A 10-ml. sample from the reaction mixture was delivered into a separatory funnel containing 100 ml. of ether and 15 ml. of 0.2 *M* acetic acid–sodium acetate buffer. The ether layer was extracted with 45 ml. of buffer in three portions, and the aqueous buffer layers were mixed with 4 ml. of Tergitol in an electrolytic beaker. Silver nitrate was added until the equivalence potential, approximately 173 mv., was reached.

To test the stability of the products to hydrobromic acid, a blank, 0.1 *M* in both hydrobromic acid and acetylenic carbinol, was prepared and analyzed for bromide ion. The bromide ion concentration was constant to 1% over the period of a month.

Rate of Production of Bromide Ions in the Presence of Azide Ions.—The presence of sodium azide in the reaction mixture necessitated a modification of the above procedure for the analysis of bromide ion, because azide obscured the previously clear maximum in the plot of Δe.m.f. *vs.* volume of silver nitrate. The sample was run into ether and was extracted with water instead of buffer solution. One milliliter of concentrated sulfuric acid was then added to the titration beaker containing the water extracts and Tergitol and the bromide was titrated by the conductometric procedure. Under these conditions the end-point potential was found to be 125 mv.

C. Treatment of Data.—First- and second-order integrated rate constants were calculated from the equations

$$\bar{k}_1 = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$\bar{k}_2 = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

In these equations a is the initial concentration of sodium hydroxide in "80%" ethanol, b is the initial concentration of organic halide and x is the amount of hydroxide that has reacted (in moles per liter) at time t. The initial rate constant $\bar{k}_2°$ was found from a plot of integrated rate constants *versus* percentage reaction, 100 (x/b).[35] A smooth curve drawn through the points was extrapolated to zero percentage reaction. The initial rate constants thus calculated were reproducible to within ±2%. The main limitation on the accuracy of $\bar{k}_2°$ was the determination of b, the initial concentration of organic halide. Because of isomerization, it was not practical to wait until a steady infinity titer was reached. Thus, four variables were involved: the weight and density of the solvent, and the weight and purity of the solute. Of these the largest variation probably occurred in the last, although it was difficult to estimate purity from the flat chromatographic peaks of the impurities.

Product Composition.—3-Bromo-3-methyl-1-butyne (4.531 g., 0.0308 mole, 0.123 *M*) was added to a solution of 1.312 g. (0.0328 mole, 0.131 *M*) of sodium hydroxide in 250 ml. of "80%" ethanol. After standing for 2 days at room temperature and then for 11 days in a refrigerator, the mixture was distilled through a 10 × 390 mm. fractionating column packed with $^1/_{16}''$ glass helices. The condenser and receiver were cooled with ice-water to prevent escape of the low-boiling 2-methyl-1-butene-3-yne (b.p. 32°). Two fractions were collected: (1) 68–77.5° (740 mm.), containing "ene-yne" and the acetylenic ether–ethanol azeotrope and (2) 77.5–78.5°, containing ethanol and water. After most of the ethanol-water azeotrope was removed, the remaining liquid was transferred to a smaller flask and a third fraction (3) 78.5–99.5°, containing mainly an acetylenic carbinol–water azeotrope, was collected. Fractions 1 and 3 were combined and analyzed by gas chromatography; the integrator was used for determination of peak area. The area under each product peak was also estimated by multiplying its height by its width at half-height. The two sets of mole per cent. composition values were not different by more than 1 mole per cent. Quantitative analysis of a mixture of known amounts of ether and carbinol established the reliability of this procedure to an accuracy of about ±2 mole per cent.

A similar procedure was followed in a determination of the relative amounts of "ene-yne," ether and carbinol formed in the first-order solvolysis, except that 29 days elapsed before the distillation was begun.

In the chromatogram of the products of the second-order reaction, in addition to the major product peaks there were two very small peaks between the olefin peak and the ether peak. In the first-order chromatogram a single small peak appeared between olefin and ether and two small peaks appeared between ether and carbinol.

Acknowledgment.—The authors are indebted to Professor G. F. Hennion, who first aroused their interest in this problem, for several valuable discussions.

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[35] O. T. Benfey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2488 (1952).

[Contribution No. 1042 from the Department of Chemistry of Indiana University, Bloomington, Ind.]

The Effects of Deuterium Substitution on the Rates of Organic Reactions. VII. Secondary Effects on the Solvolysis of 3-Halo-3-methyl-1-butynes[1]

By V. J. Shiner, Jr.,[2] Joseph W. Wilson,[3] Guenther Heinemann and Norman Solliday[4]

Received December 26, 1961

The isotopic variant of 3-bromo-3-methyl-1-butyne (I) having all six hydrogens of the two methyl groups replaced by deuterium (II), undergoes the SN1, carbonium ion solvolysis reaction in "80%" ethanol at 25° 1.84 times slower than I itself. The second-order hydroxide ion-promoted solvolysis, which is an SN1 reaction of the conjugate base, is slowed, by this deuterium substitution, by only a factor of 1.31. This is apparently most reasonably explained in terms of differing demand for hyperconjugation in the two closely related transition states. Replacement of the acetylenic hydrogen by deuterium has very little if any influence on the solvolysis rate of the analogous chloro compound. This represents a "vinylog" of α-deuterium substitution and the absence of any isotope effect is consistent with the accepted steric origin of the α-deuterium isotope effect.

Introduction

Because of their close relationship to changes in molecular structure on activation, isotope rate effects provide an especially valuable tool in the investigation of reaction mechanism or transition state structure. The importance of carbonium ion reactions in the theory and practice of organic chemistry and the rather large observed effects have led to considerable interest in the rate retardations caused by β-deuterium substitution in carbonium ion forming processes. Although these β-deuterium secondary isotope rate effects are certainly largely due to differential changes in vibration frequencies on activation, between the

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[1] (a) Taken in part from the thesis submitted by Joseph W. Wilson to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. (b) Supported in part by Grant G 5062 from The National Science Foundation, Washington, D. C.

[2] Alfred P. Sloan Research Fellow.

[3] Dow Fellow, 1960–1961.

[4] National Science Foundation Undergraduate Research Participation Fellow, summer, 1961.

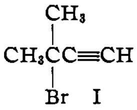
hydrogen and deuterium compounds, there is some question as to whether the vibration frequency changes are due to changes in bonding (hyperconjugation)[5,6] or non-bonding (steric)[7] interactions.

Replacement by deuterium of a hydrogen attached directly to the carbon at the reaction center also leads to an appreciable rate depression of carbonium ion forming reactions.[8] It is generally agreed that these α-deuterium secondary isotope rate effects are caused by changes in steric influences on vibration frequencies.

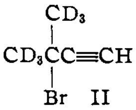
In the preceding paper[9] we have established some of the details of the mechanism of solvolysis of 3-chloro- and 3-bromo-3-methyl-1-butyne. These compounds show two solvolytic mechanisms in aqueous ethanol. One is the usual SN1, carbonium ion type and the second is an SN1-like ionization *of the conjugate base* formed in equilibrium from the starting material by loss of the acetylenic proton. It is possible to measure three different kinds of deuterium isotope effects in these reactions and each seems of especial interest. The comparison between the β-deuterium isotope effects in the first- and second-order reactions is of interest because the initial states are the same and the transition states seemingly have a minimum stereochemical difference. The γ- (or acetylenic) deuterium isotope effect in the first-order reaction is of interest because this isotopic substitution is "vinylogous" to α-deuterium substitution and this position should experience electrical effects similar to those of the reaction center but not suffer any changes in non-bonding interactions during activation.[15] Measurement of these isotope effects was, accordingly, undertaken.

Results and Discussion

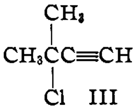
3-Bromo-3-methyl-d_3-1-butyne-4,4,4-d_3 (II) was synthesized *via* the carbinol from hexadeuterioacetone and sodium acetylide. 3-Chloro-3-methyl-1-butyne-1-*d* IV was prepared by repeated base-catalyzed exchange between 3-chloro-3-methyl-1-butyne and ethanol-*d*. Deuterium analysis showed II to contain 6.18 atom and IV, 0.85 atom of D per molecule.


I

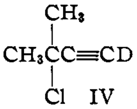
$CH_3C(CH_3)(Br)C{\equiv}CH$


II

$CD_3C(CD_3)(Br)C{\equiv}CH$


III

$CH_3C(CH_3)(Cl)C{\equiv}CH$


IV

$CH_3C(CH_3)(Cl)C{\equiv}CD$

The observed rate constants are recorded in Table I.

The β-deuterium secondary isotope rate effect (k_H/k_D) is then 1.84 in the first-order and 1.31 in the second-order reaction for the substitution of the six methyl hydrogens in I by deuterium. The isotope effect in the SN1 reaction of III, caused by replacing the acetylenic hydrogen by deuterium (IV) is nil, the rate ratio being negligibly different from 1.00.

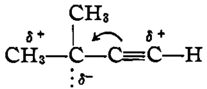
TABLE I

RATE CONSTANTS FOR SOLVOLYSIS AT 25°

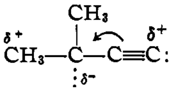
Compound	Solvent, ethanol	First order	Second order
I	"80%"	4.6[a]	11.5[b]
II	"80%"	2.5[a]	8.8[b]
III	"30%"	11.45	
IV	"30%"	11.45	

[a] Extrapolated initial integrated first-order rate constants; units are 10^{-6} sec.$^{-1}$. [b] Extrapolated initial integrated second-order rate constants for reaction with ^{-}OH; units are 10^{-3} l./mole/sec.

Since the initial state of I (or II) in the solvolysis is the same whether the first-order or second-order mechanism obtains and the transition states (V and VI) differ only by a proton, any steric influence on the difference in the two isotope effects would have to arise either from solvation differences or from different degrees of C–Br bond breakage (and other dependent, concurrent structural alterations).


V

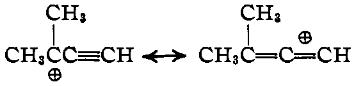
$\overset{\delta+}{CH_3}{-}\overset{CH_3}{\underset{\overset{\vdots\,\delta-}{Br}}{C}}{-}\overset{\delta+}{C}{\equiv}C{-}H$


VI

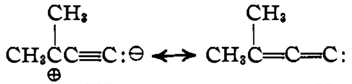
$\overset{\delta+}{CH_3}{-}\overset{CH_3}{\underset{\overset{\vdots\,\delta-}{Br}}{C}}{-}\overset{\delta+}{C}{\equiv}C{:}$

It would further seem that the degree of solvation around the central carbon atom, and therefore around the attached methyl groups, would be less in VI than in V because the charge on the central atom is less. Thus any steric crowding due to solvation would be less in VI than V and any differential isotope effect thus caused would be in the direction opposite to that observed, *i.e.*, tending to make the isotope effect larger in VI than in V instead of *vice versa*.

If we make the reasonable assumption that the *internal steric effects around the methyl groups* in the intermediate VII ↔ VIII are equivalent to those in IX ↔ X, the identity of the initial states then


VII VIII

$CH_3\overset{CH_3}{\underset{\oplus}{C}}C{\equiv}CH \longleftrightarrow CH_3\overset{CH_3}{C}{=}\overset{\oplus}{C}{=}CH$


IX X

$CH_3\overset{CH_3}{\underset{\oplus}{C}}C{\equiv}C{:}\ominus \longleftrightarrow CH_3\overset{CH_3}{C}{=}C{=}C{:}$

requires that the internal steric effects in the transition states can only differ because of differing degrees of progression along the reaction coördinates in the two reactions; *i.e.*, different degrees of C–Br bond breaking. There are two *a priori* possibilities for the order of the extent of bond breaking in the two transition states and two general postulates, one predicting one order and the other predicting the second. The first postulate, formulated and applied in the most general way by Hammond,[10] predicts that the reaction which proceeds the fastest, *i.e.*, has the lowest activation energy, will have its transition state most like the initial state. In the present example the second-order reaction is predicted by this postulate to have a smaller degree of C–Br bond breaking. If this situation actually obtains, then the *order* of isotope effects is correctly predicted by the steric explanation.

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(5) V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

(6) E. S. Lewis, *ibid.*, **5**, 143 (1959).

(7) L. S. Bartell, *J. Am. Chem. Soc.*, **83**, 3567 (1961).

(8) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *ibid.*, **80**, 2326 (1958).

(9) V. J. Shiner, Jr., and J. W. Wilson, *ibid.*, **84**, 2402 (1962).

(10) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

TABLE II

VARIATION OF ISOTOPE EFFECT WITH EXTENT OF CARBONIUM ION CHARACTER IN THE TRANSITION STATE IN SOLVOLYSIS REACTIONS[a]

R in $RC(CD_3)_2X$	$—C{\equiv}CH$	$—CH_2CH_3$	$—C_6H_5$	$—C{\equiv}C:^-$	$—\overset{\overset{H}{+\vert}}{O}C_2H_5$
X	—Br	—Cl	—Cl	—Br	$—OC_2H_5$
Rel. rate	0.3	1	5×10^2	10^9	
k_H/k_D	1.84	1.77	1.48[b]	1.31	1.12
Ref.	This work	12a	13	This work	14

[a] All in "80%" ethanol at 25°, except last entry which refers to 90% dioxane at 25°. [b] Estimated as the square for the value $C_6H_5CHClCD_3$.

However, Swain and Thornton have recently documented several examples of solvolytic reactions in which the Hammond postulate gives the wrong prediction. These authors have suggested that such results are general for ionic reactions in solution and have formulated a new rule which accommodates these exceptions and gives, in the present example, the opposite prediction.[11] Thus if the Swain–Thornton rule correctly predicts the extent of bond breaking in the transition state, the steric explanation predicts the *incorrect* order for the secondary isotope effects in the first- and second-order reactions herein reported. It would appear then that either the steric explanation of β-deuterium secondary isotope effects[7] or the Swain–Thornton rule[11] lacks the generality claimed in their original formulations.

In either case the order in the present results is correctly predicted by the hyperconjugative influence originally suggested as dominating in these secondary isotope effects.[12] Since X, having two less formal charges than IX, will contribute more importantly to IX ↔ X than VIII, which has the same number of formal charges as VII, does to VII ↔ VIII, the degree of vacancy on the central carbon atom in the second-order reaction will be less than that in the first-order reaction. The demand for hyperconjugation will be proportionately less and, to the extent that hyperconjugation causes the isotope effect, it will also be less.

Table II illustrates how a number of relevant β-deuterium secondary isotope effects in carbonium ion-type reactions vary with the apparent demand for hyperconjugation at the reaction center, or, in other words, in opposition to the ability of other substituent groups to disperse internally the charge developed.

The comparison made for the two closely related examples discussed above here extends qualitatively over almost the entire range. It might be argued that the first two isotope effect ratios in Table II are in the wrong order for this explanation since the first, and larger, number refers to a resonance-stabilized transition state and the second does not. The difference is, however, small and perhaps not experimentally significant. The difference may also reflect some inductive influence on the degree of carbonium ion vacancy.

The lack of an isotope effect on the first-order solvolysis of III, due to replacement of the acetylenic hydrogen by deuterium, is consistent with the expected lack of steric or hyperconjugative involvement of this position in the solvolysis reaction.[20] This incidentally reinforces the conclusion drawn above that the presence (or absence) of this proton should have no effect on the steric situation at the methyl groups. Since a substituent at this position should experience an electronic effect similar to that for a substituent at the reaction center,[15] the lack of any effect in the present example is consistent with the interpretation of the α-deuterium isotope effect as being the result of changes in non-bonding interactions.[8]

Experimental

With the exceptions enumerated below the compound sources, preparations and kinetic procedures were those described in the previous paper.[9]

Acetone-d_6 was prepared by the method of Shiner and Cross.[14] Combustion analysis[16] indicated a content of 6.18 atoms of D per molecule.

2-Methyl-d_3-3-butyne-2-ol-1,1,1,-d_3 was prepared by the method of Newman, Fones and Booth.[17] The higher boiling residue obtained from a starting sample of 18.3 g. (0.28 mole) of acetone-d_6 was used in the following preparation without distillation.

3-Bromo-3-methyl-d_3-1-butyne-4,4,4-d_3 was prepared using the procedure given in the previous paper[9] from the carbinol prepared as described above. The yield of bromide was 9.1 g. or 21% over-all based on the starting acetone-d_6.

3-Chloro-3-methyl-1-butyne was prepared by the method of Hennion and Nelson.[18]

3-Chloro-3-methyl-1-butyne-1-*d*.—A sample of 41 g. (0.9 mole) of ethanol-*d* was placed in a 100-ml. round-bottomed flask and 0.1 g. (0.005 mole) of sodium was added. After the sodium had dissolved, 10 g. (0.10 mole) of 3-chloro-3-methyl-1-butyne was added. The mixture was fractionally distilled. The ethanol–chloride azeotrope and some ethanol were collected from 66–75°. This was washed several times with a large excess of water and dried over anhydrous potassium carbonate. The yield was approximately 5 g. or 50%. Analysis based on the acetylenic hydrogen stretching absorbancy at approximately 3400 cm.$^{-1}$ indicated only about 70% deuteration. The exchange was repeated once again and the deuterium content approached 0.90 atom/molecule. The lack of more complete deuteration may be due to some back exchange with the wash water probably during the drying step. An n.m.r. spectrum of the deuterated sample indicated about 0.85 atom of D/molecule and also showed the presence of some of the rearranged allene chloride. This and any other impurities were reduced to <2% by v.p.c. in the sample used for kinetic measurements.

Kinetic Procedure.—The reactions in "80%" aqueous ethanol were followed using the base titration procedure

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(11) C. G. Swain and E. R. Thorton, *Tetrahedron Letters*, **6**, 211 (1961); *J. Am. Chem. Soc.*, **84**, 817 (1962).

(12) (a) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); (b) C. E. Boozer and E. S. Lewis *ibid.*, **76**, 794 (1954).

(13) B. L. Murr, Jr., Ph.D. Thesis, Indiana University, 1961, p. 97.

(14) V. J. Shiner, Jr., and Sally Cross, *J. Am. Chem. Soc.*, **79**, 3599 (1957).

(15) P. D. Bartlett and L. J. Rosen, *ibid.*, **64**, 543 (1942).

(16) V. J. Shiner, Jr., *ibid.*, **74**, 5285 (1952).

(17) M. S. Newman, W. S. Fones and W. T. Booth, Jr., *ibid.*, **67**, 1053 (1945).

(18) G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

described in the previous paper.[9] The first-order reactions in "30%" aqueous ethanol were followed conductimetrically using the procedure described by Murr.[13] The Λ_∞ and S_α for the solution of HCl in "30%" ethanol were estimated to be 213 and 96.4, respectively.[19]

The β-deuterium isotope effects in the reactions of the bromides, measured titrimetrically, are estimated to be accurate to ±4%.[9] The solvolysis rates of the chlorides were measured conductimetrically and the derived γ-deuterium isotope effect should be accurate to ±0.2%.[20]

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[19] T. Erdey-Gruz, E. Kugler and J. Hidvegi, *Acta Chim. Acad. Sci., Hung.*, **19**, 89 (1959).

[20] Comment added at the referee's suggestion. The absence of any appreciable "inverse" isotope effect in the solvolysis of IV is perhaps somewhat surprising in view of the small influences previously observed in several reactions and attributed to inductive interactions between the isotopic and reaction centers.[21] In the present example the accuracy of the rate constant determination is limited mainly by the operation of a small mass law effect[9] which prevents the reaction from following the first-order rate law precisely. The estimated error in the isotope effect ratio is ±0.2%. An "inductive" isotope effect of this order of magnitude for a deuterium in the γ-position would not be excessively small in comparison to the 1.5 ± 1.0% effect attributed to possible inductive interaction between a solvolysis reaction center and a β-situated deuterium.[21b] It seems small, perhaps, when compared with some "inductive isotope effects" observed in other reactions.[21c,d] Conclusions drawn from such comparisons are obviously very uncertain in view of the limited amount of information available and the relatively large errors in many of the observed ratios.

[21] (a) E. A. Halevi, *Tetrahedron*, **1**, 174 (1957); (b) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **82**, 2655 (1960); (c) A. J. Kresge and K. N Rao, *Chemistry & Industry*, 53 (1961); (d) H. S. Klein and A. Streitwieser, Jr., *ibid.*, 180 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Proximity Effects. XXV. Pyrolysis of Cycloöctyl and Cyclodecyl Esters[1]

BY ARTHUR C. COPE AND MARY J. YOUNGQUIST[2]

RECEIVED AUGUST 28, 1961

The acetates, benzoates, hydrogen phthalates and S-methyl xanthates of cycloöctanol and cyclodecanol have been pyrolyzed, and the pyrolysates have been analyzed with emphasis on the detection of possible transannular products. The acetates and benzoates gave open-chained α,ω-dienes and the expected cyclic olefins; small amounts of bicyclic compounds and ring contraction products were formed along with the cyclic olefins from the hydrogen phthalates. The xanthates gave only the cyclic olefins at the temperatures used.

Previously published work[3] has shown that the pyrolysis of cycloöctyl acetate yields some 1,7-octadiene and the pyrolyses of cyclodecyl acetate and cyclodecyl-S-methyl xanthate yield 1,9-decadiene along with the expected cyclic olefins. The formation of these dienes can be explained either by a direct transannular elimination or by a secondary reaction in which the cyclic olefin is further transformed to the open-chained diene. Since gas chromatography has made possible the detection and isolation of small amounts of by-products, the present work was undertaken to determine if other unusual products are formed by the pyrolysis of the acetates, benzoates, hydrogen phthalates and S-methyl xanthates of cycloöctanol and cyclodecanol.

The pyrolyses of the acetates and benzoates were carried out at 500° in a hot tube (described in the Experimental section) and the hydrogen phthalates and S-methyl xanthates were decomposed by heating them in a flask attached to a distillation column or reflux condenser. The pyrolysates were analyzed by gas chromatography and samples were isolated by the same method and identified (with one exception) by their infrared spectra. Results of the pyrolyses are summarized in Tables I and II.

In the case of the cycloöctyl esters, the acetate and benzoate were pyrolyzed at 500° to give the expected mixture of *cis*-cycloöctene, *trans*-cycloöctene and 1,7-octadiene. The yield of *cis*-cycloöctene from these two esters remained fairly constant over a series of experiments, while the yields of the *trans*-olefin and the diene varied somewhat (see Table I). This is in accord with the work of Blomquist[3] who found that the open-chained dienes also arose from pyrolysis of the *trans* isomer of the cyclic olefins and only at temperatures above 450°. Thus, slight variations in temperature or contact time of the olefin in the hot tube affect the amount of cyclic olefin that is transformed to the diene.

Cycloöctyl hydrogen phthalate was pyrolyzed at 275–400° and yielded the complex mixture of products shown in Table I. No 1,7-octadiene was formed because of the low pyrolysis temperature. The bicyclic compounds could have been formed by direct elimination of a hydrogen atom on C_3 or C_5 rather than the usual β-hydrogen atom. Another possibility is the protonation of cycloöctene (formed during the pyrolysis) to yield a carbonium ion which then rearranged to the usual products.[4]

We thought that the 1-methylcycloheptene could have been formed by further pyrolysis of bicyclo[5.1.0]octane. Pyrolysis of bicyclo[5.1.0]octane in a hot tube at 360° left the hydrocarbon unchanged; however, when samples of the hydrocarbon were heated at 300° for three to twenty hours in a sealed tube in the presence of a small amount of *n*-butyl hydrogen phthalate (added to furnish phthalic acid at the pyrolysis temperature), the pyrolysate contained 1–2% of 1-methylcycloheptene. Thus it is likely that 1-methylcycloheptene was formed in this manner during the original ester pyrolysis.

Several similar sealed tube pyrolyses were done in an attempt to explain the formation of the

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[1] Supported in part by a research grant (NSF-G5055) of the National Science Foundation. Paper XXIV, A. C. Cope, S. Moon and P. E. Peterson, *J. Am. Chem. Soc.*, **84**, 1935 (1962).

[2] National Science Foundation Predoctoral Fellow, 1957–1960; National Institutes of Health Predoctoral Fellow, 1960–1961.

[3] A. T. Blomquist and P. R. Taussig, *J. Am. Chem. Soc.*, **79**, 3505 (1957).

[4] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt and Co., New York, N. Y., 1959, p. 502.