl p-nitrobenzoate]$_{\text{initial}}$ = 0.0186M
[α-Methyl-γ-phenylallyl p-nitrobenzoate]$_{\text{initial}}$ = 0.0186M
[$NaOCH_3$]$_{\text{initial}}$ = 0.0533M
Titrant = $2.09 \times 10^{-2}M$ aqueous hydrochloric acid
Blank ($NaOCH_3$ + solvent) = 5.113 ml. of acid
Quench = 10 ml. of acetone
Aliquot = 2 ml.

Time, Sec.	Titrant, Ml.		$(k_1/[NaOCH_3]_{Av}) \times 10^4$[c]	
	MeOpNB[a]	AllylOpNB[b]	MeOpNB[a]	AllylOpNB[b]
0	4.790	4.749	—	—
17,086	4.537	4.530	2.6	2.3
31,128	4.322	4.400	3.0	2.2
55,840	4.170	4.212	2.5	2.1
75,600	4.098	4.100	2.2	2.1
106,220	4.013	3.994	1.9	1.9
177,115	3.822	3.868	1.7	1.5
1,635,000	3.532	3.580	—	—
2,200,000(∞)	3.510	3.517	—	—
			Av. 2.3 ± 0.4	2.0 ± 0.2

[a] Methyl p-nitrobenzoate. [b] α-Methyl-γ-phenylallyl p-nitrobenzoate. [c] k_1 = integrated first-order rate constant; [$NaOCH_3$]$_{Av.}$ = average base concentration throughout the interval of reaction.

a displacement reaction by alkoxide ion on the methyl carbon atom of methyl p-nitrobenzoate.[3]

The proposed mechanism has several experimentally determinable consequences. Thus, it predicts that dimethyl ether should be a product of the reaction. This prediction has been shown to be fulfilled. When the more volatile components of the reaction mixture resulting from the interaction of α-methyl-γ-phenylallyl p-nitrobenzoate and sodium methoxide (>10 half-lives) were concentrated by distillation and submitted to vapor phase chromatography, the presence of dimethyl ether among the products was established by the presence in the chromatogram of a peak whose retention time and shape were identical with those of authentic dimethyl ether. The proposed mechanism also predicts that, if step 1 is fast, the rate-determining step of the reaction is that between methyl p-nitrobenzoate and sodium methoxide and, therefore, that the rate of reaction between an allylic p-nitrobenzoate and methoxide should be essentially the same as that between authentic methyl p-nitrobenzoate and methoxide. This prediction has also been verified. Equimolar amounts of methyl and α-methyl-γ-phenylallyl p-nitrobenzoate were introduced into equal portions of a solution of sodium methoxide in methanol. We chose to introduce base as sodium methoxide (rather than as phenoxide) in order to avoid kinetic complications. An approximately threefold excess of base was used in order to speed the reaction and also to achieve conditions approaching pseudo-first order kinetics. The higher concentration of base reduced considerably the accuracy of the runs (total change in titer was, in both cases, less than 1.30 ml.) but a comparison of the data of Table II leaves no doubt that both esters reacted at the same rate by an essentially second order process.

We conclude that the facts described in this report are consistent with the above-suggested scheme.

EXPERIMENTAL

Kinetic evidence. The kinetic run described in Table I involved techniques described elsewhere.[2,5] The rate constants reported in the last column of Table I are differential second order rates. The quantity, $-d[NaOC_6H_5]/dt$, was determined at selected times from the tangent to the best curve drawn through a plot of time *vs.* ml. of titrant.

The kinetic runs described in Table II were similar to those described elsewhere[2] with only the following minor changes. Freshly cut sodium metal (3.4 g., Baker purified) was washed successively with benzene, pentane, and methanol and was then allowed to react completely with anhydrous methanol before dilution to 250 ml. of solution. By titration this solution was found to be 0.0533M in base. This solution was used to dissolve separately equimolar (1.86 mmoles) amounts of methyl p-nitrobenzoate and α-methyl-γ-phenylallyl p-nitrobenzoate to 100 ml. of solution. Each solution was then divided among glass ampoules, sealed, and placed in a constant temperature bath. At intervals ampoules of each solution were removed simultaneously and cooled to room temperature. Aliquots (2 ml.) of each solution were quenched in 10-ml. portions of acetone and titrated with standard acid. The data of columns 4 and 5 of Table II are integrated first order rates of consumption of base. In columns 6 and 7 these first order rate constants are divided by the average concentration of sodium methoxide during the interval of reaction over which the first order rates were determined.

Product evidence. After *ca.* twenty half-lives of reaction between α-methyl-γ-phenylallyl p-nitrobenzoate and sodium methoxide in methanol, described in Table II, aliquots of the reaction mixture were combined to furnish *ca.* 20 ml. of

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(3) This mechanism was first identified among the reactions of simple esters by Bunnett and co-workers[4] who showed that methyl benzoate and sodium methoxide react to form dimethyl ether by a reaction qualitatively dependent on the concentration of methoxide ion.

(4) J. F. Bunnett, M. M. Robison, and F. C. Pennington, *J. Am. Chem. Soc.*, **72**, 2328 (1950).

(5) Sodium phenoxide, kindly furnished by C. Vogel, was found to be better than 99% pure by titration.

solution which was distilled in a closed system through an 18-in. Vigreux column into a receiving flask cooled in Dry Ice–acetone. The first fraction collected (*ca.* 1 ml.) was injected into a Perkin-Elmer Vapor Fractometer (Model 154C) containing a column packed with polypropylene glycol. The instrument was fitted with a flame ionization detector, the carrier gas was nitrogen and the temperature was maintained at 100°. The resulting chromatogram contained, in additional to strong methanol absorption, a relatively sharp peak with retention time of 2.04 min. An essentially identical peak, with the same retention time, was observed in the spectrum of a solution of methanol through which dimethyl ether (Matheson Co.) had been bubbled for 5 min. immediately prior to injection.

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Rearrangement of Lactones from Substituted 3-Hydroxycyclohexanecarboxylic Acids[1]

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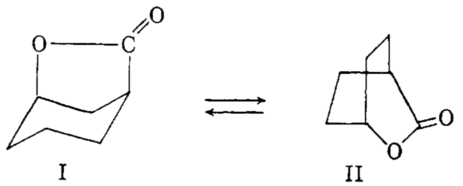
The rearrangement of hydroxy acids (or lactones) is well known, particularly in complex ring systems. In the chemistry of the diterpenes and resin acids several examples have recently been clarified.[4]

In connection with other studies[5,6] we have had occasion to observe examples of rearrangement in simple cyclohexane derivatives.

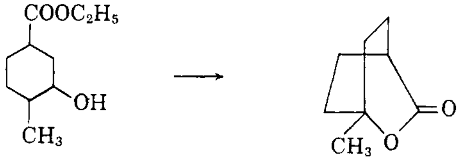
The first example is the rearrangement of the lactone of *cis*-3-hydroxycyclohexanecarboxylic acid (I) upon standing in concentrated sulfuric acid at room temperature. Though the recovery of material is not high, the predominant product is the lactone of *cis*-4-hydroxycyclohexanecarboxylic acid (II). The change from the bicyclo[3.2.1]octane system to the [2.2.2] bicyclic system is somewhat unusual.



I II

In comparable carbocyclic compounds, 2-bromobicyclo[2.2.2]octane rearranges to 2-bromobicyclo-[3.2.1]octane,[7] upon treatment with silver ion under what are presumably equilibrium conditions. Similarly[8] hydration of bicyclo[2.2.2]octene affords bicyclo[3.2.1]octanol-2 in good yield. In both cases it has been suggested that relief of bond oppositions provides a rationale for the change from the [2.2.2] system to the [3.2.1] system. On the other hand, the addition of acetic acid to bicyclo[3.2.1]-octene-2 gives bicyclo[2.2.2]octyl acetate.[9]

In the second example, we treated ethyl 3-hydroxy 4-methylcyclohexanecarboxylate with 50% sulfuric acid, under conditions which were designed to lead to lactone formation. The product of this reaction of m.p. 68–69° ($C_8H_{12}O_2$) is a δ-lactone from its infrared spectrum, and is therefore assigned structure IV.



III IV

Lehman and Paasche[10] have reported a byproduct of m.p. 69° from the Diels-Alder reaction of isoprene and acrylic acid, to which they assign the structure of 4-methyl-3-hydroxycyclohexanecarboxylic acid lactone(V). However, neither isomer of V melts at 69°[6] and it appears highly probably that the compound of Lehman and Paasche is IV.

EXPERIMENTAL[11]

4-Methyl-cis-4-hydroxycyclohexanecarboxylic acid lactone Reduction of ethyl 3-hydroxy-4-methylbenzoate with Raney nickel and hydrogen afforded a mixture of the lactones of 4-methyl-*cis*-3-hydroxycyclohexanecarboxylic acid and the ethyl-4-methyl-3-hydroxycyclohexanecarboxylates.[6] This mixture (43 g.) was heated at 45° for 16 hr. with 200 ml. of 50% sulfuric acid. The reaction mixture was diluted and extracted with ether. The ether extracts were washed with 10% sodium carbonate solution, water, and then dried. Distillation afforded a fraction, b.p. 100–130° (7 mm.) which solidified. Recrystallization from pentane afforded the lactone of 4-methyl 4-hydroxycyclohexanecarboxylic acid, m.p. 68.0–

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[1] Studies of Configuration X. Previous paper, D. S. Noyce and B. N. Bastian, *J. Am. Chem. Soc.*, **82**, 1246 (1960). Supported in part by a grant from the National Science Foundation (NSF-G5921).

[2] Eastman Kodak Company Fellow, 1954–55.

[3] Dow Chemical Corporation Fellow, 1958–59.

[4] *Cf.* L. J. Gough, T. F. Sanderson, V. I. Stenberg, and E. Wenkert, *J. Org. Chem.*, **25**, 1269 (1960); E. Wenkert and J. W. Chamberlain, *J. Am. Chem. Soc.*, **81**, 688 (1959).

[5] D. S. Noyce and H. I. Weingarten, *J. Am. Chem. Soc.*, **79**, 3098 (1957).

[6] D. S. Noyce and L. J. Dolby, abstracts of papers presented at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 1959, *J. Org. Chem.*, **26**, 1732 (1961).

[7] W. v. E. Doering and M. Farber, *J. Am. Chem. Soc.*, **71**, 1514 (1949).

[8] M. S. Newman and Y. T. Yu, *J. Am. Chem. Soc.*, **74**, 507 (1952). *Cf.* A. A. Youssef, M. E. Baup, and H. M. Walborsky, *J. Am. Chem. Soc.*, **81**, 4709 (1959).

[9] K. Alder, H. Kniger, and H. Weiss, *Ber.*, **88**, 144 (1955).

[10] E. Lehman and W. Paasche, *Ber.*, **68**, 1068 (1935).

[11] Melting points are corrected; boiling points are uncorrected. Infrared spectra were determined using a Baird Model B Infrared Spectrophotometer.