The Pyrolysis of the Epimeric d_0- and 2-d_1-2-Methylcyclohexyl-S-methyl Xanthates and Acetates[1,2]

W. SCOTT BRIGGS AND CARL DJERASSI

Department of Chemistry, Stanford University, Stanford, California

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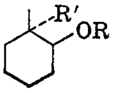
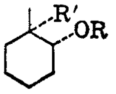
The Chugaev xanthate and ester pyrolysis reactions have been examined in the epimeric *cis*- and *trans*-2-methylcyclohexyl-S-methyl xanthates and acetates by comparison of results obtained for the unlabeled and 2-d_1-labeled substrates. While the olefinic products obtained from the pyrolysis of the *trans*-2-d_1 xanthate (**6**) and acetate (**8**) exhibit isotopic contents consistent with those to be expected through operation of a homogeneous *cis*-cyclic elimination process, the products from the *cis*-2-d_1 xanthate (**5**) and acetate (**7**) do not. In the latter compounds, kinetic deuterium isotope effects (k_D/k_H) have been calculated (1.0 in **5** and 0.67 in **7**) and from these values and isotopic content data for the 1-methyl-1-cyclohexene fraction (44% d_1 in **5** and 78% d_1 in **7**) possible ionic mechanisms have been proposed for the net *trans*-elimination process in these compounds.

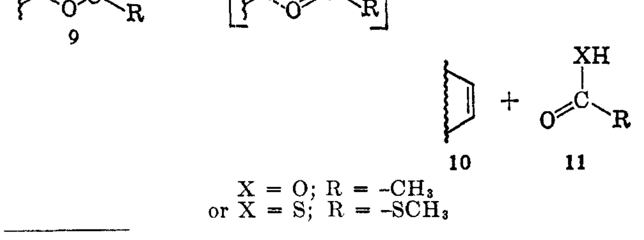
In the course of our investigation[3] of the electron impact induced elimination of the elements of xanthic and acetic acid from the epimeric 2-methylcyclohexyl-S-methyl xanthates (**1** and **2**) and acetates (**3** and **4**), we had cause to examine closely the pyrolysis of the unlabeled compounds and their 2-d_1-labeled analogs (**5–8**). The present paper records these results, which offer an interesting comparison between thermolytic and electron impact promoted phenomena.





1, R = -C(S)SCH$_3$; R' = H **2**, R = -C(S)SCH$_3$; R' = H
3, R = -C(O)CH$_3$; R' = H **4**, R = -C(O)CH$_3$; R' = H
5, R = -C(S)SCH$_3$; R' = D **6**, R = -C(S)SCH$_3$; R' = D
7, R = -C(O)CH$_3$, R' = D **8**, R = -C(O)CH$_3$; R' = D

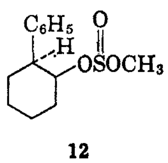
The pyrolytic elimination reaction in esters[4] and xanthates[4,5] (the Chugaev reaction) is known to result in the nearly exclusive abstraction of a *cis*-β-hydrogen atom and such elimination processes have found widespread synthetic utility as a result of this striking selectivity in the conversion of alcohols to olefins. These eliminations have been visualized as proceeding[4] by a highly concerted mode such as **9** → **10** + **11**, in which, in the activated complex, little charge separation develops and some double-bond character exists between the incipient olefinic carbon atoms. This view has been supported by the observed substituent and isotope effects.[4] In the case of esters (R = alkyl), the acid fragment **11** is stable, while that produced in the pyrolysis of xanthates (the unknown xanthic acid) undergoes subsequent decomposition to carbonyl sulfide and mercaptan (RSH).



X = O; R = -CH$_3$
or X = S; R = -SCH$_3$

While a concerted, *cis*-cyclic mechanism of the above type adequately explains the formation of the major portion of products in most pyrolytic elimination processes, minor quantities of net *trans* elimination do occur.[4,6] Such products are readily detected in cyclic systems where free rotation about carbon–carbon single bonds is precluded and it has been proposed that these products of net *trans* elimination may arise through the operation of radical[4] or ionic[6–8] mechanisms.

Esters[9,10] and S-methyl xanthates[8] of the bicyclic alcohol borneol (**15**) give, upon pyrolysis, products which can be best explained by invoking ionic intermediates[9,10] which may undergo subsequent Wagner–Meerwein rearrangement before suffering hydrogen loss. Thus, bornyl-S-methyl xanthate (**16**) yields[8] upon pyrolysis in the liquid state not only the expected bornylene (**17**), but also significant quantities of camphene (**18**) (30% optical purity) and tricyclene



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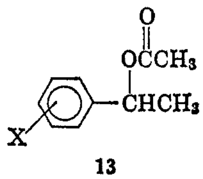

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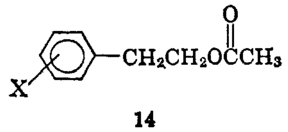

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[1] We are indebted to the National Institutes of Health for financial support (Grant No. GM-06840). The purchase of the Atlas CH-4 mass spectrometer was made possible by NASA Grant No. NsG 81-60.

[2] Taken in part from the Ph.D. dissertation submitted by W. S. B. to the Graduate School, Stanford University, 1967.

[3] W. S. Briggs and C. Djerassi, *J. Org. Chem.*, **33**, 1612 (1968).

[4] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960), and references therein.

[5] H. R. Nace, *Org. Reactions*, **12**, 57 (1962), and references therein.

(6) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 500–507.

(7) Such ionic intermediates have been proposed by G. Berti [*J. Amer. Chem. Soc.*, **76**, 1217 (1954)] to explain the large amount (70–78%) of *trans* elimination which occurs in the liquid phase pyrolysis of *cis*-methyl (2-phenylcyclohexyl) sulfite (**12**) and by Smith and co-workers [R. Taylor, G. G. Smith, and W. Wetzel, *ibid.*, **84**, 4817 (1962)] to account for the excellent correlation obtained between k_{rel} for the pyrolysis (600°K) of substituted phenylethyl acetates of types **13** and **14** with Hammett σ^+ values.

(8) (a) A. Maccoll, "Kekulé Symposium," Butterworth and Co. Ltd., London, 1959, pp 230–249; (b) for a recent review of such processes, see A. Maccoll, *Advan. Phys. Org. Chem.*, **3**, 91 (1965).

(9) C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Nature*, **190**, 715 (1961).

(10) T. Sato, K. Murata, A. Nishimura, T. Tsuchiva, and N. Wasada, *Tetrahedron* **23** 1791 (1967).

(**19**). The low optical purity of the isolated camphene suggested[9] that stepwise decomposition through a carbonium ion intermediate was operative. (See Scheme I.)

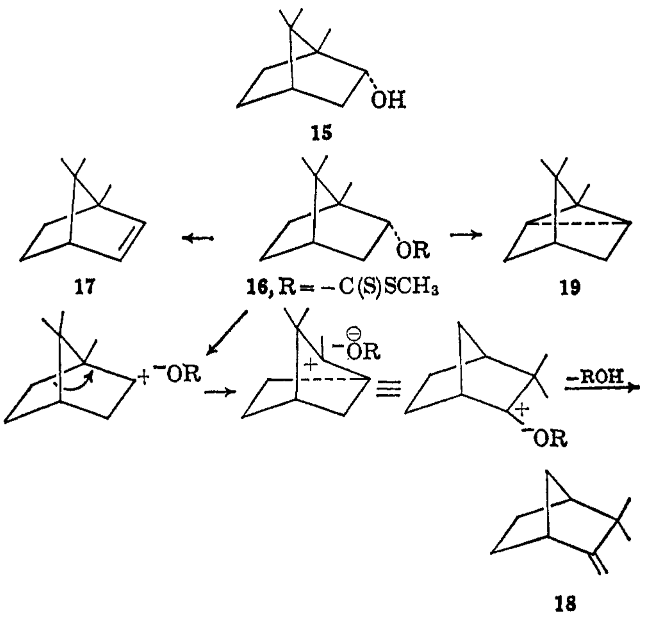
Analogous "quasi-heterolytic processes"[8] yielding ionic intermediates have been proposed[6,8,11] for the pyrolysis of alkyl halides; however, the observation of significant isotope effects in certain cases has lead to some question[4] regarding these mechanisms.

Results

Xanthates **1** and **2** and their 2-d_1-labeled analogs (**5** and **6**) were pyrolyzed at 250° as described in the Experimental Section. In a like manner, acetates **3** and **4** and their deuterated counterparts (**7** and **8**) were pyrolyzed at 400°. In Table I are summarized the percentages of the various olefinic products,[12] as determined by analytical vapor phase chromatography and the isotopic content of these products as determined by mass spectrometry.

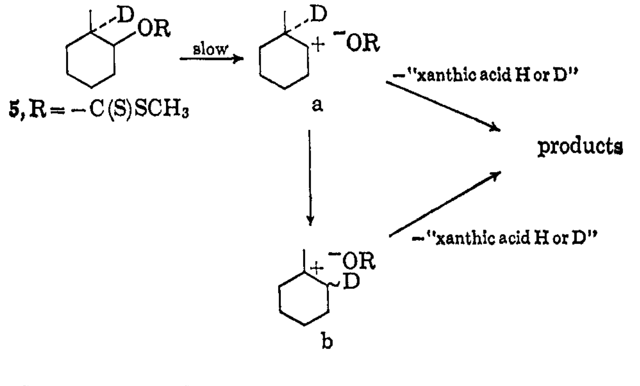
From the pyrolytic data in Table I, values of the kinetic deuterium isotope effect (k_D/k_H) for the elimination process in xanthates **1** and **2** may be calculated.[13] The values of 0.59–0.72 found for the *trans* xanthate (**2**) are in fairly good agreement with values of 0.50–0.59 previously reported[4,13] for ester pyrolyses. The *cis* xanthate (**1**), by contrast, exhibits no significant isotope effect. Inspection of the isotopic content of the olefins produced in the pyrolysis of the deuterated xanthates (**5** and **6**) (Table I) provides additional insight into the cause of this anomalous behavior.

Scheme I



While the olefins produced from the *trans* xanthate (**6**) show the expected isotopic contents for operation of a concerted, *cis*-cyclic elimination process, namely, nearly complete retention of deuterium label in the 1-methyl-1-cyclohexene and nearly complete loss of label in the formation of 1-methyl-1-cyclohexene, the results for the *cis* xanthate (**5**) are clearly not in accord with predictions. The retention of deuterium label in 44% of the 1-methyl-1-cyclohexene in this latter pyrolysis could be explained, however, by the postulation of a carbonium ion[6] intermediate of type a in one of the decomposition pathways of this isomer. This species (a) may either lose a proton or deuteron directly or undergo a 1,2-deuteride shift to yield the more stable tertiary carbonium ion (b) which subsequently loses a proton or deuteron to yield the olefinic products. In the activated complex leading to the elimination of the tertiary hydrogen in xanthate **5**, C–O bond breaking would be the dominant process, thus accounting for the lack of any observable kinetic deuterium isotope effect with this substrate. (See Scheme II.)

Scheme II



However, it should be pointed out that, since these pyrolytic studies were carried out in a hot vpc column, their degree of homogeneity is not precisely known. While a path of type **5** → a → b → products may be operating, one cannot say with certainty whether it is

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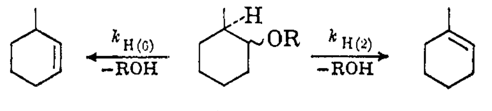
[11] A. Maccoll and E. S. Swinbourne, *Proc. Chem. Soc.*, 409 (1960).

[12] Treatment of control mixtures of each of the isomeric methylcyclohexenes under the pyrolysis and work-up conditions both neat and in the presence of equimolar quantities of glacial acetic acid or methyl mercaptan failed to produce any significant isomerization as detected by subsequent vapor phase chromatography.

[13] These values were calculated by a method analogous to that of DePuy and co-workers [C. H. DePuy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, **7**, 123 (1959)]. By consideration of the kinetic processes (1 and 2) for the unlabeled and deuterium-labeled substrates, expressions 3 and 4 may be written relating the ratios of percentages of the two olefinic products at any time *t* to the ratio of the rate constants for the two decomposition pathways, assuming that both elimination processes are of the same molecular order (and presumably both unimolecular in such pyrolysis processes).



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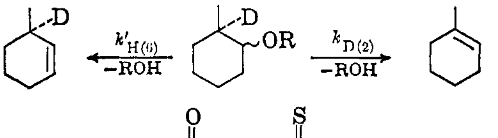
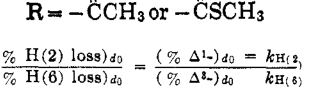


(2)



$$R = -\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \text{ or } -\overset{\overset{\displaystyle S}{\|}}{C}SCH_3$$

$$\frac{(\%\ \mathrm{H(2)\ loss})_{d_0}}{(\%\ \mathrm{H(6)\ loss})_{d_0}} = \frac{(\%\ \Delta^{1}\text{-})_{d_0}}{(\%\ \Delta^{3}\text{-})_{d_0}} = \frac{k_{H(2)}}{k_{H(6)}} \tag{3}$$

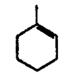
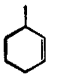
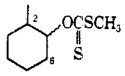
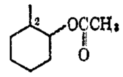
$$\frac{(\%\ \mathrm{D(2)\ loss})_{2\text{-}d_1}}{(\%\ \mathrm{H(6)\ loss})_{2\text{-}d_1}} = \frac{(\%\ \Delta^{1}\text{-})_{2\text{-}d_1}}{(\%\ \Delta^{3}\text{-})_{2\text{-}d_1}} = \frac{k_{D(2)}}{k'_{H(6)}} \tag{4}$$

By making the reasonable assumption that the rates of hydrogen loss from C-6 in the d_0 and 2-d_1 compounds are equal (*i.e.*, $k_{H(6)} \equiv k'_{H(6)}$), relations 3 and 4 may be combined to yield an expression (5) defining the kinetic deuterium isotope effect (k_D/k_H) for replacement of the C-2 hydrogen by deuterium in terms of the percentage composition of the olefinic mixture in the unlabeled and deuterium-labeled materials.

$$\frac{k_D}{k_H} = \frac{k_{D(2)}}{k_{H(2)}} = \frac{(\%\ \Delta^{3}\text{-})_{d_0} \times (\%\ \Delta^{1}\text{-})_{2\text{-}d_1}}{(\%\ \Delta^{1}\text{-})_{d_0} \times (\%\ \Delta^{3}\text{-})_{2\text{-}d_1}} \tag{5}$$

TABLE I

SUMMARY OF PYROLYTIC STUDIES ON 2-METHYLCYCLOHEXYL-S-METHYL XANTHATES AND ACETATES

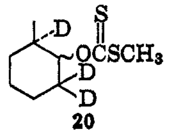
		Percentage of olefin mixture[b]		
Compound	Pyrolysis conditions[a]			k_D/k_H
				
trans-d_0 (2)	*c*	68	32	. . .
	d	65	35	. . .
	e	64	36	. . .
	f	66	34	. . .
	g	62	38	. . .
cis-d_0 (1)	*d*	29	71	. . .
	f	20	80	. . .
	g	10	90	. . .
trans-2-d_1 (6) $\left\{\begin{matrix}2\%\ d_0\\98\%\ d_1\end{matrix}\right\}$	*d*	54 (98% d_0)	46 (97% d_1)	0.62
	f	54	46	0.59
	g	54	46	0.72
cis-2-d_1 (5) $\left\{\begin{matrix}18\%\ d_0\\82\%\ d_1\end{matrix}\right\}$	*d*	28 $\left\{\begin{matrix}56\%\ d_0\\44\%\ d_1\end{matrix}\right\}$	72 $\left\{\begin{matrix}11\%\ d_0\\89\%\ d_1\end{matrix}\right\}$	1.0
	f	20	80	1.0
	g	10	90	1.0
2,6,6-d_3 (20) (97% d_3)	*d*	60	40	. . .
	e	50	50	. . .
	f	61	39	. . .
				
trans-d_0 (4)	*h*	56	44	. . .
	g	56	44	. . .
cis-d_0 (3)	*h*	9	91	. . .
	g	6	94	. . .
	i	58	42	. . .
trans-2-d_1 (8) $\left\{\begin{matrix}16\%\ d_0\\84\%\ d_1\end{matrix}\right\}$	*h*	41 (97% d_0)	59 (100% d_1)	0.56
	g	40	60	0.53
cis-2-d_1 (7) $\left\{\begin{matrix}18\%\ d_0\\82\%\ d_1\end{matrix}\right\}$	*h*	6 $\left\{\begin{matrix}22\%\ d_0\\78\%\ d_1\end{matrix}\right\}$	94 (100% d_1)	0.67
	g	4	96	0.67
	i	50	50	0.72

[a] See Experimental Section. [b] These values are corrected for the contribution of any significant quantities of the isomeric materials or isotopic contaminants and are considered reproducible to ±1%. [c] Unseasoned stainless steel, 250°. [d] Seasoned stainless steel, 250°. [e] Liquid phase, over powdered soft glass, 200°. [f] Pyrex tube, 250°. [g] Pyrex tube, 400°. [h] Seasoned stainless steel, 400°. [i] Seasoned stainless steel tube with a deposit of carbonaceous material from *ca.* 70 pyrolyses, 400°.

occurring as a true vapor phase reaction or on the walls of the hot tube as a surface-catalyzed process. In fact suggestive of at least partial intervention of such surface catalyzed processes is the observed sensitivity (Table I) of the product composition to the nature of the tube wall (seasoned stainless steel or Pyrex glass), to the presence of acidic carbonaceous residues, and to higher reaction temperature.[6] The observed temperature dependence of the anomalous 1-methyl-1-cyclohexene product in the total product mixture is, however, not that expected for total operation of a high-energy "quasi-heterolytic" process, since higher reaction temperature should result in an increase in the anomalus product rather than a decrease as noted in Table I.

The formation of a significant quantity (11%, Table I) of 3-methyl-1-cyclohexene in which all the deuterium label is lost is not easily accommodated by either the normal *cis*-cyclic elimination process or a "quasi-heterolytic" process of type **5** → a → products. and virtually demands the intervention of a surface catalyzed variant.

That this rearrangement of type **5** → b → products is not unique to the pyrolysis under conditions where surface catalysis might come into play is shown however by the pyrolysis of a mixture of 2,6,6-d_3-2-methylcyclohexyl-S-methyl xanthates (**20**) containing *cis* (30%) and *trans* (70%) isomers in the liquid state (see Experimental Section). The olefins isolated from this pyrolysis [3-methyl-1-cyclohexene (50%) and 1-methyl-1-cyclohexene (50%)] also gave anomalous isotopic contents. While the 3-methyl-1-cyclohexene fraction was 100% d_2, the 1-methyl-1-cyclohexene produced had isotopic content 94% d_2 and 6% d_3.



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The alternative radical process involving homolytic fission of the C–O bond would require a 1,2-hydrogen atom shift and would therefore not appear so likely, since, although such rearrangements have been postulated[14,15] and found[15] to occur in photochemically excited species, they are virtually absent in ground-state solution chemistry.[16–18] Such a radical process is, however, not excluded by the experimental evidence.

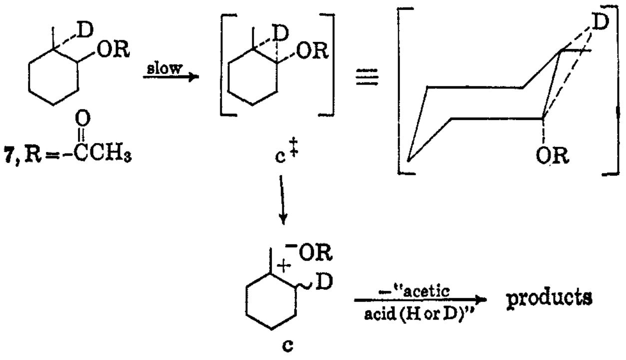
Also pertinent to any discussion of liquid phase *vs.* surface-catalyzed pyrolysis reactions is the observed close similarity of percentage of the two olefins (Table I) in the pyrolysate from *trans* xanthate **2** irrespective of the pyrolysis conditions (seasoned or unseasoned stainless steel or Pyrex tube at 250° or in the liquid phase at 200°). The *cis* xanthate (**1**), by contrast, is more sensitive (Table I) to the nature of the pyrolysis conditions, particularly the surface employed (Pyrex or stainless steel), and to the presence of acidic carbonaceous residues[19] which accumulate after extensive seasoning of the reactor. These latter deposits are presumably responsible[19] for the large proportion of net *trans* elimination both in xanthate **1** and *cis* acetate **3**, possibly through the increased intervention of heterogeneous ionic reaction paths.

The pyrolyses of *cis*-[19,20] (**3**) and *trans*-2-methylcyclohexyl acetate[20] (**4**) have been examined previously and the results in Table I are in close agreement with the values obtained by these earlier workers. Again as for *trans* xanthate **2**, the olefinic ratio from *trans* acetate **4** is nearly independent of the pyrolysis conditions, whereas that from *cis* acetate **3** exhibits greater dependence. The presence of carbonaceous deposits has a profound effect[19] (Table I) on the ratio of olefinic products produced in the pyrolysis of *cis* acetate **3**, resulting in an up to sixfold increase in the amount of 1-methyl-1-cyclohexene, the product from net *trans* elimination, under our experimental conditions.

In a manner analogous to that employed[13] in the xanthate series, values of k_D/k_H for the elimination reaction of the acetates **3** and **4** may be determined from the pyrolytic data (Table I) for the d_0 and 2-d_1 compounds. The values found for this process are 0.67 and 0.53–0.56, respectively, in fairly good agreement with those (0.50–0.59) previously reported in the literature.[4,13] Particularly interesting is the relative constancy of the value of k_D/k_H for *cis* acetate **3** (Table I) even in the presence of carbonaceous impurities.

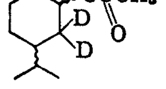
The close similarity of these pyrolytic k_D/k_H values for acetates **3** and **4** as opposed to the striking differences exhibited by xanthates **1** (1.0) and **2** (0.59–0.72) might at first suggest that in the acetates the concerted *cis*-cyclic mode of elimination is operative. However, examination of the isotopic content of the resulting olefinic products (Table I) from the deuterated compounds **7** and **8** does not support this view. While the data for the *trans* acetate (**8**) are consistent with expectations for a homogeneous *cis*-cyclic elimination process, the results for the *cis* acetate (**7**) are again anomalous. In this latter compound, 78% of the 1-methyl-1-cyclohexene produced (6% of the total olefinic product) still retains the deuterium label. One possible mechanism which might be expected to yield such isotope effect and label retention data may be visualized as 7 → c‡ → c → products. An analogous 1,2 participation of an axial hydrogen has been postulated to account for the 77-fold rate increase in the ethanolysis of 2-methylcyclohexyl tosylate on passing from the *trans* to the *cis* series.[21] (See Scheme III.)

SCHEME III



The failure of *cis* xanthate **5** to exhibit an isotope effect, interpreted as indicating spontaneous heterolysis of the C–O bond in the activated complex without requiring neighboring deuterium assistance (as was invoked in c‡ in *cis* acetate **7**), may well be a reflection of the greater acid strength[4] (and stability of the anionic species) predicted for the unknown xanthic acid compared with that of normal carboxylic acids.

Again, as for xanthates **1** and **5**, it cannot be stated with absolute certainty that these are completely homogeneous pyrolytic reactions in acetates **3** and **7**; however, in this case, the relative insensitivity of the product ratios (Table I) to tube wall construction (Pyrex or coated stainless steel) would suggest that this might be so. Particularly reassuring is the observation without comment of the analogous rearrangement process[22] in the pyrolysis of an isomer mixture of 1,3,3-d_3-carvomenthyl acetate (**21**) over glass helices at 400°.



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Thus it appears that, under the pyrolysis conditions employed in this study, the olefinic products from effective *trans* elimination in the 2-methylcyclohexyl-S-methyl xanthates and acetates may be adequately accounted for by postulating, as the major process, spontaneous (xanthates) or neighboring hydrogen

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[14] (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *J. Amer. Chem. Soc.*, **87**, 1410 (1965); (b) H. Kristinsson and G. W. Griffin, *ibid.*, **88**, 378 (1966); (c) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

[15] D. I. Schuster and I. S. Krull, *J. Am. Chem. Soc.*, **88**, 3456 (1966).

[16] C. Walling in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 416 ff.

[17] L. H. Slaugh, *J. Amer. Chem. Soc.*, **81**, 2262 (1959).

[18] D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).

[19] Similar effects of acidic carbonaceous residues have been reported by W. J. Bailey and L. Nicholas [*J. Org. Chem.*, **21**, 854 (1956)] in their pyrolysis studies on *cis*-2-methylcyclohexyl acetate.

[20] R. T. Arnold, G. G. Smith and R. M. Dodson, *ibid.*, **15**, 1256 (1950).

[21] (a) W. Hückel and H. D. Sauerland, *Ann.*, **592**, 190 (1955); (b) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 143.

[22] A. G. Thomas and B. Willhalm, *J. Chem. Soc., Sect. B*, 219 (1966).

assisted (acetates) heterolysis of the C–O bond yielding ion pairs, followed by direct proton loss or 1,2-hydride shift and subsequent proton loss from the cationic species.

Experimental Section[23]

Preparation of d_0- and 2-d_1-Labeled Xanthates and Acetates (1–8) and 2,6,6-d_3-2-Methylcyclohexyl-S-methyl Xanthate (20).—These materials were prepared and characterized as described earlier.[3]

Pyrolysis of *trans*-2-Methylcyclohexyl-S-methyl Xanthate (2) and 2,6,6-d_3-2-Methylcyclohexyl-S-methyl Xanthate (20) in the Liquid Phase.—The crude xanthate (containing a fair amount of dimethyl trithiocarbonate as an impurity) was pyrolyzed over powdered soft glass in a flask equipped with a nitrogen inlet tube and a Vigreux column by heating in a Wood's metal bath at 200–210°.[24] The pyrolysate was collected in a Dry Ice–isopropyl alcohol cooled trap. In each case, the pyrolysate was analyzed by vpc on a 15% Apiezon L column (10 × 0.25 in.) at 100°.

The pyrolysate from xanthate **20** was separated by preparative vpc employing the above conditions and the material corresponding in retention time to 3-methyl-1-cyclohexene (or methylenecyclohexane) was examined by nmr spectroscopy. The spectrum of this compound exhibited as its main features a signal centered at δ 5.55 ppm (1 H, HC=C) and a closely spaced doublet (J = 1 cps) centered at δ 0.95 ppm (3 H, $-CH_3$). No signals were apparent for either terminal methylene (δ 4.6) or cyclopropane hydrogens (δ <1.0) in this material, nor was evidence found for the presence of cyclopropane hydrogens[3] in the nmr spectrum of the 1-methyl-1-cyclohexene fraction from this pyrolysis.

Conditions for All Other Pyrolysis Studies on 2-Methylcyclohexyl Acetates and S-Methyl Xanthates.—All pyrolyses were carried out in a Varian Aerograph Model 202A gas chromatograph fitted with either a 2 ft × 0.25 in. Greenville Tube, Inc., Type 304, W & D stainless steel tube equipped with a small plug of Pyrex glass wool at the entrance (and previously seasoned by *ca.* 30 pyrolyses of 10-μl samples of xanthates and acetates under the conditions listed below) or a 2 ft × 6 mm length of no. 7740 Pyrex tube with a small plug of Pyrex glass wool at the entrance. In both cases injector liners of 2-mm Pyrex tube were employed. The temperature conditions were as follows: xanthates, injector block 175°, column 250°, detector block 150°, helium flow *ca.* 20–60 ml/min over 5 min, estimated contact time with hot zone 0.5–1 min, sample size 2–10 μl; acetates, injector block 175°, column 400°, detector block 150°, helium flow conditions *ca.* 15–25 ml/min over 5 min, estimated contact time with hot zone 0.5–1 min, sample size 2–10 μl.

General Procedure.—The sample was injected at the requisite temperature and minimum flow rate. After 2 min, the flow rate was raised uniformly to the maximum value over the ensuing 3 min. The pyrolysate was collected in a 4-mm glass U-tube with liquid nitrogen cooling. When visible evidence of continued pyrolysate flow had ceased, the tube was removed, 20 μl of anhydrous ether added, and the sample examined by analytical gas chromatography on 20% Apiezon L column (10 ft × 0.25 in.) at 100°. Preparative gas chromatography employing the same conditions yielded the pure isomeric olefins whose isotopic contents were determined from the molecular ion regions of the 70-eV mass spectra. Olefinic compositions were determined by the cut and weigh method on the analytical vpc traces.

Registry No.—**1**, 15288-12-7; **2**, 15288-13-8; **3**, 15288-14-9; **4**, 15288-15-0; **5**, 15288-22-9; **6**, 15288-17-2; **7**, 15285-97-9; **8**, 15285-91-3; **20**, 15296-85-2.

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[23] All compounds were purified by vapor phase chromatography (vpc) and characterized by infrared spectroscopy and mass spectrometry as described in ref 3. Olefinic products were analyzed and purified by vpc on a Varian Aerograph Model 202B chromatograph employing the columns listed. Mass spectra of olefinic products were recorded by Dr. A. M. Duffield on an Atlas CH-4 mass spectrometer equipped with a Model TO-4 ion source and heated gas cartridge inlet system maintained at 200°. Ionizing conditions are as follows: ion source temperature, 200°; ionizing voltage, 70 eV; and ionizing current, 10 μA. Nmr spectra were run by Dr. Y. Kanazawa and Mr. R. C. Ronald on a Varian Associates Model A-60 spectrometer in deuteriochloroform solution and using tetramethylsilane (δ 0.00) as an internal standard.

[24] Pyrolysis of xanthate **20** containing dimethyl trithiocarbonate under these conditions and that of a purified sample in the absence of powdered soft glass and with the bath temperature maintained at 250° yielded identical results.

Ozonolysis. X. The Molozonide as an Intermediate in the Ozonolysis of *cis* and *trans* Alkenes[1a]

LOIS J. DURHAM AND FRED L. GREENWOOD[1b]

Department of Chemistry, Stanford University, Stanford, California 94305

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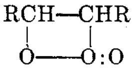
Low temperature (−130°) nmr spectral studies of the ozonation mixtures which were prepared from dichlorodifluoromethane solutions of the stereoisomers of 2-butene, 2-pentene, and 3-hexene gave evidence for the existence of molozonides. The *cis* molozonides could be observed to decompose at −130° to the usual ozonolysis products, whereas the *trans* molozonides required warming to −100° before they were converted into the usual ozonolysis products.

It was Staudinger[2] who first made the suggestion that the observed alkene–ozone reaction products were actually secondary reaction products which arose from a primary addition product. By analogy to the moloxide which at that time was postulated as the primary autoxidation product of alkenes and which was formulated as a 1,2-dioxetane, he called the primary alkene–ozone reaction product a molozonide and formulated it as



$$\begin{array}{l} \mathrm{RCH{-}CHR} \\ \;\;\,| \qquad\;\;\, | \\ \;\;\mathrm{O{-}{-}O{:}O} \end{array}$$

It was not until 1960 that firm, indirect experimental evidence for the existence of the molozonide appeared when Criegee and Schröder,[3] reported that treatment of the ozonation mixture from *trans*-di-*t*-butylethylene with isopropyl Grignard reagent gave rise to *dl*-2,2,5,5,-tetramethylhexane-3,4-diol. Subsequently, it

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[1] (a) A preliminary report on part of this work has been published: L. J. Durham and F. L. Greenwood, *Chem. Commun.*, 843 (1967). (b) F. G. is indebted to the Chemistry Department, Stanford University, and particularly to Dr. H. S. Mosher, for their hospitality and to the Petroleum Research Fund of the American Chemical Society for partial financial support during sabbatical leave from Tufts University.

[2] H. Staudinger, *Ber.*, **58**, 1088 (1925).

[3] R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).