Rearrangement of Esters in the Gas Phase. IV. Fate of an Oxygen Tracer in the Rearrangement of Crotyl Trifluoroacetate

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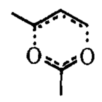
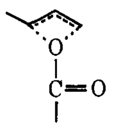
Abstract: Crotyl trifluoroacetate, labelled in the ether position with ^{18}O, was allowed to rearrange in the gas phase at 268° to the α-methylallyl ester. The carbonyl oxygen contained most of the label in the product, and there was little loss of position of label in the starting material, showing that the major reaction goes through a six-membered cyclic transition state resembling that of a Cope rearrangement. Detectable amounts of oppositely labelled materials showed reaction through one or both of two four-membered ring transition states, and the rate constants were about one-tenth those of the Cope-like process. The rearrangement of the oxygen label in benzyl trifluoroacetate at 395° was also observed. The similarity of this rearrangement to the oxygen-scrambling process in the crotyl ester suggests that reaction with two oxygens in a four-membered ring transition state, resembling the SNi mechanism, is an appropriate mechanism for both reactions. It was, however, impossible to rule out the alternative transition state containing one oxygen in a four-membered ring for the crotyl ester, and heterogeneous processes for both systems are not excluded.

The interconversion of α- and γ-substituted allylic esters has been described,[1] and was believed to represent a "Dioxa-Cope" rearrangement passing through the six-membered cyclic transition state A. The possible four-membered cyclic transition state B was not rigorously excluded, although the observation that allyl-α-d_2 trifluoroacetate and allyl ^{18}O-trifluoroacetate rearranged at the same rate within experimental error showed that if B occurred as a major route, then the alternative four-ring mechanism C, which does not lead to allylic rearrangement, must occur to about the same extent as B.


A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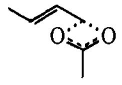
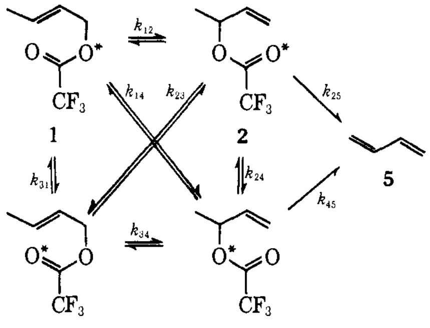

C

The substituent effects, namely, marked acceleration by electron-donating groups in the α or γ position of the allyl moiety and by electron-withdrawing X groups, indicated a transition state of substantial charge separation. In the extreme, this might yield an ion pair which could conceivably collapse with random recombination of the ends of the allylic cation and the carboxylate anion. This appears unlikely, both because of the high energy of separated charges, and because even in solution, where an ion pair has been strongly supported,[2] the postulated fragments do not combine randomly in the cases that have been studied with ^{18}O tracers. Nevertheless, the mechanism is entirely consistent with both the substituent effects and the previously reported tracer results. A further suggestion of an ion-pair intermediate arises from the very large Arrhenius *A* factors reported for the fastest rearrangements, apparently inconsistent with the six-membered cyclic transition state, as estimated by O'Neal and Benson.[3] It therefore seemed worthwhile to explore these possibilities using an allylic ester with a simultaneous label at both the allylic and carboxylate positions.

We have chosen to study in this way crotyl trifluoroacetate, marked with ^{18}O in the ether oxygen. This was chosen because it was one of the most tractable esters in terms of reproducibility, it reacted very rapidly, gave one of the largest *A* factors, and gave readily separated products. Scheme I shows the compounds concerned and interconversions considered.

Scheme I



In Scheme I, the asterisk respresents excess ^{18}O. Reactions with transition state A are **1** ⇄ **2** and **3** ⇄ **4**, those with transition state B are **1** ⇄ **4** and **2** ⇄ **3**, and those with transition state C are **1** ⇄ **3** and **2** ⇄ **4**. In the scheme, rate constants are defined for one direction only, for example, k_{12}; the reverse reaction **2** → **1** is assigned the rate constant k_{21}. A mixture of **1** and **3** is separable from a mixture of **2** and **4**, but the analysis of a mixture of **1** and **3** is most conveniently accomplished by separation of the two oxygens, followed by an analysis of one (or both) fractions. It is convenient to saponify the ester, then determine the ^{18}O content of the alcohol by combustion.

A possible reaction with transition state C (analogous to processes **1** → **3** or **2** → **4**) with negligible possibilities of structural rearrangement is that of benzyl ester illustrated by reaction I. The rate is measured here.

$$C_6H_5CH_2{}^{18}OCOCF_3 \rightleftarrows C_6H_5CH_2OC^{18}OCF_3 \qquad (I)$$

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[1] E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Amer. Chem. Soc.*, **90**, 662 (1968).

[2] H. L. Goering and M. M. Pombo, *ibid.*, 82, 2315 (1960).

[3] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 71, 2903 (1967).

Results

The labelled crotyl ester was prepared by the sequence

$$CH_3CH{=}CHCH(OCH_3)_2 \xrightarrow[H^+]{H_2{}^*O} CH_3CH{=}CHCH{=}{}^*O \xrightarrow[AlCl_3]{LiAlH_4}$$

$$CH_3CH{=}CHCH{-}{}^*OH \xrightarrow{(CF_3CO)_2O} CH_3CH{=}CHCH_2{}^*OCOCF_3$$

The reaction was followed in a diffusively stirred flow system. The rate of the isotopically normal reaction has been measured before,[4] and from this work, neglecting oxygen isotope effects, we may write $k_{12} = k_{34} = 6.93 \times 10^{-3}$ sec^{-1} and $k_{21} = k_{43} = 6.78 \times 10^{-3}$ sec^{-1} at 268°. Parenthetically, we may note that the current results from the ^{18}O compound, while not primarily aimed at getting these rearrangement rate constants, confirmed these numbers. The extent of reaction at constant flow rate became constant in less than 1 hr and remained unaltered for 3 days; the absence of detectable seasoning effects suggests the absence of any important heterogeneous component. Nevertheless, the vessel was seasoned for several days with ordinary ester before introducing the labeled one. The isomeric esters in the effluent from the reaction were trapped and then separated by gas chromatography. Each ester was then cleaved to the corresponding alcohol, the alcohols were again purified by gas chromatography, and then analyzed for ^{18}O by the combustion method of Doering and Dorfman,[5] using a mass spectrometric comparison of the 44 and 46 mass unit peaks of the resulting carbon dioxide. A new feature not previously observed[4] was the presence of a small amount of *cis*-crotyl trifluoroacetate. It was present in the starting material and the amount changed very little, so it may be irrelevant to the reaction.

Benzyl trifluoroacetate, from benzyl alcohol ^{18}O, prepared following Doering and Dorfman,[5] was passed through the reactor at 325°, and the recovered ester was reconverted to the alcohol and analyzed for ^{18}O.

The results of these experiments are presented in Table I.

It can be readily seen from the table that most of the label is lost on isomerization, and therefore, *the major course of the reaction is by way of the six-membered transition state.* However, a perceptible amount of reaction by way of some other route, for example, one or both of the four-membered cyclic transition states exists.

Table II shows the gas chromatographic analysis of the individual components in the exit stream, and Table III shows the mole fraction of the differently labeled materials, as calculated from the entries in Tables I and II, using equations such as (1) and (2).

$$(\mathbf{1}) = [(\mathbf{1}) + (\mathbf{3})](^{18}O \text{ excess in crotyl alcohol})/4.014\% \tag{1}$$

$$(\mathbf{3}) = [(\mathbf{1}) + (\mathbf{3})] - (\mathbf{1}) \tag{2}$$

The values of (**1**) and (**4**) so obtained are as good as the accuracy of the whole procedure. (**2**) and (**3**) are determined by differences, and since (**3**) is small, its accuracy is very low.

Table I. Isotopic Composition of Products from Thermal Rearrangement of Mass Esters

Compound	Flow rate, ml/sec[a,b]	Ether ^{18}O[c] content, %
cis **1**	∞	4.041[d]
trans **1**	∞	4.041
trans **1** + **3**	0.28	3.952
trans **1** + **3**	0.10	3.798
cis **1** + **3**	0.28	(3.815)[d,e]
cis **1** + **3**	0.10	3.790[d]
2 + **4**	0.28	0.576
2 + **4**	0.10	0.649
$C_6H_5CH_2OH$	*f*	4.376
$C_6H_5CH_2OCOF_3$	∞	4.424
$C_6H_5CH_2OCOCF_3$	0.74	3.276

[a] Flow rates corrected to reacting temperature, 268° for the crotyl ester, 325° for the benzyl ester. [b] The symbol ∞ denotes an analysis of unreacted starting material. [c] Individual CO_2 samples agree well enough to justify this number of significant figures, but one less is justified for the whole process, including the degradation and combustion. These contain the natural abundance of 0.204% ^{18}O. [d] The *cis*-alcohol was characterized by its nmr spectrum, but was never obtained free from *trans* and was a minor component in all samples, including the starting materials. The analyses given are for samples rich in the *cis* isomer, not corrected for the content of *trans* isomer. The amount was always small and there is, therefore, no evidence on whether it participates slowly in the rearrangement or not. [e] The mass spectrum showed excessive atmospheric contamination and the result is therefore of low accuracy. [f] This sample is one of benzyl alcohol before esterification.

Table II. Analysis of Exit Stream from Flow System Starting

U, ml/sec	(**1**) + (**3**)[a]	(**2**) + (**4**)	(**5**)[b]
0.28	0.48	0.39	0.13
0.10	0.36	0.36	0.27

[a] *cis* and *trans* **1** (and **3**) were not separated in this analysis. The fraction of *cis* ester is presumably the same as that of the *cis* alcohol obtained on hydrolysis and is substantially less than 10% of the total. [b] The retention time of butadiene was short and the analysis is not of high precision. The values nevertheless are in agreement with those measured by MacDonald earlier,[4] as are the relative amounts of crotyl trifluoroacetate and the rearranged ester.

Table III. Mole Fractions of Isotopically Isomeric Products

Flow rate, *U*, ml/sec	Mole fraction of esters			
	1	**2**	**3**[a]	**4**
0.28	0.469	0.352	0.011	0.0378
0.10	0.337	0.318	0.0228	0.0418

[a] These values, obtained by difference, are of fairly low precision.

Discussion

Let us first consider for simplicity a scheme appropriate for producing all substances but with $k_{14} = k_{41} = k_{32} = k_{23} = 0$. Using the earlier values for the structural rearrangement[4,6] and neglecting isotope effects, we write $k_{12} = k_{34} = 6.93 \times 10^{-3}$ sec^{-1} and $k_{21} = k_{43} = 6.78 \times 10^{-3}$ sec^{-1}.

It is convenient to calculate first the nearly equal rate constants k_{25} and k_{45} from the steady-state equation (3)

$$(U/V)(\mathbf{5}) = k_{25}(\mathbf{2}) + k_{45}(\mathbf{4}) \simeq k_{25}[(\mathbf{2}) + (\mathbf{4})] \tag{3}$$

in which the approximation is only in the neglect of the oxygen isotope effect. Table II then gives the rough

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(4) J. M. MacDonald and E. S. Lewis, unpublished results. This work is described in ref 1 as part I of this series. The condensed results of this work are contained in Table II of ref 1.

(5) W. von E. Doering and E. Dorfman, *J. Amer. Chem. Soc.*, 75, 5597 (1953).

(6) These values are presumably more accurate than those derived from Table II, since the experiments were designed for rate data rather than product isolation.

values of $k_{25} = 4.62 \times 10^{-4}$ and 3.96×10^{-4} sec^{-1} for the two flow rates, which are in satisfactory agreement with MacDonald's more reliable value $k_{25} = 4.24 \times 10^{-4}$ sec^{-1} at this temperature,[4] which we shall use hereafter.

The steady state in **4** is given by eq 4.

$$k_{24}(\mathbf{2}) + k_{34}(\mathbf{3}) = (\mathbf{4})[(U/V) + k_{42} + k_{43} + k_{45}] \quad (4)$$

The two values of $k_{42} - k_{24}$ from the two flow rates in Table III are then 7.89×10^{-4} and 5.90×10^{-4}. The rather small value of (3) makes the second term on the left smaller than the first, thus the low accuracy does not invalidate the answer.

The steady state in **3** is given by eq 5, but the sensitivity to (3) is now large and in fact the solutions for k_{13}

$$k_{13}(\mathbf{1}) + k_{43}(\mathbf{4}) = \mathbf{3}[(U/V) + k_{31} + k_{34}] \quad (5)$$

$= k_{31}$ are -3.6×10^{-4} and -3.5×10^{-4} sec^{-1}. These meaningless negative numbers reflect the fact that (**4**) > (**3**) in both experiments; we believe that the uncertainty in (3) is responsible for this nonsense.

It is possible analogously to analyze the data using the alternative modes for getting the products **3** and **4**, namely, $k_{13} = k_{31} = k_{24} = k_{42} = 0$ but $k_{14} = k_{32}$ and $k_{23} = k_{41}$, and $k_{14}/k_{41} = k_{12}/k_{21}$.

The steady state in **4** is eq 6 which yields 7.5×10^{-4}

$$k_{14}(\mathbf{1}) + k_{34}(\mathbf{3}) = \mathbf{4}[(U/V) + k_{41} + k_{43} + k_{45}] \quad (6)$$

and 10.6×10^{-4} sec^{-1} for the two flow rates. The use of the steady state in **3** still gives negative flow rates, for the same reasons as before. There is not much to choose between the two schemes or any combination of them, about the only conclusion that can be drawn is that whatever the mode of shuffling it is of the order of one-tenth the rate of the rearrangement process. The limitation on the rearrangement kinetics is primarily in the difficulties of the analysis and separation, rather than in the flow system used. It should be noted that there were not enough good results to ascertain that the reactions are first order, which is very likely, or that the secondary reactions were homogeneous. In this connection, if a reaction contributes less than 10%, it would be very difficult to demonstrate that it is homogeneous, even if the evidence for homogeneity of the major reaction is quite clear.

One further piece of evidence which is compatible with the first scheme (k_{13}, $k_{24} \neq 0$) and cannot readily be explained by reactions such as $\mathbf{1} \rightarrow \mathbf{4}$ is the observation of isotopic rearrangement in benzyl trifluoroacetate, presented in Table I. The rate constant of this reaction (at 325°) calculated from the single observation is 2.1×10^{-3} sec^{-1}, assuming a first-order rate law. It is reasonable to guess that the rate of this reaction might be enough changed by temperature and the difference between benzyl and crotyl for both of these to undergo a C-type mechanism,[7] but again, we have no evidence that either reaction is homogeneous.

Whatever the mechanism of the minor reaction, and the accompanying paper[8] emphasizes the prevalence of surface reactions, a major course following mechanism A is indicated, and we confirm further that the reaction resembles the less polar Cope rearrangement.

Experimental Section

Crotonaldehyde Dimethyl Acetal. The procedure used by Todd and Teich[9] for the preparation of the diethyl acetal was followed. Crotonaldehyde (77 g, 1.07 moles) and trimethyl orthoformate (133 g, 1.25 moles) were stirred while a solution of 3.5 g of ammonium nitrate in 125 ml of methanol was added slowly. After addition of the last solution the mixture was heated at reflux for 20 min, cooled, diluted with 1 l. of ether, and washed with three 200-ml portions of dilute ammonium hydroxide and then with two 100-ml portions of water. The ether layer was dried with anhydrous grandular sodium carbonate, filtered, and most of the ether was removed by distillation through a spinning band column and 96 g (78%) of material boiling at 118–120° was obtained (lit.[10] bp 118–120°).

The 60-mc nmr spectrum showed a doublet of relative area of 3 at δ 1.7, a singlet area of 6 at 3.2, a split doublet of area 1 at 4.68, and a complicated multiplet of area 2 at 4.85–6.15.

Crotonaldehyde-^{18}O. Crotonaldehyde dimethyl acetal (64 g, 0.55 mole) was stirred while water (10 g, 0.55 mole) containing 5.2° excess ^{18}O, and then 2 drops of dilute sulfuric acid was added. On stirring the solution became quite cool and the two layers became homogeneous. This solution was diluted with 200 ml of ether and solid anhydrous granular sodium carbonate was added to neutralize the catalytic acid and to remove any water present. The sodium carbonate was removed by filtration and most of the ether was distilled through a Vigreux column. The residue was then slowly distilled through a spinning band column until the head temperature could not be kept below 70°. The residue of 4.15 g was not purified further, but gas chromatographic analysis showed the presence of only crotonaldehyde and a small amount of methanol. To the residue was added about 100 ml of ether and a very small amount of benzoquinone as preservative.

Crotyl Alcohol-^{18}O. Crotonaldehyde was reduced to crotyl alcohol with aluminum hydride (AlH_3) according to the method of Jorgenson.[11] Aluminum chloride, anhydrous (44 g, 0.33 mole), was cooled in a flask and with stirring 250 ml of ether was slowly added. Lithium aluminum hydride (28 g, 0.7 mole) in 750 ml of ether was cooled to ice bath temperature and the aluminum chloride solution was added dropwise with stirring. The entire solution was warmed to room temperature to precipitate the lithium chloride, after which the mixture was cooled again in an ice bath. The stabilized crotonaldehyde-^{18}O solution in ether mentioned above was diluted to 250 ml with ether and was added dropwise to the aluminum hydride solution. After completion of the addition the ice bath was removed and stirring was continued for 4 hr, after which time 50 ml of water was cautiously added to destroy the excess hydride. Dilute sulfuric acid was then added to form a solid and then a gelatinous precipitate. The ether layer was decanted and the solid material was extracted with several portions of ether. The combined ether extracts were dried over anhydrous granular sodium sulfate, filtered, distilled through a Vigreux column, and the residue was distilled through a spinning band column to give 32 g of material boiling at 118–120°. This material was identical with authentic crotyl alcohol and represented about 90% yield from crotonaldehyde dimethyl acetal.

Mass spectrometric analysis of the carbon dioxide produced from a sample showed that the crotyl alcohol contained 4.106% ^{18}O in excess of the 0.204% natural abundance.

Crotyl Trifluoroacetate-alkyl-^{18}O. Crotyl alcohol-^{18}O (20 g, 0.28 mole) was cooled in an ice bath and stirred while trifluoroacetic anhydride (70 g, 0.33 mole) was added dropwise, and worked up conventionally with ice cold water and distilled through a spinning band column. The fraction boiling at 105–106° (41.5 g, 89%) was collected. The material was indistinguishable from that prepared by MacDonald.[4]

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(7) The type C transition state, a 1,3-sigmatropic rearrangement, has formal analogy in solution to reactions which really go in two steps by way of ions, but it has no close analogy in the gas phase. It has a less direct analogy to the S$_{\rm N}$i reactions of chloroformates, which, however, are showing increasing evidence of heterogeneity [E. S. Lewis and K. Witte, *J. Chem. Soc., B*, 1198 (1968)], and has relation to the thermal rearrangements of aryl thioncarbamates to thiolcarbamates [K. Miyazaki, *Tetrahedron Lett.*, 2793 (1968)] which seem very unfavorable substances for an ionic course.

(8) E. S. Lewis and E. R. Newman, *J. Amer. Chem. Soc.*, 91, 7455 (1969).

(9) D. Todd and S. Teich, *ibid.*, 75, 1894 (1953).

(10) I. N. Nazarov, S. M. Makin, B. K. Kruptsov, and V. A. Mironov, *Zh. Obshch. Khim.*, 29, 106 (1959).

(11) M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

Hydrolysis of Crotyl Trifluoroacetate-alkyl-^{18}O. In order to analyze for the amount of label present at the alkyl position, it was necessary to convert the ester to the alcohol. Alkyl-^{18}O-labelled crotyl trifluoroacetate (5 g, 0.03 mole) was slowly added with stirring to sodium hydroxide (2.5 g, 0.06 mole) in 50 ml of water at ice bath temperature. After warming to room temperature the aqueous solution was extracted with four 75-ml portions of ether which were combined and dried over anhydrous granular sodium sulfate, decanted, and then thoroughly dried over anhydrous powdered magnesium sulfate. The ether was filtered and all but a small amount was removed by distillation through a Vigreux column. The residue was then purified by preparative gas chromatography using a 10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb W column in an Aerograph A-700 Autoprep. The crotyl alcohol was collected and found to be a mixture of *cis* and *trans* isomers consisting mostly of the *trans* form. The *cis* isomer could not be obtained pure, but nmr analysis showed that the methylene protons were shifted from δ 4.1 for *trans*- to δ 4.25 for *cis*-crotyl alcohol. The splitting pattern also changed but could not be analyzed carefully because of the presence of the *trans* isomer in the *cis*-crotyl alcohol.

Combustion and analysis of the carbon dioxide produced from a sample of a mixture of the *cis*- and *trans*-crotyl alcohol showed 3.479% excess ^{18}O. No 3-buten-2-ol was found that would correspond to S$_N$2′ attack by hydroxide ion on the crotyl trifluoroacetate. The somewhat low ^{18}O content was not further studied since an alternative ester cleavage described below was used. Since this experiment was not duplicated, it probably should not be given much significance.

Hydrazine Hydrate Treatment of Crotyl Trifluoroacetate-alkyl-^{18}O. Another method for preparation of the alcohol from the ester was tried because the saponification was mistakenly believed to lead to side reactions. It proved to be very simple and convenient. Alkyl-^{18}O-labelled crotyl trifluoroacetate (5 g, 0.03 mole) was stirred at ice bath temperature while hydrazine hydrate (5 g, 0.10 mole) was slowly added. The mixture was heated on a steam bath for 20–30 min, cooled, and poured into 300 ml of ether. The two layers were vigorously stirred magnetically and the excess insoluble hydrazine hydrate was separated from the ether layer which was dried with anhydrous powdered magnesium sulfate. This ether was filtered, distilled to a residue of about 5 ml, and then the crotyl alcohol was obtained pure by preparative gas chromatography using the same conditions mentioned above. A small amount of *cis*-crotyl alcohol was found as before, but no 3-buten-2-ol was present. Trifluoroacethydrazide was not identified or isolated. Analysis of the carbon dioxide from this sample showed the crotyl alcohol contained 4.041% excess ^{18}O.

Hydrazine Hydrate Treatment of Kinetic Samples. The same procedure as above was used to isolate crotyl alcohol and 3-buten-2-ol from mixtures of the trifluoroacetates. Sample 1 weighed 7.5 g while sample 2 weighed 7.0 g, and they were treated, respectively, with 7.5 and 7.0 g of hydrazine hydrate. Ether extraction, drying, distillation, and then preparative gas chromatography gave *cis*- and *trans*-crotyl alcohol and 3-buten-2-ol which were converted into carbon dioxide and analyzed for ^{18}O content.

Benzyl Alcohol-^{18}O. The method of Doering and Dorfman[5] was followed closely in order to prepare this compound. Dichlorodiphenylmethane was treated with water containing 5.2% ^{18}O to produce benzophenone-^{18}O. Perbenzoic acid oxidation of the benzophenone-^{18}O gave phenyl benzoate-carbonyl-^{18}O which was reduced with lithium aluminum hydride to benzyl alcohol-^{18}O. The over-all yield was 35% or 6.5 g of alcohol. Analysis of the carbon dioxide produced from a sample of this material showed that it contained 4.376% ^{18}O.

Benzyl Trifluoroacetate-alkyl-^{18}O. Trifluoroacetic anhydride (15 g, 0.071 mole) was slowly added with sirring to benzyl alcohol-^{18}O (6.0 g, 0.056 mole) in an ice bath. After warming to room temperature gas chromatographic analysis showed no alcohol remaining so the solution was poured into a separatory funnel containing about 150 g of ice covered with 100 ml of petroleum ether. After vigorous agitation the aqueous layer was removed and extracted with another 100-ml portion of the ether. The combined extracts were washed with two 50-ml portions of cold saturated aqueous sodium carbonate, once with 50 ml of ice water, filtered through a cone of anhydrous granular sodium sulfate, and then dried with anhydrous powdered magnesium sulfate. The petroleum ether extract was filtered, distilled to 40° through a Vigreux column, and the last traces of the ether were removed at 1 mm pressure with the distillation flask heated to about 130°. The residue of 11.0 g (97%) was analyzed by gas chromatography and was found to contain only benzyl trifluoroacetate identical with previously synthesized unlabelled material which had been distilled. This residue was not distilled in order to prevent any possible scrambling of the label at the high temperature needed.

Hydrazine hydrate treatment of benzyl trifluoroacetate-^{18}O. Using the same conditions as for the allylic esters, 4 g of starting ester was treated with 5 g of hydrazine hydrate and purified in the normal manner using the same preparative gas chromatograph conditions. Analysis showed 4.424% ^{18}O in the benzyl alcohol produced from starting ester.

^{18}O Analysis. The carbon dioxide is trapped in vials in liquid nitrogen and the vials are sealed under a pressure of about 1 mm while still cold. The bromine in chloroform–carbon tetrachloride bubbler was not used as a scrubber in the preparation of the carbon dioxide samples.

Analyses of the *m/e* 46 and 44 peaks were carried out by Mr. Sam Carroll in a Consolidated Engineering Type 21-701 mass spectrometer using an ionizing voltage of 50 eV and scanning the two peaks three times with increasing plate voltage and three times with decreasing plate voltage.

The ^{18}O content of a sample can be calculated if the *m/e* 46/44 ratio of standard tank carbon dioxide containing only the natural abundance (0.204%) of ^{18}O is known.

Several standard samples of tank carbon dioxide were run during the course of analyzing the samples produced from the various alcohols. The total ^{18}O content, x, of a substance containing only one oxygen, can be calculated according to the equation

$$\frac{0.99796x + 0.00204(1 - x)}{0.00408(1 - x)} = \frac{46/44 \text{ ratio of standard}}{46/44 \text{ ratio of sample}}$$

Kinetic Procedures. The stirred flow system used has been described in part before,[1] the crotyl system was studied in the apparatus described as I in that reference. Nitrogen at a controlled flow rate was bottled through the ester in a water-jacketed vaporizer held at 50° by circulation of thermostated water. The ester containing stream then passed into a 202.0-ml spherical Pyrex reaction vessel kept at 268.8° in a 1:1 sodium nitrate–sodium nitrite molten salt bath held constant by a commercial proportional temperature controller. A calibrated copper–constantan thermocouple was used to monitor the reactor temperature. The entrance and exit tubes of the reactor were kept at greater than 50% with heating tapes and samples were collected in Dry Ice–acetone cooled traps. Flow rates were measured with a 10-ml soap bubble flowmeter and the perfect gas law was used to correct the observed flow rate at room temperature to the temperature of the reactor.

Samples of the exit gas were withdrawn through a rubber serum stopper mounted on the heated exit tube and were injected by means of an electrically heated 1-ml gas tight syringe into an Aerograph Model 600 "HyFi" gas chromatograph equipped with a flame ionization detector. Analysis was done on a 9 ft × $^1/_8$ in. column of butanediol succinate on Chromosorb P while the areas of the peaks corresponding to compounds exiting from the reactor were automatically computed and recorded by an Infotronics Model CRS-10HB digital readout system integrator.

One hour after flow was started using unlabelled crotyl trifluoroacetate, the relative peak areas at a given flow were virtually identical with the values found by MacDonald.[4] Three days later the ratios of the three compounds coming out of the reactor were still the same.

Kinetic Samples. Since the kinetic behavior of this system has been closely investigated,[4] only a few samples of the exit gas were taken during the collection of these gases for analysis of the ^{18}O content. Starting with pure crotyl trifluoroacetate containing ^{18}O label at the alkyl position, two samples were collected with the vaporizer at 50° and the reactor at 268.8°. Sample 1 was collected over a 19-hr period at a corrected flow rate of 0.28 ml/sec and 7.5 g of material consisting of about 48% starting material, 39% rearranged ester, and 13% butadiene was obtained. Sample 2 was collected over a 48-hr period at a corrected flow rate of 0.10 ml/sec and 7.0 g of liquid consisting of about 36% crotyl ester, 36% rearranged ester, and 27% butadiene was obtained.

The stirred flow system used for benzyl trifluoroacetate was essentially that described by Lewis and Witte,[6] and is that described as II in ref I. The major difference is that thermostating was accomplished with a closely fitting externally heated aluminum block, instead of the fused salt bath. The vaporizer was held at

60°, the reactor at 325°, and 5 g of benzyl trifluoroacetate-^{18}O was collected in an ice bath trap over a 4-day period using a corrected flow rate of 0.74 ml/sec. Under these conditions about 0.5% toluene was formed as the only other product. At lower flow rates or higher temperatures considerable amounts of toluene (up to 50% at 375°) were detected in samples of the exit gas from the reactor. Seasoning of the reaction vessel and determination of the most severe conditions that could be used with minimum toluene formation was carried out for 1 week prior to introduction of ^{18}O-labelled material.

Benzyl alcohol was obtained from the material which had passed through the reactor by treating the ester with hydrazine hydrate as above.

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Addition Reactions of 4,4-Dimethylcyclohexadienylidene[1]

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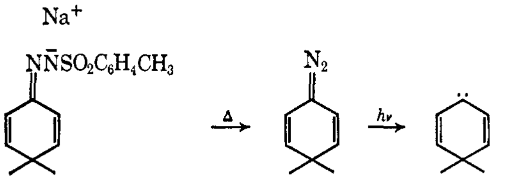
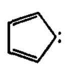
Abstract: Diazo-4,4-dimethylcyclohexadiene (**1**) has been synthesized and decomposed under a variety of conditions. The resultant carbene, 4,4-dimethylcyclohexadienylidene (**2**), adds stereospecifically to *trans*-4-methyl-2-pentene and nearly so to *cis*-4-methyl-2-pentene. Adducts are also formed with dienes, acetylenes, and benzene. Remarkably, the product of addition to benzene is in the norcaradiene form. A comparison of relative rates of addition of **2** and cyclopentadienylidene (**3**) to olefins reveals differences which may indicate a quasi-aromatic structure for **3**.

Pyrolysis of the sodium salt of 4,4-dimethylcyclohexadienone tosylhydrazone yields the deep purple diazo-4,4-dimethylcyclohexadiene (**1**)[3] in *ca.* 22% of theory. While the diazo compound seems stable indefinitely at −78° under nitrogen, it decomposes rapidly at room temperature to a glistening golden yellow azine. Nonetheless careful handling permits the examination of the photochemical decomposition of this compound and thereby the study of 4,4-dimethylcyclohexadienylidene (**2**).

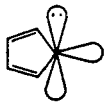


1 2

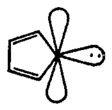
Beyond yielding additional information on the properties of internally stabilized carbenes, it was hoped that a comparison of properties with those of cyclopentadienylidene (**3**) would be instructive. In particular, it was hoped that substantial differences in the behaviors of **2** and **3** would appear indicating special properties attributable to an aromatic structure (**3a**) for **3**. Were the two free electrons to be located in the π system, one might expect different, if not precisely predictable, properties for **3**. Gleiter and Hoffmann[5] have reported extended Hückel calculations in which **3a** and the more conventional **3b** (in which the free electrons occupy the sp^2-like orbital) emerge of comparable energies. Even though the properties of **3** become known during the course of this work and seemed quite unspectacular,[6-9] it remained to provide an appropriate model against which the lack of strangeness could be measured. The carbene **2** seemed a good choice as it can not attain the six π electron aromatic system of **3a** and should be a simple divinylcarbene. A possible escape *via* the vinylcarbene–cyclopropene rearrangement studied by Closs[10] appeared only a remote possibility in this case as did intramolecular insertion or aromatization.



3



3a



3b

Cyclohexadienylidenes, while not previously unknown, have not been studied in detail. Examples of aromatizations in steroidal systems are known[11] and Fry[12] has generated 4-methyl-4-trichloromethylcyclohexadienylidene from the corresponding tosylhydrazone salt.[12] No systematic study was undertaken in the latter case, nor was the diazo compound isolated.

The structure of **1** was evident from its spectra. The infrared spectrum is dominated by a band at 2049 cm^{-1}

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[2] (a) Alfred P. Sloan Research Fellow, 1967–1969; (b) Olin Matheson Research Participant, 1968.

[3] Although we have experienced no trouble with this material, this relative of the notoriously capricious diazocyclopentadiene[4] should be treated with great caution.

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