

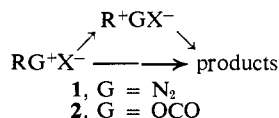
The Reactions of *cis*- and *trans*-4-*tert*-Butylcyclohexyl and *erythro*- and *threo*-3-Phenyl-2-butyl Chloroformates and Chlorides with Silver Hexafluoroantimonate in Acetic Acid. A Comparison with Deaminations and Solvolyses

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Abstract: The acetate and olefin products from the reactions of *cis*- and *trans*-4-*tert*-butylcyclohexyl and *erythro*- and *threo*-3-phenyl-2-butyl chloroformates and chlorides with silver hexafluoroantimonate in acetic acid are identified and found to be consistent with the hypothesis that the reactions of the chloroformates are similar to deaminations and are different from the reactions of the chlorides, which, in turn, resemble solvolyses. Deuterium labeled reactants are used to delineate the rearrangement reactions of both types of chloroformates. It is established by oxygen-18 labeling that the products from the 4-*tert*-butylcyclohexyl substrates do not arise from acetic (4-*tert*-butylcyclohexyl)carbonic anhydride. The acetates from the reaction of *cis*- and *trans*-*N*-(4-*tert*-butylcyclohexyl)-sulfanyl amines with nitrosyl hexafluoroantimonate in acetic acid are found to be similar to those from the corresponding chloroformates. The results are interpreted in terms of silver assisted reactions of the chloroformates primarily by initial ionization (k_c) to an ion pair in which the cation resembles the reactant and in terms of silver assisted reaction of the chlorides predominantly by classical nucleophilic participation by neighboring groups (k_Δ) or solvent (k_s). These proposals are in accord with previous suggestions for deaminations and solvolyses and are noted to provide an appealing mechanistic rationale for distinction between those reactions as well.

A similarity between the silver promoted dehalodecarboxylation of alkyl chloroformates and the deamination of primary alkyl amines has been suggested and attributed¹⁻³ to the resemblance between nitrogen and carbon dioxide as leaving groups in the low-energy processes which may be formulated as leading from the diazonium ion **1** or the carboxylium ion **2** to an intermediate carbonium ion or to products. On the other hand, reactions of alkyl chlorides with silver ion,



although kinetically complex, appear to give products and involve processes which resemble those of solvolyses.^{4,5} In mechanistic explanations of the product differences observed on deamination of a primary amine and solvolysis of the corresponding sulfonate, a critical role is assigned to the small energy required to break the carbon heteroatom bond in deamination, but interpretations have differed on the timing of bond breakage and on the nature and environment of any intermediates formed thereafter.⁶⁻²⁴ One difficulty en-

countered in attempting to identify the fundamental differences between deaminations and solvolyses is that effects due to necessary variations in reagents, counterions, temperature, and solvents are difficult to assess. For example, most deaminations are considered to involve a diazonium ion associated with a counter species which can significantly affect the fate of the ion^{8,11-13,16,22,25} but which is, except in a few cases,^{12,16} different from the counter species in the solvolytic reaction to which the deamination is compared.

Comparison of the products from the reactions of

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(2) For an excellent review, see D. N. Kevill, "The Chemistry of Acyl Halides," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1972, p 381.

(3) D. N. Kevill, W. A. Reis, and J. B. Kevill, *Tetrahedron Lett.*, 957 (1972); W. E. Dupy, H. R. Hudson, and D. A. Karam, *ibid.*, 3193 (1972), and references cited therein.

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(11) R. A. Moss, *Chem. Eng. News*, 28 (Nov. 22, 1971); R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967).

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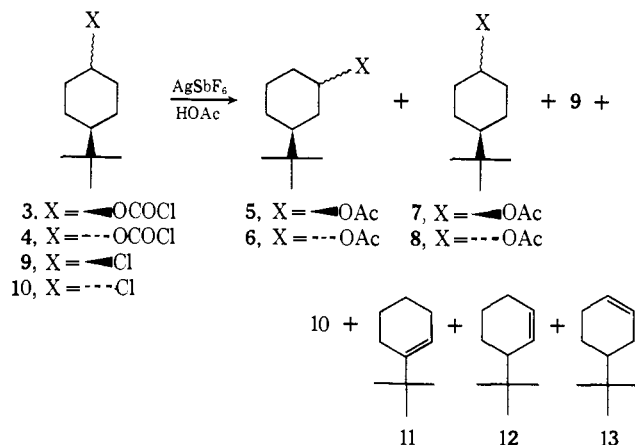
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alkyl chloroformates and chlorides with silver hexafluoroantimonate under the same conditions offers an opportunity to obtain information about reactions which appear to have rather different energies of activation but leaving groups differing formally only in the elements of a stable nonnucleophilic species. The substrates selected for comparison are the conformationally rigid 4-*tert*-butylcyclohexyl and conformationally free 3-phenyl-2-butyl secondary systems which have been investigated extensively in deaminations and solvolyses.^{6-10,21,26} The fact that these substrates give significantly different product ratios in these reactions has been attributed to control of product formation by the same factors which dictate the ground state conformation of the reactants.^{6-11,13,15-17,19,20,23,25-27} The present study of the acetate and olefin products from the reactions of *cis*- and *trans*-4-*tert*-butylcyclohexyl and *erythro*- and *threo*-3-phenyl-2-butyl chloroformates and chlorides with silver hexafluoroantimonate in acetic acid shows that the suggested analogies to deamination and solvolyses are viable and provides a basis for discussion of the mechanistic differences between such processes.

Results

***cis*- and *trans*-4-*tert*-Butylcyclohexyl Substrates.** The reaction of *cis*-4-*tert*-butylcyclohexyl chloroformate (**3**) with silver hexafluoroantimonate in dry acetic acid for 3 hr at ambient temperature gives carbon dioxide, silver chloride, *cis*- and *trans*-3-*tert*-butylcyclohexyl acetates (**5** and **6**), *cis*- and *trans*-4-*tert*-butylcyclohexyl acetates (**7** and **8**), *cis*- and *trans*-4-*tert*-butylcyclohexyl chlorides (**9** and **10**), and 1-, 3-, and 4-*tert*-butylcyclohexenes (**11**, **12**, and **13**, respectively) (Scheme I) in

Scheme I



the yields indicated in Table I. The same products are formed (Scheme I) in different amounts from the *trans* chloroformate **4** (Table I) under the same conditions. The structures of **7-11** and **13** were established by glpc analysis and spectral comparison with authentic materials, while **5**, **6**, and **12** were identified on the basis of their spectral properties. The yields of the organic products are within experimental error of 100% from both chloroformates.

(26) C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer, "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, p 1347.

(27) Conformational control in deaminations is known not to imply the exclusive involvement of groups which are *trans* to the departing nitrogen. For example, Collins, *et al.*, observe migrations of *cis* phenyl rings in secondary propyl systems^{8a} and Cohen, *et al.*, have shown that olefin arises from *cis* eliminations in cyclohexyl systems.²⁵

Table I. Yields of Products in Mole Per Cent from the Reactions of *cis*- and *trans*-4-*tert*-Butylcyclohexyl Chloroformates (**3** and **4**) and Chlorides (**9** and **10**) with Silver Hexafluoroantimonate in Acetic Acid at Ambient Temperature

Products	Reactant			
	3 ^a	4 ^a	9 ^a	10 ^b
5	1.2 ± 0.9	0.8 ± 0.3	0.2 ± 0.06	0.9 ± 0.12
6	8.2 ± 0.3	2.9 ± 0.6	2.3 ± 0.3	1.2 ± 0.3
7	3.6 ± 0.3	8.3 ± 0.6	0.5 ± 0.06	4.3 ± 0.3
8	3.5 ± 0.3	29.2 ± 1.0	1.4 ± 0.3	0.7 ± 0.3
9	14.7 ± 0.6	4.1 ± 2.7		
10	1.5 ± 0.6	36.7 ± 2.7		
11	6.6 ± 0.6	6.3 ± 0.9	1.4 ± 0.3	1.6 ± 0.3
12	3.8 ± 0.9	1.3 ± 0.3	0.7 ± 0.3	2.1 ± 0.6
13	59.3 ± 5.7	15.3 ± 0.8	28.1 ± 3.0	19.6 ± 4.5

^a Reaction time, 3 hr; errors are three times the standard deviations of at least three glpc determinations. ^b Reaction time, 48 hr; errors as specified in footnote *a*.

Carbon dioxide is produced quantitatively and the yields of silver chloride from **3** and **4** are 84 and 62%, respectively; the material balance for chloride is satisfied by the formation of 4-*tert*-butylcyclohexyl chlorides, which have predominantly retained configuration in each case. A trace of material with a retention time identical with that of *cis*-2-*tert*-butylcyclohexyl acetate was also observed for each reaction. The *trans* chloroformate **4** also gave a small amount of an unidentified material with a retention time comparable to that reported for 2-*tert*-butylbicyclo[3.1.0]hexane.¹⁰

The *cis*- and *trans*-4-*tert*-butylcyclohexyl chlorides are visually less reactive to silver hexafluoroantimonate in acetic acid than are the chloroformates. The *cis* chloride **9** reacts in 3 hr at ambient temperature to give 30% silver chloride and 35% organic products **5-8** and **11-13** (Scheme I) in the yields indicated in Table I. The reactivity of **9** in 3 hr suggests that some of the products observed in the reaction of *cis*-4-*tert*-butylcyclohexyl chloroformate (**3**) may be due to subsequent reaction of the *cis* chloride initially formed. An upper limit can be placed on the influence this secondary reaction could have on the product yields. At the end of the reaction of **3**, a yield of 16.2% 4-*tert*-butylcyclohexyl chloride was found, of which 14.7% is **9**. If it is assumed that as a maximum this amount represents 65% of the amount of **9** initially formed (*i.e.*, that 35% reacted), then 24.5% *cis* chloride could have been formed from the reaction. In 3 hr this amount of **9** could react to give 0.05% *cis*-3-acetate, 0.6% *trans*-3-acetate, 0.1% *cis*-4-acetate, 0.4% *trans*-4-acetate, 0.4% 1-olefin, 0.1% 3-olefin, and 6.9% 4-olefin, relative to the values in Table I. In no case do the potential corrections change a trend or affect a conclusion which might be made concerning the product ratios from the reaction of the *cis* chloroformate.

The *trans* chloride **10** does not react to give a detectable amount of silver chloride with silver hexafluoroantimonate in acetic acid at ambient temperature for 3 hr, but after 48 hr a 33% yield of silver chloride is produced and the same organic products as those observed previously are obtained (Scheme I) in the yields indicated in Table I. Although both chloride isomers give predominant elimination and overall inversion in the formation of the unrearranged acetates, the products from **10** could reflect some acid-catalyzed additions of acetic acid to the olefins and some equili-

bration of the olefins at the longer reaction time not covered by the product stability control experiments discussed below. However, the reaction of the *cis* chloride **9** was allowed to proceed for 36 hr to give a 59% yield of silver chloride, and the product ratios obtained (see Experimental Section) were found to correspond sufficiently closely to those reported in Table I for the 3-hr reaction to suggest that major amounts of product isomerization or destruction do not occur even at the longer reaction times used for **10**.

The reaction of *trans*-4-*tert*-butylcyclohexyl chloroformate (**4**) was carried out in the presence of 1 equiv of 4-*tert*-butylcyclohexene (**13**) in order to determine the stability of a representative olefin to the reaction conditions. After 12 hr at ambient temperature, glpc analysis showed $114.0 \pm 3.7\%$ **13**, based on starting chloroformate as 100%. A parallel reaction with no added olefin gave $19.5 \pm 0.7\%$ **13** under otherwise identical conditions. If **4** reacts to the same extent in the presence of 1 equiv of **13** as it does with no added olefin, then as much as $5.5 \pm 3.8\%$ of 4-*tert*-butylcyclohexene could undergo secondary reaction under these conditions. It should be noted, however, that in the reaction with added **13** the silver chloride yield was reduced to 55% from 68% in the absence of olefin. If the yield of **13** from 4-*tert*-butylcyclohexyl chloroformate is adjusted for the amount of silver chloride formed, then only 115.8% olefin would be expected, a value well within experimental error of that observed. In a more severe test of the stability of **13**, molar amounts of silver chloride and hexafluoroantimonoic acid were produced from 1 equiv of silver hexafluoroantimonate and hydrogen chloride gas in the presence of 1 equiv of 4-*tert*-butylcyclohexene in acetic acid. Analysis of the reaction after the mixture had been stirred for 3 hr at ambient temperature showed formation of 1.3% *trans*-3-*tert*-butylcyclohexyl acetate, 1.1% *cis*-4-*tert*-butylcyclohexyl acetate, 0.3% *cis*-3-*tert*-butylcyclohexyl acetate, and 0.2% *trans*-4-*tert*-butylcyclohexyl acetate, based on **13**, for a total of 2.9% addition of acetic acid to the olefin. These values are considered to represent the maximum amount of acid-catalyzed addition of acetic acid which could occur in the chloroformate reactions, since in the actual reactions neither olefin nor hexafluoroantimonoic acid is present in concentrations as high as those in the control. In neither control was there evidence of isomerization of 4-*tert*-butylcyclohexene to 1- or 3-*tert*-butylcyclohexene.

In order to determine the origin of the products from **3** and **4** the reactions of the *cis*- and *trans*-4-*tert*-butylcyclohexyl-2,2,6,6-*d*₄ chloroformates (**3-d**₄ and **4-d**₄) with silver hexafluoroantimonate in acetic acid were investigated. The products are shown in Scheme II, and the yields are summarized in Table II. The location of the deuterium atoms as shown in Scheme II for **6-d**₄, **7-d**₄, **8-d**₄, **13-d**₃, and **13-d**₄ is based on the proton magnetic resonance spectra, as cited in Table III. The isotopic substitutions in **5-d**₄ and **12-d**₄ are considered to be the same as for **6-d**₄, since these products are presumed to be formed from the same precursor, the 3-*tert*-butylcyclohexyl-3,4,5,5-*d*₄ cation (**14**), which results from a 1,2-deuteride shift. The error limits given in Table III reflect difficulties in obtaining data with small samples and are sufficiently large that only qualitative conclusions about the origin

Scheme II

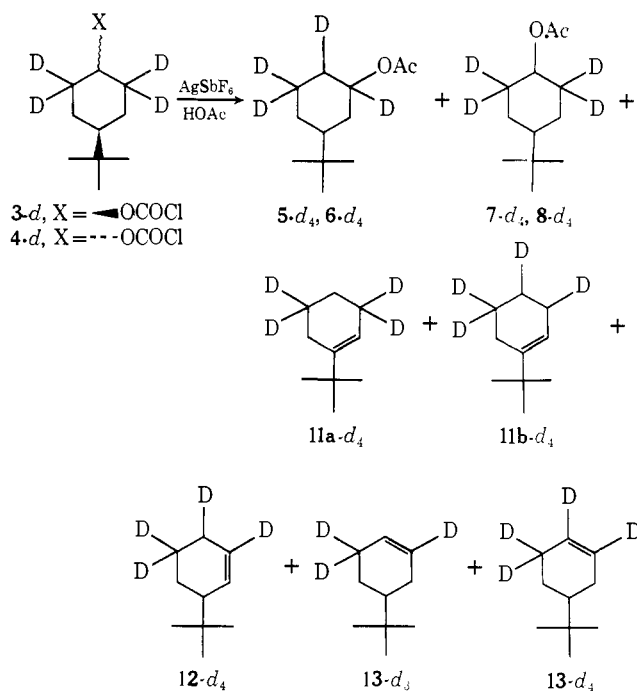


Table II. Yields of Products in Mole Per Cent from the Reaction of *cis*- and *trans*-4-*tert*-Butylcyclohexyl-2,2,6,6-*d*₄ Chloroformates (**3-d**₄ and **4-d**₄) with Silver Hexafluoroantimonate in Acetic Acid at Ambient Temperature for 3 hr

	3-d ₄ ^a	4-d ₄ ^a
5-d ₄	1.4 ± 6.3	0.7 ± 0.3
6-d ₄	9.9 ± 0.6	2.6 ± 0.3
7-d ₄	4.4 ± 0.9	8.3 ± 1.8
8-d ₄	4.1 ± 0.9	30.7 ± 2.4
9-d ₄ , 10-d ₄	18.2 ± 3.9	42.4 ± 3.6
11-d ₄	8.3 ± 0.9	5.0 ± 0.5
12-d ₄	4.2 ± 1.5	1.4 ± 0.3
13-d ₃ , 13-d ₄	52.0 ± 4.8	7.8 ± 0.4

^a Errors are three times the standard deviation for at least three glpc determinations.

Table III. Nmr Analysis of Products from the Reactions of 4-*tert*-Butylcyclohexyl-2,2,6,6-*d*₄ Chloroformates with Silver Hexafluoroantimonate in Acetic Acid at Ambient Temperature for 3 hr

Product	Starting chloroformate	1- or olefinic protons ^a	Other ring protons ^a	<i>tert</i> -Butyl protons ^b
13-d ₃ , 13-d ₄	3-d ₄	0.8 ± 0.9 (2) ^c	5 ± 0.6 (7)	9
	4-d ₄	0.7 ± 0.9 (2)	5 ± 1.5 (7)	9
8-d ₄	3-d ₄	0.9 ± 0.3 (1)	5 ± 1.2 (9)	9
	4-d ₄	1.0 ± 0.3 (1)	5 ± 1.2 (9)	9
7-d ₄	3-d ₄	1.0 ± 0.6 (1)	5 ± 0.9 (9)	9
	4-d ₄	0 ± 0.3 (1)	5 ± 0.9 (9)	9
6-d ₄	3-d ₄	0 (1)	6 ± 1.8 (9)	9
	4-d ₄	0 (1)	6 ± 1.5 (9)	9
5-d ₄	3-d ₄	0 (1)	6 ± 1.5 (9)	9
	4-d ₄	Not collected		

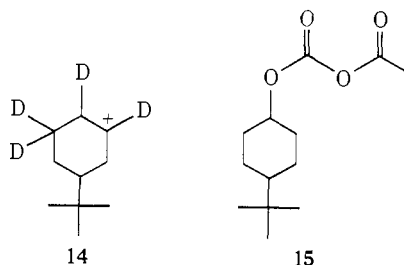
^a Average of 3-5 integrations of 60-MHz proton spectra; errors are reported as three times the standard deviations. ^b Arbitrarily assigned a value of nine protons as a standard. ^c Numbers in parentheses represent the total number of protons and deuteriums on the position in question.

of the products can be based on these deuterium distributions.

Comparisons of the reaction of **3** with that of $3-d_4$ and of **4** with $4-d_4$ show that only the yield of 4-*tert*-butylcyclohexene (**13**) is appreciably affected by the deuterium substitution. The yield of **13** is reduced by *ca.* 10% of its yield from the *cis* isomer **3** and by *ca.* 50% of its yield from the *trans* isomer **4**, a result which is consistent with the expected operation of primary isotope effects²⁸ in the formation of $13-d_3$. However, the 4-*tert*-butylcyclohexene formed from $3-d_4$ and $4-d_4$ may have less than the one olefinic proton expected in the pmr spectra of $13-d_3$, which could reflect the presence of some $13-d_4$ from **14**.

An interesting feature of the reactions of **3**, **4**, and **9** is the formation of 1-*tert*-butylcyclohexene (**11**) as 9, 28, and 5%, respectively, of the total olefin yields in each case. The above control experiment, which establishes the stability of **13** to the reaction conditions, can be taken to suggest that **11** does not arise by olefin isomerization. The olefin **11** is also produced from **10** but in that case has not been rigorously excluded as a secondary reaction product from isomerization of the other olefins. Mass spectral analysis of the 1-*tert*-butylcyclohexene from $3-d_4$ and $4-d_4$ shows it to contain 99 and 97% of the original label, respectively. The allylic and nonallylic ring protons and deuteriums can be resolved in the nmr spectra and those data can be combined with the assignment of 1-*tert*-butylcyclohexyl-3,3,5,5- d_4 (**11a-d₄**) and 1-*tert*-butylcyclohexyl-3,4,5,5- d_4 (**11b-d₄**) as the most reasonable products²⁹ to establish the ratios of **11a-d₄**:**11b-d₄** as $39 \pm 2:61 \pm 3$ from $3-d_4$ and $51 \pm 4:49 \pm 4$ from $4-d_4$. The possibility that **11b-d₄** arises not by consecutive 1,2-hydride shifts but *via* protonation of 3-*tert*-butylcyclohexene (**12-d₄**) formed by a proton loss from **14** can be excluded for three reasons. First, if **12-d₄** is converted to **11b-d₄** by such a process even with a maximum isotope effect, *ca.* 14% exchange of deuterium for protium would be expected. Second, both **3** and **4** give about the same amount of **11** but **3** gives more than twice as much **12** as does **4**; if **11** resulted from **12**, the reaction which produces more **12** should produce more **11**. Finally, the control experiments established that **13** is not converted to **12** or **11**, a process which should very closely parallel any possible conversion of **12** to **11**.

The intermediacy of *cis*- and *trans*-acetic (4-*tert*-butylcyclohexyl)carbonic anhydrides (**15**) is possible in the



(28) Other smaller isotope effects might also be expected in these reactions: V. J. Shiner and J. G. Jewett, *J. Amer. Chem. Soc.*, **87**, 1382 (1965).

(29) 1,2- and 1,3-hydride shifts have been reported for a variety of cyclohexyl systems: (a) Y. G. Bundel, V. A. Savin, M. N. Ryabtsev, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **165**, 1303 (1965); *Engl. Trans.*, 1198; (b) see, however, C. C. Lee and J. E. Kruger, *J. Amer. Chem. Soc.*, **87**, 3986 (1965) and C. J. Collins, *Chem. Rev.*, **69**, 543 (1969); (c) J. E. Nordlander and T. J. McCrary, *J. Amer. Chem. Soc.*, **94**, 5133 (1972); (d) J. B. Lambert, G. J. Putz, and C. E. Mixan, *ibid.*, **94**, 5132 (1972); (e) H. Hogeveen and A. A. Kiffen, *Recl. Trav. Chim. Pays-Bas*, **91**, 1205 (1972).

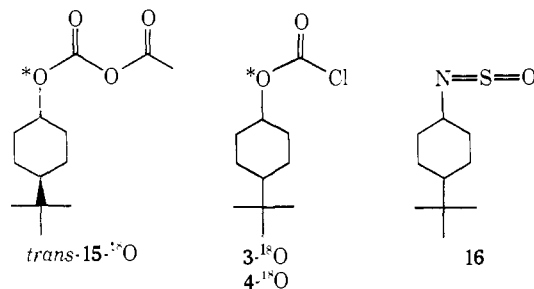
reactions of **3** and **4** with silver hexafluoroantimonate in acetic acid. If this is the case, the relationship between the reactants, possible carbonium ion intermediates, and products would be obscured. In particular, the conversion of **15** to unrearranged and retained acetate would be expected to occur without cleavage of the alkyl-oxygen bond.³⁰ In fact, when 1 equiv of *trans*-**15** is allowed to react in the presence of **4** and silver hexafluoroantimonate in acetic acid the yield of **8**, the unrearranged and retained acetate, is increased to about 120% from *ca.* 30% in the absence of *trans*-**15**. In order to show that the conversion of *trans*-**15** to **8** does involve retention of the oxygen-alkyl bond, the decomposition of *trans*-**15** ¹⁸O labeled with 1.86% ¹⁸O in the cyclohexyl oxygen was allowed to proceed in the presence of 1 equiv of silver hexafluoroantimonate and 10 mol % **4**, and the evolved carbon dioxide was collected, analyzed by mass spectrometry, and found to contain almost no excess oxygen-18 (Table IV).

Table IV. Oxygen-18 Labeling of Carbon Dioxide from the Reaction of Cyclohexyl Oxygen Labeled Acetic (*trans*-4-*tert*-Butylcyclohexyl)carbonic Anhydride (*trans*-**15**-¹⁸O) with Silver Hexafluoroantimonate in Acetic Acid^a in the Presence of 10% Unlabeled **4**

Source of CO ₂	<i>f</i> ¹⁸ O in CO ₂ ^b	<i>f</i> ¹⁸ O excess	Relative % enrichment
Reaction of unlabeled 4 with AgSbF ₆ in HOAc	0.266 ± 0.008 ^c	0	0
Pyrolysis of 4 - ¹⁸ O used to prepare <i>trans</i> - 15 - ¹⁸ O	2.122 ± 0.003	1.856 ± 0.017	100
Reaction of <i>trans</i> - 15 - ¹⁸ O with AgSbF ₆ in HOAc in the presence of 10% unlabeled 4	0.285 ± 0.003	0.019 ± 0.008	1.13 ± 0.44 ^d

^a Reaction run in the presence of 10 mol % unlabeled **4**. ^b Calculated from $f^{18}O = (b + 2c)/2$, where *a*, *b*, and *c* are intensity values for *m/e* 44, 46, and 48 normalized so that $a + b + c = 100$. ^c Errors reported as standard deviations of at least four scans from isotope ratio mass spectrum. ^d Corrected for 10% unlabeled **4** in the reaction mixture.

However, it was established by analysis of the carbon dioxide evolved from the reactions of *cis*- and *trans*-cyclohexyl oxygen-18 labeled reactants, $3-^{18}O$ and $4-^{18}O$, respectively, that **15** does not play an important



(30) (a) D. S. Tarbell and E. J. Langosz, *J. Org. Chem.*, **24**, 774 (1959); E. J. Langosz, *ibid.*, **26**, 2161 (1961); (b) C. J. Michejda, D. S. Tarbell, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **84**, 4113 (1962); (c) D. S. Tarbell, *Accounts Chem. Res.*, **2**, 296 (1969).

role in the conversions of the chloroformates to products. The carbon dioxide resulting from the reaction of 4-¹⁸O containing 23.6% oxygen-18 in the cyclohexyl oxygen has $96.6 \pm 2.5\%$ of the label from the chloroformate, while the carbon dioxide from 3-¹⁸O bearing 24.4% oxygen-18 contains $99.0 \pm 2.5\%$ of the label (Table V). Clearly both *cis*- and *trans*-4-*tert*-butyl-

Table V. Oxygen-18 Labeling of Carbon Dioxide from the Reaction of Cyclohexyl Oxygen Labeled *cis*- and *trans*-4-*tert*-Butylcyclohexyl Chloroformate 3-¹⁸O and 4-¹⁸O with Silver Hexafluoroantimonate in Acetic Acid

Source of CO ₂	<i>f</i> ¹⁸ _O in CO ₂ ^a	<i>f</i> ¹⁸ _O excess	Relative % enrichment
Reaction of unlabeled 4 with AgSbF ₆ in HOAc	0.27 ± 0.01 ^b		0
Pyrolysis of cyclohexyl oxygen labeled 4	23.63 ± 0.33 ^c	23.36 ± 0.33	100
Reaction of cyclohexyl oxygen labeled 4 with AgSbF ₆ in HOAc	22.83 ± 0.23 ^c	22.56 ± 0.23	96.57 ± 1.68
Pyrolysis of cyclohexyl oxygen labeled 3	24.44 ± 0.40 ^d	24.17 ± 0.40	100
Reaction of cyclohexyl oxygen labeled 3 with AgSbF ₆ in HOAc	24.20 ± 0.46 ^c	23.93 ± 0.46	99.01 ± 2.51

^a Calculated from $f^{18}_O = (b + 2c)/2$, where *a*, *b*, and *c* are intensity values for *m/e* 44, 46, and 48 normalized so that $a + b + c = 100$. ^b Error reported as standard deviation of four scans from isotope ratio mass spectrum. ^c Errors reported as standard deviations of six scans from isotope ratio mass spectrum. ^d Error reported as standard deviation of six scans each for two independent samples from isotope ratio mass spectrum.

cyclohexyl chloroformates react primarily by cleavage of the alkyl-oxygen bond, although **4** could be giving minor amounts of **8** via *trans*-**15**.

As previously noted, comparisons of deaminations with other reactions considered to involve similar cationic species are difficult because of necessary differences in reactants, counter species, and reaction conditions. The reaction of isocyanates or *N*-sulfinylamines with nitrosyl salts³¹ appears to provide a suitable system for comparison with the present studies in that a diazonium species may be formed without a nucleophilic counter species. It has been noted, however, that possible olefinic products are unstable to reactions of *N*-sulfinylamines and nitrosating agents in chlorobenzene.¹ The reaction of *N*-(4-*tert*-butylcyclohexyl)-sulfinylamine (**16**) with nitrosyl hexafluoroantimonate at ambient temperature for 1.5 hr gives **5** ($0.7 \pm 0.3\%$), **6** ($1.1 \pm 0.6\%$), **7** ($7.9 \pm 0.9\%$), and **8** ($31.2 \pm 3.3\%$) from the *trans* isomer and **5** ($0.5 \pm 0.3\%$), **6** ($1.9 \pm 1.2\%$), **7** ($1.7 \pm 1.5\%$), and **8** ($2.6 \pm 1.8\%$) from the *cis* isomer. The ratios of these products are in reasonable agreement with the ratios of the same products from the reactions of the corresponding chloroformates. It was shown that 4-*tert*-butylcyclohexene is not stable to the

(31) G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lucas, *J. Amer. Chem. Soc.*, **88**, 5328 (1966).

conditions for reaction of *trans*-**16**, but the olefin does not simply add acetic acid to form the *tert*-butylcyclohexyl acetates since the yields of the acetates are not affected.

threo- and **erythro**-3-Phenyl-2-butyl Substrates. The reactions of *threo*- and *erythro*-3-phenyl-2-butyl chloroformates (**17** and **18**) with silver hexafluoroantimonate in acetic acid for 1 hr give *threo*- and *erythro*-3-phenyl-2-butyl acetates (**19** and **20**), 2-methyl-1-phenylpropyl acetate (**21**), *threo*- and *erythro*-3-phenyl-2-butyl chlorides (**22** and **23**), *cis*- and *trans*-2-phenyl-2-butene (**24** and **25**), and 2-methyl-1-phenyl-1-propene (**26**) (Scheme III) in the yields shown in Table VI. The structures

Scheme III

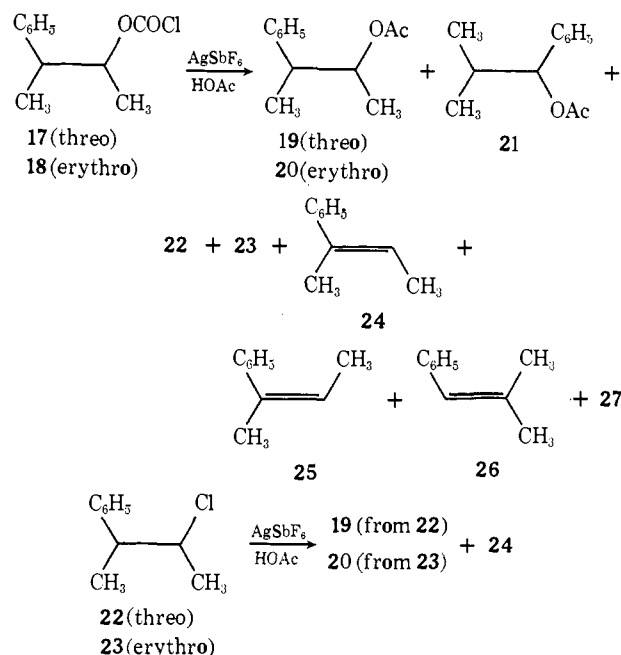


Table VI. Yields of Products in Mole Per Cent from the Reactions of *threo*- and *erythro*-3-Phenyl-2-butyl Chloroformates (**17** and **18**) and Chlorides (**22** and **23**) with Silver Hexafluoroantimonate in Acetic Acid at Ambient Temperature for 1 hr

Products	Reactant			
	17 ^a	18 ^a	22 ^a	23 ^a
19	17.0 ± 2.1	2.0 ± 0.6	33.6 ± 4.8	
20	4.7 ± 0.9	29.9 ± 3.0		40.8 ± 4.5
21	39.0 ± 4.5	4.3 ± 0.3		
22	8.7 ± 1.8	0.4 ± 0.6		
23	1.0 ± 0.9	8.0 ± 1.5		
24	8.5 ± 2.1	18.2 ± 4.8	4.2 ± 1.5	3.2 ± 1.5
25	3.5 ± 1.2	6.4 ± 3.0		
26	3.7 ± 1.2	1.3 ± 0.3		
27	5.7 ± 1.2	9 ± 6		

^a Errors are three times the standard deviations of at least three glpc determinations.

of the products were established by glpc and spectral comparison with authentic materials. In addition, 3-methyl-2-phenyl-1-penten-4-one (**27**), which results from acylation of the olefins under the reaction conditions, and traces of 2-phenyl-1-butene (**28**) are obtained from both isomers. The yields of silver chloride are 81 and 78% and the yields of the organic products are 92 and 80% from **17** and **18**, respectively. Both chloroformates show some leakage between diastereo-

meric types and give significant amounts of methyl migration (**21** and **26**) in addition to possible phenyl and hydrogen migrations.

The reactions of *threo*- and *erythro*-3-phenyl-2-butyl chlorides (**22** and **23**) with silver hexafluoroantimonate in acetic acid for 1 hr give 40 and 41% silver chloride, respectively. The remainder of the chlorides are unreacted. From **22** the organic products are **19** and **24**, totaling 38%, and from **23** the products are **20** and **24**, totaling 44% (Scheme III and Table VI). The chlorides give substitution products with retention of diastereomeric integrity, consistent with only neighboring phenyl participation, along with small amounts of olefin. Reactions of 8.3% chloride **22** and of 9.5% chloride **23** in the presence of the chloroformate **17** show that about one-third and one-fourth, respectively, of the added chlorides may be converted to the expected acetates **19** and **20** under the reaction conditions (Table VI).

The formation of **27** appears to involve the acylation of the 2-phenyl-2-butenes.³² In an experiment designed to provide samples of **27** for structural assignment and for comparison with the reaction product, this ketone was isolated from a reaction of gaseous hydrochloric acid with silver hexafluoroantimonate and a mixture of the 2-phenyl-2-butenes in acetic acid.

Control experiments on the stabilities of the products and of 2-phenyl-2-butyl acetate (**29**), a possible product,



to the reaction conditions were carried out by addition of an amount of the material to be tested equivalent to its actual or expected yield to a reaction of **17** and silver hexafluoroantimonate in acetic acid. The secondary acetate products **19**, **20**, and **21** are stable to the reaction conditions but the tertiary acetate **29** is not. Addition of an amount of **29** equivalent to a 26.8% yield in the control experiment results in the absence of **29** among the products and a yield of $37 \pm 10\%$ of **24**, **25**, **26**, and **27**, compared with a yield of $21 \pm 6\%$ in the absence of **29**. Although these values could be considered within the maximum error of one another, more probably this difference reflects the conversion of about one-half of **29** to the observed products with the other half being converted to unidentified materials. In any case, it is clear that **29** is not stable to the reaction conditions.

Of the olefinic products, only 2-methyl-1-phenyl-2-propene (**26**) gives a recovery within the experimental error expected. The other olefins, *cis*- and *trans*-2-phenyl-2-butene (**24** and **25**) and 2-phenyl-1-butene (**28**), yield olefin mixtures which are consistent with incomplete acid-catalyzed interconversion³³ of **24**, **25**, **26**, and **28** but not conversion to the acetates **19**, **20**, and **21** or the ketone **27**. Although the experimental errors are high, the yields of these materials are consistent with the total olefin added, suggesting that conversion

to undetected products is slow under these reaction conditions.

The reactions of the chloroformates **17** and **18** with silver hexafluoroantimonate in acetic acid to give **21** and **26** clearly show that methyl migration occurs but the other products do not provide information about the participation of other groups. The reaction of *threo*-3-phenyl-2-butyl-1,1,1,3-*d*₄ chloroformate (**17-d**₄) was carried out and the location of deuterium in the products was established by proton and deuterium magnetic resonance to obtain information about possible phenyl and hydrogen participation. The results, summarized in Scheme IV and Table VII, show that

Scheme IV

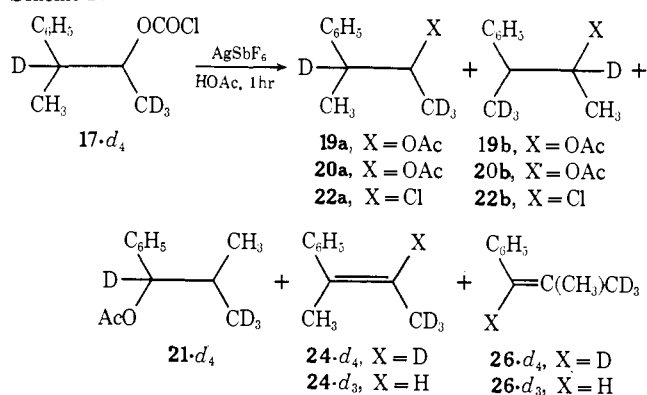


Table VII. Ratios of Products from the Reaction of *threo*-3-Phenyl-2-butyl-*d*₄ Chloroformate (**17-d**₄) with Silver Hexafluoroantimonate in Acetic Acid at Ambient Temperature for 1 hr

Products	Ratio ^a
19-ta : 19-tb	2.3 : 1
20-ea : 20-eb	1.7 : 1
22-ta : 22-tb	3 : 2
26-d ₄ : 26-d ₃ : 24-d ₄ : 24-d ₃	1 : 1 : 2 : 2

^a Errors are estimated as $\pm 20\%$.

all three groups do migrate in the formation of the substituted and olefinic products. The *threo* acetates, **19a** and **19b**, and the *threo* chlorides, **22a** and **22b**, have about the same amount ($35 \pm 10\%$) of the original label scrambled, consistent with *trans* phenyl participation in the formation of these substituted products.^{26,34} The *erythro* acetates, **20a** and **20b**, also show about 30% scrambling, consistent with *cis* phenyl participation, among other possibilities.^{8,35} Methyl migration is involved in the formation of racemic **21-d**₄, **26-d**₃, and **26-d**₄, presumably *via* the isopropylphenyl carbonium ion. The presence of **26-d**₃ implies deuterium loss by equilibration with the medium or by interchange of tertiary hydrogens in the intermediate ion.³⁶ The labeling patterns of **24-d**₃ and **24-d**₄ are consistent with deuteride migration but a quantitative estimate of the amount of migration and elimination would be complicated by the possible equilibration of deuterium and hydrogen as well as the unknown effect the labeling

(32) C. D. Nenitzescu and A. T. Balaban, "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, Chapter 37.

(33) (a) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3883 (1949); (b) D. J. Cram and M. R. V. Sahyun, *ibid.*, **85**, 1257 (1963); (c) R. S. Schwartz, H. Yokokawa, and E. W. Graham, *ibid.*, **94**, 1247 (1972).

(34) E. I. Snyder, *J. Amer. Chem. Soc.*, **91**, 5118 (1969).

(35) C. J. Collins, *Advan. Phys. Org. Chem.*, **2**, 1 (1964), and references cited therein.

(36) G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 5571 (1966); M. Saunders and P. Vogel, *ibid.*, **93**, 2559, 2561 (1971).

Table VIII. A Comparison of Product Yields from the Reactions of *cis*- and *trans*-*N*³-4-*tert*-Butylcyclohexyl-*N*³-*p*-nitrophenyltriazines (30 and 31) and *cis*- and *trans*-4-*tert*-Butylcyclohexyl *p*-Nitrobenzenesulfonates (32 and 33) in Acetic Acid at 25° with Products from the Reactions of *cis*- and *trans*-4-*tert*-Butylcyclohexyl Chloroformates (3 and 4) and Chlorides (9 and 10) with Silver Hexafluoroantimonate in Acetic Acid

Product	Reactant							
	Cis				Trans			
	3 ^a	30 ^b	9	32 ^c	4 ^a	31 ^{b,d}	10 ^e	33 ^c
<i>cis</i> -3- <i>tert</i> -Butylcyclohexyl acetate (5)	1.4 ± 0.9	2.2	0.6 ± 0.3	0.1	1.3 ± 0.6	0.3	3.0 ± 0.3	1.6
<i>trans</i> -3- <i>tert</i> -Butylcyclohexyl acetate (6)	9.5 ± 0.3	5.3	6.6 ± 0.6	5.0	4.6 ± 0.9	0.6	3.9 ± 0.6	0.3
<i>cis</i> -4- <i>tert</i> -Butylcyclohexyl acetate (7)	4.2 ± 0.3	3.6	1.4 ± 0.3	0.6	13.0 ± 0.9	10.8	14.1 ± 0.9	21.4
<i>trans</i> -4- <i>tert</i> -Butylcyclohexyl acetate (8)	4.1 ± 0.3	3.5	4.0 ± 0.3	11.5	45.6 ± 4.8	73.5	2.3 ± 0.6	0.2
1- <i>tert</i> -Butylcyclohexene (11)	7.6 ± 0.6	2.3	4.0 ± 0.6		9.9 ± 1.5		5.3 ± 1.5	0.4
3- <i>tert</i> -Butylcyclohexene (12)	4.4 ± 0.9	9.4	2.0 ± 0.2	1.6	2.1 ± 0.6	0.6	6.9 ± 1.8	4.4
4- <i>tert</i> -Butylcyclohexene (13)	68.9 ± 5.7	73.9	81.2 ± 3.0	81.2	23.9 ± 3.6	14.1	64.1 ± 15.3	72.0

^a Yields normalized to 100% excluding chloride products. ^b H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965). Yield normalized to 100% excluding amine products from total recoveries of 77–85%. ^c N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968). Yields normalized to 100% from total recoveries of 96%. The reactions were carried out in the presence of 1 equiv of sodium acetate, and the amount of sodium acetate was shown not to affect the product ratios. ^d A 0.2% yield of *trans*-2-*tert*-butylcyclohexyl acetate is also reported. ^e This reaction was allowed to proceed for 48 hr, as opposed to 3-hr reactions for the other chlorides and chloroformates, and some acetate products could be due to addition of acetic acid to the olefins.

might have on the conversion of any tertiary acetate corresponding to 29, 24-*d*₃, or 24-*d*₄.

The relationship of the group migrations in the deuterated substrate 17-*d*₄ to corresponding migrations in the isotopically unsubstituted 17 depends on a number of isotope effects of unknown magnitude.³⁷ However, if the secondary isotope effects are similar for phenyl and methyl migration, extrapolation of the results from 17-*d*₄ to the product yields from 17 suggests that *ca.* 70% of 19 and 20 arises from *trans* phenyl participation or that 15–20% of the reaction of 17 involves such a process. The same assumption suggests that 43% of 17 reacts by methyl migration, giving 21 and 26, while 3% of 17 reacts with *cis* phenyl participation to give 20. The formation of 24-*d*₄ from 17-*d*₄ clearly shows that deuteride migration occurs. A corresponding hydride migration would be expected in the reaction of 17, but its extent is difficult to assess in the absence of information about the isotope effects for the migration and elimination steps. If the isotope effects are equal and greater than 5, the products 24-*d*₃ and 24-*d*₄ from 17-*d*₄ would indicate that *ca.* one-half of 24 and 25 arises from hydrogen migration. However, if the isotope effects are equal and less than 5 or if the isotope effect for participation is greater than for elimination, the amount of migration would be higher.^{38,39} Accordingly, 9–18% of 17 may be considered to react with hydrogen migration. Products shown by the reaction of 17-*d*₄ to be inconsistent with participation by a nominally *trans* group amount to 12%, including 1.3% of 20, in addition to the *cis* phenyl migration giving *ca.* 3.4% 20 from 17, 1.7% of 22, and 5% of 19, as well as 1% of 23. This value could be as high as 21% if one-half of 24 and 25 is formed by elimination without migration.

The origin of the products from the reaction of the

(37) (a) V. J. Shiner, "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., ACS Monograph, Van Nostrand Reinhold Co., New York, N. Y., 1970, Chapter 2; (b) *ibid.*, Chapter 2; (c) for examples of isotope effects in ion pairing, see S. G. Smith and D. J. W. Goon, *J. Org. Chem.*, **34**, 3127 (1969); B. L. Murr and M. F. Donnelley, *J. Amer. Chem. Soc.*, **92**, 6686 (1970); V. J. Shiner and R. D. Fisher, *ibid.*, **93**, 2553 (1971).

(38) For example, the k_H/k_D ratio for unsymmetrical axial deuteride participation in the solvolysis of 4-*tert*-butylcyclohexyl tosylates is 2.2²⁸ and the intramolecular k_H/k_D ratio for the dehydration of partially deuterated *tert*-butyl alcohol with a sulfurane is 1.54.³⁹

(39) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 4328 (1971).

erythro chloroformate 18 can be analyzed in the same way, albeit without the insight provided by a deuterium labeling experiment. Accordingly, from 18, *trans* phenyl participation could account for 20 and 23 or 38% of the product, *trans* methyl migration for 21 and 26 or 6%, and *trans* hydrogen migration for 24 and 25 or 17–34% if it is presumed that no more than one-half of these olefinic products arises by direct elimination. In the case of 18 the products 19, 22, and perhaps one-half of the olefins, or a total of 19–21%, would not involve *trans* neighboring group participation. Hydrogen migration followed by elimination would not be distinguishable from direct elimination.

Discussion

A test of the proposed analogies between silver-assisted dehalodecarboxylation of chloroformates and deamination of amines and between silver-assisted dehalogenation of chlorides and solvolysis of sulfonates is provided by product comparisons from the different reactions for the same substrates under comparable conditions. It is such product studies which stimulated investigation and rationalization of differences in deaminations and solvolyses,^{6–25} and it is the presumed analogy of nitrogen and carbon dioxide as stable non-nucleophilic leaving groups, leading to similar arrays of reactive intermediates, that is central to the proposed analogy between dehalodecarboxylation and deamination.

Product Comparisons. (a) 4-*tert*-Butylcyclohexyl Substrates. The reactions of both *cis*- and *trans*-4-*tert*-butylcyclohexyl chloroformates (3 and 4) with silver hexafluoroantimonate in acetic acid are considerably faster than those of the corresponding chlorides (9 and 10), and the products formed are significantly different from each reactant (Table I). The products from the acetolyses of *cis*- and *trans*-*N*³-4-*tert*-butylcyclohexyl-*N*³-*p*-nitrophenyltriazines (30 and 31),⁴⁰ reactions considered to involve the corresponding diazonium ions,⁵ and of *cis*- and *trans*-4-*tert*-butylcyclohexyl *p*-nitrobenzenesulfonates 32 and 33,⁴¹ typical

(40) H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965).

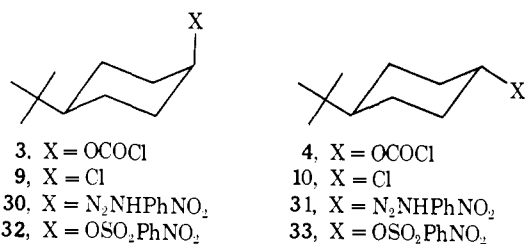
(41) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968).

Table IX. Neighboring Trans Group Participation in the Reactions of *threo*- and *erythro*-3-Phenyl-2-butyl Substrates in Acetic Acid at Ambient Temperature

Reactant	Products	Total product yield ^a	Group participation ^b			Products inconsistent with trans participation ^b	
			Phenyl	Methyl	Hydrogen ^c	Elimination	Other processes
<i>threo</i> -3-Phenyl-2-butyl chloroformate (17)	Acetate, chloride	92	16–21	45	10–19	0–9	12
<i>threo</i> -3-Phenyl-2-butyl-amine ^{d,e}	Acetate, alcohol	50	12	32	24		32
<i>threo</i> -3-Phenyl-2-butyl chloride (22)	Acetate, olefin	100	89			11 ^f	
<i>threo</i> -3-Phenyl-2-butyl-tosylate ^{d,g}	Acetate, olefin	88	57			40 ^f	3
<i>erythro</i> -3-Phenyl-2-butyl chloroformate (18)	Acetate, chloride, olefin	80	48	8	21–43	0–17	3
<i>erythro</i> -3-Phenyl-2-butylamine ^{d,e}	Acetate, alcohol	50	68 ^h	6	20		6
<i>erythro</i> -3-Phenyl-2-butyl chloride (23)	Acetate, olefin	100	93			7 ^f	
<i>erythro</i> -3-Phenyl-2-butyl tosylate ^{d,g}	Acetate, olefin	91	74			25 ^f	2

^a Yields are given in mole per cent relative to starting material consumed. ^b Participations are normalized to the total product yields indicated in column three. ^c Maximum values as some olefins may arise without hydrogen migration. ^d Data from ref 26. ^e D. J. Cram and J. E. McCarty, *J. Amer. Chem. Soc.*, **79**, 2866 (1957). ^f Olefins **24** and **25** could result from hydrogen participation and migration: D. J. Cram, *ibid.*, **74**, 2137 (1952). ^g D. J. Cram, *ibid.*, **71**, 3863 (1949); reaction at 75°. ^h This value contains any unrearranged erythro isomer and is a maximum.

solvolysis reactions, both reported by Whiting and co-workers at 25° in acetic acid, are compared in Table VIII with the products from the reactions of **3**, **4**, **9**, and



10 with silver hexafluoroantimonate in acetic acid at ambient temperature. The yields of products have been normalized to 100% and the yields of the amine and chloride have been deleted from the reactions of the triazines and chloroformates, respectively, to remove apparent differences which might result from different amounts of internal return.

In general, all of the *cis* substrates give more elimination and less substitution than the *trans* isomers, but the product ratios are different for each case. Nonetheless, a correspondence of products from the chloroformates and the triazines is notable in comparing the second and third and sixth and seventh columns of Table VIII, and a difference between these products and those from chlorides and *p*-nitrobenzenesulfonates listed in the fourth and fifth and eighth and ninth columns is also clear. However, there also appears to be a greater difference between the products from the triazines and benzenesulfonates than between the chloroformates and chlorides. Comparisons within the *cis* and *trans* systems show these trends most clearly.

The *cis* chloroformate **3** and the *cis* triazine **30** give considerable elimination to the 4-olefin **13**, equal amounts of the 4-acetates **7** and **8**, and significant amounts of rearrangement to the 3-acetates **5** and **6**, the 1-olefin **11**, and the 3-olefin **12**. The *cis* chloride **9** and

cis-*p*-nitrobenzenesulfonate **32** give predominant inversion in the formation of the 4-acetates, along with more elimination and less rearrangement than **3** and **30**, but the rearranged 3-acetates contain a somewhat larger excess of *trans* isomer **5** over *cis* isomer **6** than is the case for the corresponding triazine or chloroformate. The trends in the product yields for chloride **9** and *p*-nitrobenzenesulfonate **32** are clearly parallel, with the latter showing greater tendency for inversion to the 4-acetates and less rearrangement in the olefins. On the other hand, both the chloroformate and chloride give about twice as much 1-olefin **11** as 3-olefin **12**, a result which contrasts with the absence of the 1-olefin from the reaction of the *p*-nitrobenzenesulfonate **32** and the *ca.* fourfold excess of **12** to **11** from the triazine **30**.

The *trans* chloroformate **4** and triazine **31** show at least a sixfold decrease in elimination to olefins and at least an 18-fold increase in retention in the 4-acetate relative to the corresponding chloride **10** and *p*-nitrobenzenesulfonate **33**.⁴² A parallel between the chloride **10** and the *p*-nitrobenzenesulfonate **33** is also found in that the 4-substituted product from **10** and **33** is mainly inverted, although **33** results in more inversion in the 4-acetates and less rearrangement in the olefins. It should be noted that quantitative comparisons involving **10** are somewhat uncertain because of the possibilities of secondary reactions (*vide supra*). Again the chlorides and chloroformates produce considerably more 1-olefin **11** than do the triazine or *p*-nitrobenzenesulfonate.

(b) **3-Phenyl-2-butyl Substrate.** Direct product comparison of the reactions of *threo*- and *erythro*-3-phenyl-2-butyl chloroformates and chlorides with silver hexafluoroantimonate in acetic acid to the classical work of Cram, *et al.*,^{23,26,33a,43} on the deamination of the 3-

(42) These preferences are obtained by considering the ratios of the relevant products. For example, the ratio of olefins to other products from **4** is 35.9:64.1 \cong 1:2 and from **10** is 76.3:23.7 \cong 3:1 and (1:2) (3:1) \cong 6.

(43) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3863 (1949).

phenyl-2-butylamines and the solvolysis of 3-phenyl-2-butyl tosylates in acetic acid shows the correspondence of deamination and dehalodecarboxylation and the contrast of these reactions to dehalogenation and solvolysis. Comparisons made in terms of the neighboring groups involved in trans participation are summarized in Table IX. The threo chloroformate **17** and the corresponding amine favor methyl migration, with hydrogen migration and phenyl participation occurring to lesser extents. In contrast, the threo chloride and tosylate react with dominant phenyl participation. The erythro chloroformate **18** and erythro amine show effective competition of hydrogen and methyl migration with the major process of phenyl participation, which again stands in contrast to the more dominant phenyl group participation observed for the erythro chloride and tosylate.

(c) Conclusions from Product Comparisons. The comparisons in Tables VIII and IX reveal that in general the products from the silver-promoted dechlorodecarboxylation of the chloroformates **3**, **4**, **17**, and **18** are similar to those formed on deamination of the corresponding amines and substantially different from the products of reaction of the corresponding chlorides **9**, **10**, **22**, and **23** with silver ion, with the latter yielding products similar to those from solvolysis. The first analogy is also supported by the close correspondence of the acetate products from the chloroformates **3** and **4** with those from the corresponding sulfnylamines **16**. These comparisons and the following mechanistic discussion are directed to transformations in the carbon portion of the substrates. The present work does not provide information about the role of silver in assisting these reactions or the possible complexities therefrom.^{4,5} Despite the differences which might be expected in comparing silver-assisted and other reactions, the parallel suggested on the basis of a correspondence of leaving groups is clearly found for silver-assisted dechlorodecarboxylation and deamination and for silver-assisted dechlorination and solvolysis in both the conformationally rigid and conformationally free secondary systems. If in the reactions of chloroformates and chlorides the roles of chloride, silver, and hexafluoroantimonate are comparable, then the product differences from these reactants can clearly be attributed to the elements of carbon dioxide. A reasonable explanation for this effect is that the high stability of carbon dioxide contributes substantially to lowering critical activation energies in the reactions of the chloroformates. This hypothesis applies whether or not a carboxylium ion is an intermediate and is consistent with the role assigned to nitrogen in deaminations.⁶⁻²⁵ A potentially useful suggestion from these results is that chloroformates, which are easily obtained from alcohols, could serve as readily available precursors of the novel cations often sought by reactions considered to involve diazonium ions.

Mechanism. The viability of the analogy between silver-promoted dehalodecarboxylation and deamination, however, does not define the details of the reaction. Deaminations are interpreted in terms of (1) reaction *via* ion pairs,^{8-18, 22, 25} (2) the intermediacy of free, unencumbered carbonium ions,^{6, 23} or (3) direct reactions of diazonium ions.^{7, 21} These three interpretations are not mutually exclusive but focus on different

points as critical along the reaction pathway. Historically, the latter two proposals appear to have arisen out of an apparent need to explain the differences in products between deaminations and solvolyses, at a time when the latter were considered to involve prototypical carbonium ions. Any one of these rationales can provide an explanation for the facts that the stereochemistry of the reactant and the nature of the leaving group strongly influence the products.

The correspondence between solvolyses and silver-promoted dehalogenation for the secondary halides **9**, **10**, **22**, and **23** appears more informative mechanistically. Solvolyses in secondary systems are now known not to involve carbonium ions which would be interconverted when produced from isomeric precursors but to proceed *via* neighboring group (k_{Δ}) and solvent (k_s) assisted noninterconverting pathways,^{44, 45} and such a scheme has been shown to apply to acetolyses of cyclohexyl^{29c, d} and 3-phenyl-2-butyl substrates.^{26, 44} It is interesting that acceptance of this mechanism in general for sulfonate solvolyses of secondary systems removes the previously apparent need for rationalization of the difference between deamination and solvolyses in these systems in terms of different kinds of carbonium ions or special reactions of carbonium ion precursors.⁴⁵ If the analogy can be extended from solvolysis to the reactions of the chlorides **9**, **10**, **22**, and **23**, these compounds may be considered to react, probably as silver-substrate complexes, largely by neighboring group (k_{Δ}) and solvent (k_s) participation, although some ionization also occurs. Evidence on the latter point is the formation of small amounts of retained 4-acetates in the reactions of the 4-*tert*-butylcyclohexyl chlorides **9** and **10**. Small amounts of similarly retained product from the reactions of **22** and **23** would not have been detected.⁴⁶

If the silver-promoted reaction of the halide involves small amounts of ionization and the role of the elements of carbon dioxide in the silver-promoted reaction of the chloroformates is assigned to be that of facilitating carbon-oxygen heterolytic bond cleavage, the reactions of the chloroformates should involve a substantial amount of ionization.⁴⁷ In fact, if the reactions of **3**, **4**, **17**, and **18** are considered to proceed mainly by silver-assisted ionization (k_c), the difference between the reactions of the chloroformates and the chlorides becomes readily

(44) M. L. Brookhart, F. A. L. Anet, D. J. Cram, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 5659 (1966); A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969); M. G. Jones and J. L. Coke, *ibid.*, **91**, 4285 (1969); H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970), and references cited therein. For a recent summary, see D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972). The definitions for k_{Δ} (neighboring group participation), k_s (solvent assistance with covalent bonding), and k_c (ionization) are consistent with the latter reference.

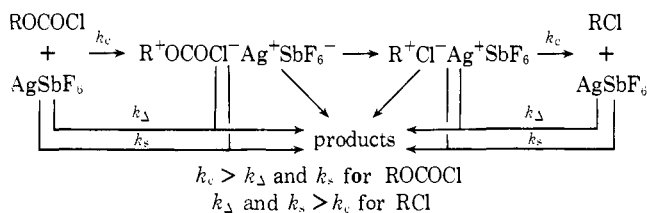
(45) The discrete processes designated by k_{Δ} and k_s could, of course, involve ion pair species, but in the present context the term carbonium ion is used for the species produced by ionization, k_c , which can provide products directly and/or enter the k_{Δ} and k_s pathways.

(46) T. Cohen and J. Solash, *Tetrahedron Lett.*, 2513 (1973), have recently reported a predominance of ionization with retention in the reaction of *trans,trans*-2-bromodecalin with silver perchlorate and silver fluoroborate in acetonitrile.

(47) The idea that participation is a function of transition state energy, clearly stated by S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952), over two decades ago in terms of the requirements of driving force for neighboring group participation, has been borne out by subsequent studies. For recent examples, see P. G. Gassman and A. F. Fentiman, *ibid.*, **92**, 2549 (1970), and E. N. Peters and H. C. Brown, *ibid.*, **95**, 2397 (1973), and references cited therein.

explicable in terms of different partitioning between k_c , k_Δ , and k_s processes. This engagingly, and perhaps deceptively, simple rationale is summarized in Scheme V for the silver-promoted reactions of the chloroform-

Scheme V



ates and chlorides. The initial ionic species from the chloroformate could react to give products directly or *via* participation or lose carbon dioxide to give a second ionic aggregate which, in turn, could give products, including chloride.⁴⁸ Carbonium ion components of ion aggregates are well preceded for analogous reactions^{4,5,8-18,49} and have been noted to provide an alternative path to the products from participation,⁴⁴ since both neighboring groups and solvents are expected to interact with the electron-deficient center. Competition between the three processes is obviously possible for the initial reactant, but the processes represented by k_Δ and k_s remain discrete.⁴⁵

A facile initial silver-assisted ionization of the chloroformate or reaction of a subsequent carboxylium ion could proceed *via* a transition state which strongly resembles starting material.⁵⁰ This, of course, is not to imply that all components of the species produced by such transition states have the lowest conceivable energy of a free species and an important feature of the present proposal is that the carbonium ion formed as a part of the first ion aggregate closely resembles the reactant (*vide infra*). Scheme V could well be elaborated by including higher silver ion aggregates⁴ and other ion pairs.⁴⁵

Interpretation of the results of the reactions of the *cis*- and *trans*-4-*tert*-butylcyclohexyl chloroformates and chlorides in light of Scheme V is illustrative. The majority of products from the chlorides **9** and **10** can be readily understood in terms of solvent displacement and hydrogen participation and elimination. The 4-*tert*-butylcyclohexyl acetates are mostly inverted from each chloride and are considered to arise mainly by solvent participation, although the importance of the retained product in suggesting some ionization has been noted. The major reaction product in both cases is 4-*tert*-butylcyclohexene (**13**). The formation of **13** from the *trans* chloride **10** could involve nonchair forms of the cyclohexane ring analogous to suggestions for the corresponding solvolysis,^{41,51a} a *cis* elimination in which the leaving chloride complexed to silver acts as a base,^{25,51b} or, in the case of this relatively inert chloride, an ionization process. Rearrangement by

(48) Internal return of halide or halide silver ion complexes has been reported: Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, **87**, 4778 (1965); P. G. Gassman and R. L. Cryberg, *ibid.*, **91**, 2047 (1969); ref 22, p 432.

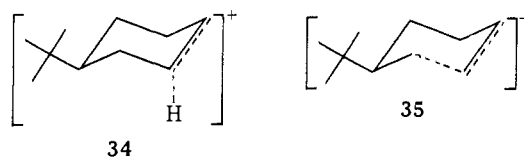
(49) S. Winstein, B. Appell, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, No. 19, 109 (1965), and references cited therein and subsequent work.

(50) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955); J. E. Leffler, *Science*, **117**, 340 (1953).

(51) (a) V. J. Shiner and J. G. Jewett, *J. Amer. Chem. Soc.*, **87**, 1383 (1965); (b) J. Zavada, J. Krupicka, and J. Sicher, *Collect. Czech. Chem. Commun.*, **33**, 1393 (1968).

1,2-hydrogen participation can account for the 3-substituted products **5** and **6**, the 3-olefin **12**, and some of the olefin **11**, although a choice between the intermediacy of a 3-*tert*-butylcyclohexyl cation or internal return⁴¹ to 3-*tert*-butylcyclohexyl chloride cannot be made. The remainder of **11** appears to arise by formal 1,3-hydrogen migration perhaps *via* a protonated cyclopropane.^{29b} While it might be expected that the 3-acetates **5** and **6** which arise from the configurationally similar chloroformates and chlorides after hydride transfer would be similar, the ratios of inversion to retention for these cases are 6.8:1 for **3**, and 11:1 for **9**, and 1:3.7 for **4**, and 1:1.3 for **10**. Either common intermediates are not formed even after rearrangement or **5** and **6** are produced from common species which are formed in different amounts from the corresponding chloroformates and chlorides. The 1.4 and 2.3% retention found for the 4-*tert*-butylcyclohexyl acetates from **9** and **10**, respectively, clearly does not fit into participation processes and provides evidence for some ionization. The retained 4-acetates are found in the amounts of 0.6 and 0.2% in the solvolyses of the corresponding *p*-nitrobenzenesulfonates. The amount of silver-assisted ionization of the chlorides could be somewhat greater than that indicated by the retained 4-acetates if some of the hydrogen migration and elimination products arise after carbon-chlorine bond cleavage.

The reactions of the *cis*- and *trans*-4-*tert*-butylcyclohexyl chloroformates (**3** and **4**) may be accommodated by the predominant silver-assisted ionization (k_c) process of Scheme V, provided that the cation formed in each case as part of the ion aggregate reflects the geometry of the reactant. Such a "memory effect"⁹ might be achieved by the intermediacy of species in which the σ bonds which are *trans* coplanar with the carbon-oxygen bond being broken overlap with the vacant *p* orbital to give species represented as **34** and



35 from the *cis* and *trans* chloroformates, respectively. Such participation might be expected in an intermediate by the favorable geometry for orbital overlap in these substrates even if overlap were not necessary to assist the ionization. The cation **34** would be expected to give elimination to 4-olefin **13** as well as rearrangement and loss of carbon dioxide to a second ion aggregate. The latter could produce an ion free of its counter species, the postulated precursor of a stereochemically indiscriminate attack on the 4 position,⁵² giving **7** and **8**. The 3-acetates **5** and **6** and olefins **11** and **12** could arise from ionic intermediates at either stage. The delocalization suggested for **35** is important in providing a

(52) (a) S. D. Elkovich and J. G. Traynham, *J. Org. Chem.*, **38**, 873 (1973), have reported an extensive study of the products of reaction of several *cis*- and *trans*-4-*tert*-butylcyclohexyl systems. Only lead tetraacetate oxidation of the corresponding carboxylic acid appeared to give a secondary cation sufficiently free of a counter species to provide a common mixture of 53:47 4-substituted acetates from the different precursors. (b) For a general summary of deamination of cyclohexylamines, see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 89.

rationale for the predominant retention of configuration in the 4-acetate; essentially the postulate is that this stabilization is maintained to the stage of solvent attack. It is also apparent that **35** would give substantially less elimination than **34** and that this would occur at a later stage in the reaction sequence. The other acetate and olefinic products could also arise from subsequent ionic species.

If participative delocalization of the type suggested for **34** and **35** does not involve a change in reactant geometry, it is equivalent to the "vertical stabilization" of Traylor, *et al.*⁵³ The present case does not provide definitive information about the geometry or symmetry of the proposed intermediates and more symmetrical or partially bridged structures, such as have been noted to be part of a continuum for which "vertical stabilization" provides a limit,⁵⁴ are possible. In fact, a symmetrically bridged ion analogous to **35** has been suggested in deaminations of the cyclohexylamines.⁷ However, that cation is not favored for the present because it would be expected to be readily convertible to corner and edge protonated bicyclo[3.1.0]hexanes,^{7,55} which in the cases of **3-d₁** and **4-d₁** would further result in deuterium scrambling into the 1, 2, and 3 positions. Neither proton nor deuterium nmr gives any indication that substantial amounts of deuterium are present on the olefinic position of 1-*tert*-butylcyclohexene from **4-d₁**, although as little as 10% should have been detected.

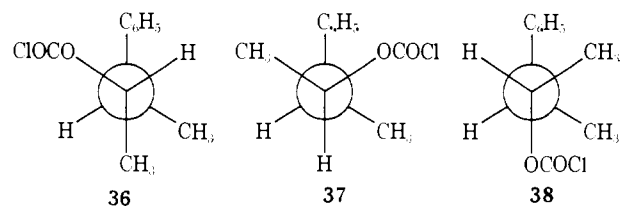
The reduced selectivity in product formation from the chloroformates relative to that from chlorides, which is apparent by comparison of the products from **3** with **9** and from **4** with **10** (Table VIII), can be taken to reflect a decreased differentiation between competing pathways, a characteristic of facile reactions noted to be a consequence of decreased activation energies.^{21,22} The effect of deuterium substitution in reducing the yields of the 4-olefin **13** by *ca.* 12% in comparing **3** to **3-d₁** (from 59.3 ± 5.7 to 52.0 ± 4.8%) and by *ca.* 50% from **4** to **4-d₁** (from 15.3 ± 0.8 to 7.8 ± 0.4%) is also consistent with such a compression of activation energies. The *cis* substrate **3-d₁**, which gives a reactive intermediate having some delocalization in the axial carbon-deuterium bond, would be expected to show a lower isotope effect for elimination than the *trans* isomer. The larger isotope effect on the product ratios from the *trans* isomer **4-d₁** is consistent with elimination occurring at a point where activation energies are less compressed and therefore farther along the reaction pathway for **4-d₁** than for **3-d₁**.

The 1-*tert*-butylcyclohexene (**11**), suggested above to be the product of 1,3- and consecutive 1,2-hydride shifts from both **3** and **4**, does not fit the previously discussed patterns. Significant amounts of **11** are formed from the chloroformates **3** and **4** and chlorides

9 and **10** (Table VIII), but only minor amounts appear from triazine **30** and no **11** is reported from the triazine **31** or the nitrobenzenesulfonates **32** and **33**. The formation of **11** could be considered a novel reaction of the silver halide containing ionic aggregates of Scheme V which can be formed from either the chloroformates or chlorides. However, it is also possible that **11** results from acid- and/or silver-catalyzed ring opening of a bicyclo[3.1.0]hexane^{10,56,57} or that scrambling of the label occurs in some other undetected precursor to **11**. Although this point has not been resolved in the present work, the similar amounts of scrambling from **3-d₁** and **4-d₁** suggest that **11** has very similar precursors from **3**, **4**, **9**, and **10**, consistent with some ionization.

The group participations and migrations observed for *threo*- and *erythro*-3-phenyl-2-butyl chlorides and chloroformates are readily accommodated by Scheme V. Solvolyses of the *threo* and *erythro* tosylates have been analyzed in detail in terms of k_{Δ} and k_s ²⁶ and the product correspondence between the tosylates and the chlorides **22** and **23** suggests that the latter react by similar pathways. The operation of conformational control in the deamination of 3-phenyl-2-butylamines, first presented in the classic work of Cram and McCarty,^{23,27} also rationalizes the similar group migrations found in the silver-promoted reactions of the chloroformates **17** and **18** (Table IX).

Consistent with conformational control in Scheme V, the resemblance of the transition states and intermediates to reactants assures that the migrations can be rationalized in terms of the same factors which control the conformer population or in terms of reactions competitive with bond rotations interconverting the conformers. For example, in the case of the *threo* isomer **17**, the favored methyl participation (Table IX) in migration may be understood in terms of transition states which show a conformational preference similar to that of **36** over **37** and **38**,^{23,55} or in terms of **36**, **37**, and **38**, leading to open ions which subsequently react



rapidly relative to bond rotation. The existence of an open ion is supported by the *cis* phenyl migration in **17-d₁** as well as by analogy⁸ and is provisionally preferred in the present interpretation. The product differences between the 3-phenyl-2-butyl chloroformates and chlorides is clearly consistent with the former reacting mainly by ionization and the latter mostly by participation. Specifically, ions **39** and **40** are considered to be the carbonium ion component of the major ion pairs formed from the *threo* and *erythro* chloroformates, respectively, with corresponding ions formed to lesser degrees from other conformations for each diastereomer.

(56) T. J. Cogdell, *J. Org. Chem.*, **37**, 2541 (1972).

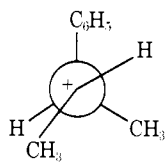
(57) L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Amer. Chem. Soc.*, **94**, 9222 (1972); P. G. Gassman and T. Nakal, *ibid.*, **94**, 5497 (1972); W. G. Dauben and A. J. Kiebania, *ibid.*, **94**, 3669 (1972).

(58) C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, **31**, 1000 (1966), and references cited therein.

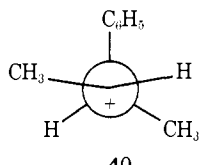
(53) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971), and references cited therein. See also J. A. Bone and M. A. Whiting, *Chem. Commun.*, 115 (1970); T. J. Mason, M. J. Harrison, J. A. Hall, and G. D. Sargent, *J. Amer. Chem. Soc.*, **95**, 1849 (1973).

(54) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 3794 (1973); see also W. J. Hehre and P. C. Hikerty, *ibid.*, **94**, 5918 (1972), and R. Hoffmann, L. Radom, J. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *ibid.*, **94**, 6221 (1972). See also D. F. Eaton and T. G. Traylor, *ibid.*, **96**, 1226 (1974).

(55) J. L. Fry and G. J. Karabatsos, "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 553-554.



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Scheme V with the attendant provisions of facile formation of a silver halide ionic aggregate also provides an effective rationalization for the formation of bridgehead bicyclo[2.2.1]-substituted products from the corresponding chloroformates and of cyclopropane from *n*-propyl chloroformates,¹ reactions which also resemble deaminations.

It should be clear that Scheme V and the above interpretation are essentially a rationalization of product similarities in terms of recent concepts of nucleophilic substitution in secondary systems. No doubt all of the reactions could be proven on closer examination to be different in detail. For example, differences have been noted between solvolyses and silver-promoted ionizations of different halides.^{4,5,46} Nonetheless, the general resemblance of the products from the reactions of the chloroformates to those from deaminations and of the products from the reactions of the halides to those from solvolyses in the present work suggests that the former be placed together and considered to involve considerably more ionization than the latter, which appear to involve predominant covalent solvent and neighboring group participation.

The reaction pathways proposed do have considerable precedent. The important role which may be played by ion pairs in deaminations has been noted by many workers,^{8-12,16,18,20,22,25,59} although the possibilities that these intermediates are not a single species or an equilibrium mixture of subspecies is often noted in differences ascribed to nonequilibrium of the ions with respect to bond rotation, counterion position, and solvation.^{6,8-12,22,24,25,60,61} The proposal of the conversion of the chloroformates to an ionic aggregate containing a carbonium ion which resembles the reactant may be considered preceded by the early^{23,62} and subsequent^{6,8-10,22} versions of the "hot" carbonium ion or the cation part of the ion pairs suggested in deaminations.¹⁶ The resemblance of the transition states leading to these intermediates to the ground

(59) For some recent cases, see J. H. Bayless, A. T. Jurewicz, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4466 (1968); I. Lillien and L. Handloser, *ibid.*, **93**, 1682 (1971); T. Cohen, A. R. Naniewski, G. M. Deeb, and C. K. Shaw, *ibid.*, **94**, 1786 (1972); S. J. Cristol, J. R. Mohrig, and G. T. Tiedeman, *J. Org. Chem.*, **37**, 3239 (1972).

(60) For recent cases and pertinent discussion, see J. A. Berson, R. T. Luibrand, N. G. Kundu, and D. G. Morris, *J. Amer. Chem. Soc.*, **93**, 3075 (1971); C. J. Collins, I. T. Glover, M. D. Eckart, V. F. Raaen, B. M. Benjamin, and B. S. Benjamin, *ibid.*, **94**, 899 (1972); C. J. Collins and B. M. Benjamin, *J. Org. Chem.*, **37**, 4358 (1972); W. Hüchel and H. J. Kern, *Justus Liebig's Ann. Chem.*, **728**, 49 (1969); D. E. Applequist, M. R. Johnston, and F. Fisher, *J. Amer. Chem. Soc.*, **92**, 4614 (1970); H. Hart and J. L. Brewbaker, *ibid.*, **91**, 716 (1969).

(61) The recent work of C. D. Ritchie and P. O. I. Virtanen, *J. Amer. Chem. Soc.*, **94**, 4966 (1972), and C. D. Ritchie, *Accounts Chem. Res.*, **5**, 348 (1972), which suggests that nucleophilicities may be controlled by desolvation energies, could be taken to provide support for the importance of solvation effects in these reactions, although in deaminations such effects could well be due to solvent reorganization being competitive with reaction rather than to the existence of unsolvated carbonium ions in solution.

(62) D. Y. Curtin and M. C. Crew, *J. Amer. Chem. Soc.*, **76**, 3719 (1954); J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **76**, 4501 (1954); D. Semenow, C. H. Shih, and W. G. Young, *ibid.*, **80**, 5472 (1958). The latter reference attributes the term "hot" carbonium ion to Professor Winstein.

states of the reactant, along with a decreased lack of selectivity among alternative pathways, is implicit in the compressed energy scale for these reactions.^{20-22,63} At least one interpretation of deaminations in terms of k_{Δ} and k_s processes has appeared.⁶⁴

The present results do not provide an unambiguous distinction between the postulated carbonium ion intermediate and competition between formation of such an ion with direct reaction to products from a carboxylum ion **1**.^{1,2,65} However, we provisionally prefer the former in that it seems easier to explain the lack of carbonic anhydride in the reactions of **3** and **4**, to understand the retention from **4** and the *cis* participation in **17**, and to rationalize the general similarity of dehalodecarboxylations and deaminations in terms of carbonium ions. Carboxylum ions^{66,67} could well be present as precursors to the intermediate carbonium ions but are not implicated by the present results.

It is interesting to note that the above scheme, which rationalizes the difference between silver-promoted dehalodecarboxylation of chloroformates and dehalogenation of chlorides in terms of different initial partitioning between participation (k_{Δ} and k_s) and ionization (k_c) and which is derived from earlier proposals for deaminations and solvolyses, provides a straightforward rationale for the differences in those reactions also. It is not necessary that ionization be the dominant reaction pathway under all conditions, and a competitive scheme for deamination could be used to interpret the increased diversity of pathways noted for some deaminations as the ability of the solvent to support ionization increases.⁷ In essence, the long-studied uniqueness of deaminations appears still attributable to the frequently noted⁶⁻²⁵ facile formation of nitrogen accompanying ionization. Similar behavior has also been suggested for other substrates bearing especially stable leaving groups.⁶⁸

Summary

The reactions of *cis*- and *trans*-4-*tert*-butylcyclohexyl and *erythro*- and *threo*-3-phenyl-2-butyl chloroformates with silver hexafluoroantimonate in acetic acid at ambient temperature give product ratios which are very

(63) That such compression need not always reduce selectivity has been shown by J. A. Berson, J. W. Foley, J. M. McKenna, H. Junge, D. S. Donald, R. T. Luibrand, N. G. Kundu, W. J. Libbey, M. S. Poonian, J. J. Gajewski, and J. B. E. Allen, *J. Amer. Chem. Soc.*, **93**, 1299 (1971).

(64) W. Kirmse, D. Hasselmann, and O. Seipp, *Chem. Ber.*, **105**, 850 (1972).

(65) Such a suggestion would be analogous to the proposal that deamination reactions proceed by branching at the point of the diazonium ion **2**.²¹⁶

(66) Carboxylum ions can be postulated to provide possible rationales for a variety of reactions in which alkoxy carbonyl groups migrate: R. M. Acheson, *Accounts Chem. Res.*, **4**, 177 (1971); P. Schmidt, R. W. Hoffmann, and J. Backes, *Angew. Chem., Int. Ed. Engl.*, **11**, 513 (1972); J. Kagan, D. A. Agdeppa, and S. P. Singh, *Helv. Chim. Acta*, **55**, 2252 (1972); K. Friedrich and H. Straub, *Chem. Ber.*, **103**, 3363 (1970).

(67) Concerted migration of alkoxy carbonyl groups has also been reported: J. A. Berson and R. G. Saloman, *J. Amer. Chem. Soc.*, **93**, 4620 (1971).

(68) For a summary see ref 1 and, e.g. (a) deoxidations: P. S. Skell and I. Starrer, *J. Amer. Chem. Soc.*, **81**, 4117 (1959); J. Langrebe, *Tetrahedron Lett.*, 105 (1965); (b) decarboxylations: J. J. Keating and P. S. Skell, *J. Amer. Chem. Soc.*, **91**, 695 (1969); R. R. Sheldon and J. K. Kochi, *Org. React.*, **19**, 279 (1972); (c) ionization of alkyl mercurals: F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **85**, 363 (1963); (d) ionization of alkyl coppers: C. L. Jenkins and J. K. Kochi, *ibid.*, **94**, 843 (1972); (e) ionization of sulfoxonium species: H. Kwart, E. N. Givens, and C. J. Collins, *ibid.*, **91**, 5532 (1969).

similar to those produced on deaminations of the same substrates and different from those found for solvolyses. The previously suggested analogy between silver-promoted reactions of chloroformates and deaminations is considered to be strongly supported by this product correspondence. Reactions of *cis*- and *trans*-4-*tert*-butylcyclohexyl and *erythro*- and *threo*-3-phenyl-2-butyl chlorides with silver hexafluoroantimonate in acetic acid give product ratios similar to those from solvolyses. The difference between the reactions of the chlorides and chloroformates is attributed to the facile loss of carbon dioxide from the chloroformates and can be analyzed in terms of predominant ionization of the chloroformates (k_c), as opposed to predominant solvent or group participation (k_s and k_d) for the chlorides. Such a mechanistic distinction also seems to apply to comparisons of deaminations and solvolyses.

Experimental Section⁶⁹

Gas-Liquid Partition Chromatography (glpc). Glpc was performed on Aerograph Models A-90-P3 and 1860 with thermal conductivity and flame ionization detection, respectively. Product yields are reported in mole per cent based on starting chloroformate and were determined by use of internal standards with corrections for differences in detector responses between products and internal standards unless otherwise noted. The columns used were: 10-ft \times $\frac{1}{8}$ -in. 10% Dow 710 (column A); 10-ft \times $\frac{1}{8}$ -in. 20% Ucon LB550X (column B); 12-ft \times $\frac{3}{8}$ -in. XF-1150 Chromosorb P (column C); 7-ft \times 0.25-in. 30% Ucon LB550X (column D); 6-ft glass 10% DEGS (column E); 150-ft BDS wall coated open tubular column (column F); 6-ft \times 0.25-in. 20% Carbowax (column G); 2-ft \times 0.25-in. 16% SE-30 (column H); 50-cm \times 0.25-in. 15% Dow 710 and 5% Bentone 34 (column I). Errors are calculated from the standard deviation of peak areas obtained by planimetric measurement.

Materials. Glacial acetic acid (Du Pont) was refluxed with 1–3% acetic anhydride and distilled at atmospheric pressure under dry nitrogen. Silver hexafluoroantimonate and nitrosyl hexafluoroantimonate, obtained from the Ozark-Mahoning Co., were dried at room temperature over P_2O_5 at 0.3 mm for a minimum of 3 days and stored in amber bottles under dry nitrogen.

cis- and *trans*-4-*tert*-butylcyclohexanols were separated from the commercial mixture (Aldrich) by chromatography on activated alumina and identified by mp and nmr criteria.^{70,71}

trans-4-*tert*-Butylcyclohexanol-2,2,6,6- d_4 and *cis*-4-*tert*-butylcyclohexanol- d_4 were prepared in 58 and 82% yields by lithium aluminum hydride and lithium tri-*sec*-butylborohydride⁷² reduction, respectively, of 4-*tert*-butylcyclohexanone-2,2,6,6- d_4 (ms, $98.7 \pm 0.1\%$ d_4). The purity was established (column A) and the assignments were consistent with nmr and ir spectral data: *trans* isomer, mp 80–81°; *cis* isomer, mp 81–82°.

trans-4-*tert*-Butylcyclohexanol-¹⁸O and *cis*-4-*tert*-butylcyclohexanol-¹⁸O were prepared in 80 and 66% yield by reduction of 4-*tert*-butylcyclohexanone-¹⁸O (prepared by exchange with water containing excess ¹⁸O) as with the deuterated ketone. The amount of ¹⁸O incorporation was determined after conversion to the chloroformate (Table IV).

General Procedure for the Preparation of 4-*tert*-Butylcyclohexyl

(69) Melting points were determined on a Buchi or Thomas-Hoover capillary melting point apparatus and are uncorrected. Nmr spectra were obtained on Varian Models A-60-A, A-56/60, HA-100, HR-220, or T-60 spectrometers by Mr. Robert Thrift and associates or by the authors. Chemical shifts are reported in δ , ppm, relative to the internal standard tetramethylsilane unless otherwise noted. Deuterium nmr spectra were obtained at 15.4 MHz on the HA-100 spectrometer and chemical shifts are reported in δ , ppm, relative to external deuteriochloroform. Ir spectra were obtained on Perkin-Elmer Models 137, 237B, or 521 spectrometers. Mass spectra were recorded by Mr. C. Cook and associates on a Varian MAT CH-5 spectrometer. Elemental analyses were carried out by Mr. J. Nemeth and associates.

(70) S. Wilstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

(71) R. V. Lenticux, R. K. Kullnig, H. J. Birnstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80**, 6098 (1958).

(72) H. C. Brown and S. Krishnamurthy, *J. Amer. Chem. Soc.*, **94**, 7159 (1972).

Chloroformates. An anhydrous ether solution of the alcohol and 1 equiv of dry pyridine were added dropwise to a cold (-20°) five- to tenfold excess of phosgene in anhydrous ether. After being allowed to warm to ambient temperature overnight under a positive nitrogen flow, the reaction mixture was washed with 5% aqueous hydrochloric acid, 5% aqueous sodium bicarbonate, and water and dried ($MgSO_4$). The solvent was then removed to give the product.

cis-4-*tert*-Butylcyclohexyl chloroformate (3) was prepared from *cis*-4-*tert*-butylcyclohexanol in 90% yield as a pale yellow liquid;⁷³ ir (liquid film) 2950, 2865, 1785 (C=O), 1484, 1366, 1236, 1185, 1160, 1103, 1048, 870, 810; nmr (CCl_4) δ 5.00 (broad s, 1), 2.3–1.0 (broad m, 9), 0.87 (s, 9).⁵²

trans-4-*tert*-Butylcyclohexyl chloroformate (4) was prepared from *trans*-4-*tert*-butylcyclohexanol in 86–90% yield as a clear colorless liquid;⁷³ ir (liquid film) 2950, 2849, 1786 (C=O), 1458, 1161, 1115, 1017, 884, 833, 800; nmr (CCl_4) δ 4.60 (broad m, 1), 2.4–1.0 (broad m, 9), 0.86 (s, 9).⁵²

cis-4-*tert*-Butylcyclohexyl-2,2,6,6- d_4 chloroformate (3- d_4), *trans*-4-*tert*-butylcyclohexyl-2,2,6,6- d_4 chloroformate (4- d_4), *cis*-4-*tert*-butylcyclohexyl chloroformate-¹⁸O (3-¹⁸O), and *trans*-4-*tert*-butylcyclohexyl chloroformate-¹⁸O (4-¹⁸O) were prepared from the corresponding isotopically labeled alcohols. Deuterium content expected from the 98.7% label of the ketone was consistent with the nmr spectra. The ¹⁸O content was determined by pyrolysis and the purified CO_2 was analyzed by mass spectrometry as summarized in Table V.

cis-4-*tert*-Butylcyclohexyl chloride (9) and *trans*-4-*tert*-butylcyclohexyl chloride (10) were isolated from mixtures (glpc, column B, 130°) obtained by heating 3 and 4, respectively, to 140° by preparative glpc (column C, 160°). The ir and nmr spectra are consistent with published data and serve to distinguish the isomers.⁷⁴

Acetic (*trans*-4-*tert*-butylcyclohexyl)carbonic anhydride (*trans*-15) was prepared according to the general procedure of Michejda, Tarbell, and Saunders^{30b} from 4, 0.244 g (1.11 mmol), 0.0665 g (1.11 mmol) of acetic acid, and 0.113 g (1.11 mmol) of triethylamine in anhydrous ether at 0° under dry argon. The filtrate, after removal of triethylamine hydrochloride, was washed with dilute aqueous HCl, dilute aqueous sodium bicarbonate, and water and dried ($MgSO_4$), and the ether was removed to give 0.22 g (82%) of a clear liquid;⁷³ ir (liquid film) 2985, 2865, 1835 and 1773 (C=O), 1484, 1458, 1370, 1264, 1144, 1119, 1027, 1006, 942, 922; nmr (CCl_4) δ 4.40 (broad m, 1), 2.3–0.9 (broad m, 9), 2.10 (s, 3), 0.83 (s, 9).

Acetic (*trans*-4-*tert*-butylcyclohexyl)carbonic anhydride-¹⁸O (*trans*-15-¹⁸O) was prepared as described above from a sample of *trans*-4-*tert*-butylcyclohexyl chloroformate-¹⁸O. The ¹⁸O content was assumed to be 1.86 atom % excess, the same as that of the starting chloroformate.

N-(*cis*-4-*tert*-Butylcyclohexyl)sulfinylamine (*cis*-16) was prepared by mixing 1.55 g (10 mmol) of *cis*-4-*tert*-butylcyclohexylamine,^{75a} 0.79 g (10 mmol) of pyridine, and 1.2 g (10 mmol) of thionyl chloride in anhydrous benzene, followed by filtration and evaporation of the solvent *in vacuo*. The brownish semisolid thus obtained was washed several times with pentane and the combined washings were concentrated to give a brown liquid, which afforded 0.38 g (20%) of *N*-(*cis*-4-*tert*-butylcyclohexyl)sulfinylamine on molecular distillation;⁷³ bp $<75^\circ$, 0.2 mm; ir (CCl_4) 2907, 2841, 1471, 1441, 1361, 1235, 1111, 1092, 1026, 1000, 930, 905, 883; nmr (CCl_4) δ 4.73 (broad, s, 1), 2.0–1.0 (broad m, 9), 0.87 (s, 9).

N-(*trans*-4-*tert*-Butylcyclohexyl)sulfinylamine (*trans*-16) was prepared from *trans*-4-*tert*-butylcyclohexylamine,⁷⁵ 1.55 g (10 mmol), pyridine, 0.79 g (10 mmol), and thionyl chloride, 1.2 g (10 mmol), in anhydrous benzene. The same isolation procedure as above gave a dark liquid, and molecular distillation (bp $<70^\circ$, 0.1 mm) gave 1.0 g (52%) of a clear, colorless liquid;⁷³ ir (CCl_4) 2907, 2841, 1473, 1443, 1238, 1119, 1100, 900; nmr (CCl_4) δ 4.38 (broad m, 1), 2.1–0.9 (broad m, 9), 0.85 (s, 9).

cis- and *trans*-4-*tert*-Butylcyclohexyl acetates⁷⁰ (7 and 8), *cis*- and *trans*-2-*tert*-butylcyclohexene^{70,73} (13), and 1-*tert*-butylcyclo-

(73) Analyses were carried out for all elements except oxygen and the values obtained were within $\pm 0.30\%$ of the calculated values.

(74) F. D. Greene, C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964), and references cited therein.

(75) (a) W. Hüchel and K. Heyder, *Chem. Ber.*, **96**, 220 (1963); (b) D. V. Nightingale, J. D. Kerr, J. A. Gallagher, and M. Maienthal, *J. Org. Chem.*, **17**, 1017 (1952).

hexane^{73,76} (**11**) were prepared and identified by standard procedures.⁷⁷

Reactions of *cis*- and *trans*-4-*tert*-Butylcyclohexyl Chloroformates and Chlorides with Silver Hexafluoroantimonate in Acetic Acid. The reactions were carried out by addition of the chloroformate or chloride to a 5–10% excess of the silver salt in dry acetic acid under argon at ambient temperature for 3 hr unless otherwise noted. After the reactions had been quenched by pentane and water rinses, the reaction mixtures were filtered, more water was added, the mixtures were extracted twice with pentane, and the combined pentane extracts were washed twice with water and dried (Na₂SO₄). Analysis of the organic products was achieved by glpc (column B) at 95° for the *tert*-butylcyclohexenes with bromobenzene as internal standard and at 150° for all other products with 4-*tert*-butylcyclohexanone as internal standard without concentration. Material for isolation experiments carried out for product identification was concentrated at ambient temperature and reduced pressure prior to preparative glpc. Material balances are within experimental error of 100% on all runs.

Silver chloride yields were determined gravimetrically as the ammonium hydroxide soluble solid from the reaction mixtures from the reactions of **3** and **4**. Essentially quantitative yields of carbon dioxide were obtained as barium carbonate from two barium hydroxide traps when the reaction mixture was constantly swept by a slow stream of dry argon.

The yields reported in Table I were obtained by reaction of 0.124 g (0.567 mmol) of **3** with 0.207 g (0.590 mmol) of silver hexafluoroantimonate in 3.0 ml of acetic acid and by reaction of 0.136 g (0.622 mmol) of **4** with 0.221 g (0.643 mmol) of silver hexafluoroantimonate in 3.0 ml of acetic acid, both for 3 hr, followed by glpc analysis.

The products were isolated for identification in separate experiments. Typical is the reaction of 1.04 g (4.75 mmol) of *cis*-4-*tert*-butylcyclohexyl chloroformate with 1.74 g (5.05 mmol) of silver hexafluoroantimonate in 7.0 ml of acetic acid, which was allowed to proceed for 12 hr and found by analytical glpc to be very similar to the 3-hr reaction. The peaks corresponding to 1- and 4-*tert*-butylcyclohexenes were collected separately by preparative glpc (column C, 130°) and gave ir and nmr spectra and glpc retention times identical with those of authentic materials. The peak corresponding to 3-*tert*-butylcyclohexene (**12**) could not be isolated in pure form because of its small amount and poor resolution from the other olefins under preparative conditions. Consequently, **12** was collected as a mixture with 1-*tert*-butylcyclohexene and gave nmr signals at δ 5.63 and 0.89 in a ratio of 2:9 when signals due to 1-*tert*-butylcyclohexene were subtracted. The peaks corresponding to *cis*- and *trans*-4-*tert*-butylcyclohexyl chlorides (**7** and **10**) and to the *cis*- and *trans*-4-*tert*-butylcyclohexyl acetates (**8** and **9**) were collected (column D, 180°) and gave nmr and ir spectra and glpc retention times identical with those of authentic materials. The same glpc conditions provided the 3-*tert*-butylcyclohexyl acetates; the peak with shorter retention time is assigned as the *trans* axial isomer⁷³ **6** on the basis of the 6–8 Hz half-width and δ 5.07 ppm chemical shift of its 1-proton:⁷¹ ir (CCl₄) 2941, 2849, 1727 (C=O), 1475, 1445, 1364, 1256, 1230, 1111, 1045, 1017, 958; nmr (CCl₄) δ 5.07 (broad s, 1), 2.2–1.0 (broad m, 9), 2.00 (s, 3), 0.88 (s, 9).

The second peak is assigned as the *cis* (equatorial) isomer on the basis of the 15–20 Hz half-width and δ 4.53 ppm chemical shift of its 1-proton:⁷¹ ir (CCl₄) 2874, 2801, 1727 (C=O), 1471, 1451, 1362, 1236, 1027, 1011, 962, 894; nmr (CCl₄) δ 4.53 (broad m, 1), 2.1–0.93 (broad m, 9), 1.95 (s, 3), 0.91 (s, 9).

In addition to the above products, a very small peak (<0.2%) with retention time identical with that of authentic *cis*-2-*tert*-butylcyclohexyl acetate was observed. No peak corresponding to authentic *trans*-2-*tert*-butylcyclohexyl acetate was observed.

The products from a similar reaction of *trans*-4-*tert*-butylcyclohexyl chloroformate gave spectral data identical with those collected from the *cis* isomer. A very small (<0.1%) peak corresponding to *cis*-2-*tert*-butylcyclohexyl acetate, but no peak corresponding to *trans*-2-*tert*-butylcyclohexyl acetate, was observed. A very small peak was also observed just prior to 1-*tert*-butylcyclohexene (**11**), but it could not be collected in amounts sufficient to obtain spectral data. A possible reaction product reported to

have a retention time similar to that of 1-*tert*-butylcyclohexene is 2-*tert*-butylbicyclo[3.1.0]hexane.¹⁰

The general procedure for the reaction of the 4-*tert*-butylcyclohexyl chlorides was the same as for the chloroformate reactions, although the rate of precipitation of silver chloride was visually considerably slower than for the chloroformates. The reaction of 0.0557 g (0.319 mmol) of *cis*-4-*tert*-butylcyclohexyl chloride and 0.120 g (0.349 mmol) of silver hexafluoroantimonate in 1.5 ml of acetic acid for 3 hr at ambient temperature gave 0.014 g (31%) of silver chloride. Glpc analysis on column B gave the yields summarized in Table I. The reaction of the *cis* chloride was also carried out for 36 hr and gave 59% silver chloride, 2.3% 1-*tert*-butylcyclohexene, 1.5% 3-*tert*-butylcyclohexene, 47.0% 4-*tert*-butylcyclohexene, 5.9% *trans*-3-*tert*-butylcyclohexyl acetate, 1.9% *cis*-4-*tert*-butylcyclohexyl acetate, 0.9% *cis*-3-*tert*-butylcyclohexyl acetate, and 2.9% *trans*-4-*tert*-butylcyclohexyl acetate.

The reaction of *trans*-4-*tert*-butylcyclohexyl chloride was very slow and was carried out for 48 hr to give a 33% (0.014 g) yield of silver chloride from 0.519 g (0.298 mmol) of *trans*-4-*tert*-butylcyclohexyl chloride and 0.112 g (0.325 mmol) of silver hexafluoroantimonate in 1.4 ml of acetic acid and the organic products are reported in Table I.

Product stability control experiments were carried out with 4-*tert*-butylcyclohexene.⁷⁷

Reactions of *cis*- and *trans*-4-*tert*-Butylcyclohexyl-Chloroformate 2,2,6,6-*d*₄ (3-*d*₄ and 4-*d*₄). The reactions of the deuterated chloroformates were carried out in a manner analogous to those described for the undeuterated compounds. In analytical runs, 0.0558 g (0.250 mmol) of 3-*d*₄ and 0.0879 g (0.256 mmol) of silver hexafluoroantimonate in 1.4 ml of acetic acid and 0.0314 g (0.141 mmol) of 4-*d*₄ and 0.0514 g (0.149 mmol) of silver hexafluoroantimonate in 0.8 ml of acetic acid in separate reactions gave the results presented in Table II.

In a preparative reaction, 0.812 g (3.64 mmol) of 4-*d*₄ in 5.0 ml acetic acid was added to 1.31 g (3.80 mmol) of silver hexafluoroantimonate in 15.0 ml of acetic acid. After it had been stirred for 3 hr, the reaction mixture was filtered and worked up as described above. The yield of silver chloride was 0.288 g (55%). The organic products were isolated by preparative glpc (column D; the olefins at 150° and the remaining products at 180°). The distribution of protons on the various cyclohexyl ring positions was determined by integration of the peaks corresponding to these positions relative to the *tert*-butyl signal and the results are given in Table III. The products of 3-*tert*-butylcyclohexene and *cis*-3-*tert*-butylcyclohexyl acetate were not collected. The results of a similar isolation and nmr spectral analysis of the products of the reaction of 0.881 g (3.95 mmol) of 3-*d*₄ with 1.46 g (4.25 mmol) of silver hexafluoroantimonate in 20 ml of acetic acid for 3 hr are also reported in Table III. The yield of silver chloride was 0.426 g (75%).

A more detailed study was made of 1-*tert*-butylcyclohexene, which was isolated from the reaction mixtures after preparative glpc (column D, 150°). The 1-olefin from the reaction of 4-*d*₄ showed a molecular ion at *m/e* 142 on mass spectral analysis, corresponding to four deuterium atoms per molecule. More detailed analysis for total deuterium content by isotope ratio mass spectrometry gave 97.0 ± 0.7% retention of the original four deuterium atoms per molecule. The 60-MHz nmr spectrum of 1-*tert*-butylcyclohexene-*d*₄ shows a singlet at δ 5.40 for the olefin proton, a singlet at δ 1.03 for the *tert*-butyl protons, and broad partially resolved multiplets at 2.0 and 1.6, corresponding to the allylic and nonallylic saturated ring protons, respectively. The ratio of signals at 100 MHz gives a ratio of olefinic:saturated ring:*tert*-butyl protons of 1.0:4.1:9.0 and an allylic to nonallylic proton ratio of 2.5:1.5. A 15.4-MHz deuterium nmr spectrum shows no evidence for an olefinic deuterium and gives a ratio of 1.5:2.5 for allylic and nonallylic deuterium by planimeter integration of a time-averaged spectrum of 28 scans.

The 1-*tert*-butylcyclohexene from the reaction of the *cis*-3-*d*₄ also shows a molecular ion at *m/e* 142 in the mass spectrum, corresponding to 99.3 ± 0.6% retention of the original four deuterium atoms per molecule. Analysis of the 100-MHz proton nmr spectrum gives a 1.0:4.0:9.0 ratio for the olefinic, saturated ring, and *tert*-butyl protons, respectively, and a ratio of 2.7:1.3 for the allylic to nonallylic protons. Deuterium nmr at 15.4 MHz shows no evidence for an olefinic deuterium and gives an allylic to nonallylic deuterium ratio of 1.3:2.7 by planimeter integration of a spectrum resulting from 16 time-averaged scans.

Reaction of Acetic (*trans*-4-*tert*-butylcyclohexyl)carbonic Anhydride (*trans*-15) in the Presence of **4 and Silver Hexafluoroanti-**

(76) H. L. Goering, R. L. Reeves, and H. H. Fry, *J. Amer. Chem. Soc.*, **78**, 4926 (1956).

(77) See paragraph at end of paper regarding supplementary material.

monate in Acetic Acid. A solution of 0.0604 g (0.250 mmol) of acetic (*trans*-4-*tert*-butylcyclohexyl)carbonic anhydride and 0.0504 g (0.230 mmol) of **4** in 2.0 ml of acetic acid was added to a solution of 0.176 g (0.510 mmol) of silver hexafluoroantimonate in 2.0 ml of acetic acid. The precipitation of silver chloride and evolution of carbon dioxide were evident shortly after mixing. The reaction mixture was stirred at ambient temperature for 6 hr and the reaction was then quenched, filtered, and worked up as described above for the chloroformate reactions. The yield of carbon dioxide as barium carbonate was 0.081 g (177% based on chloroformate, 71% of theoretical including the mixed anhydride). Glpc analysis (column B, 150°) showed about four times the amount of *trans*-4-*tert*-butylcyclohexyl acetate expected for the reaction of **4**, while all other product ratios were as expected for the reaction of the chloroformate alone. Although absolute yields were not obtained, the ratio of *trans*-/*cis*-4-*tert*-butylcyclohexyl acetates of 14:1 indicates formation of 70–80% of *trans*-4-*tert*-butylcyclohexyl acetate as the major product from the mixed anhydride.

Reaction of Acetic (*trans*-4-*tert*-Butylcyclohexyl)carbonic Anhydride-¹⁸O with Silver Hexafluoroantimonate in the Presence of 10 mol % **4.** By the same procedure as reported above, but in a vacuum manifold, reaction was effected between 0.054 g (0.224 mmol) of *trans*-**15**-¹⁸O, a small amount of unlabeled **4** (0.004 g, 0.02 mmol), and a solution of 0.079 g (0.230 mmol) of silver hexafluoroantimonate in 1.0 ml of acetic acid. The evolution of CO₂ ceased after 20 min and the evolved CO₂ was collected and purified and the results of the mass spectral data are given in Table IV.

Reactions of *cis*- and *trans*-4-*tert*-Butylcyclohexyl Chloroformate-¹⁸O (3**-¹⁸O and **4**-¹⁸O).** A solution of silver hexafluoroantimonate (0.065 g, 0.189 mmol) in 1.0 ml of acetic acid was allowed to react with **4**-¹⁸O (0.040 g, 0.182 mmol) in 0.5 ml of acetic acid after the solutions had been degassed by three warm and freeze (−78°) cycles. After the reaction had been allowed to proceed at room temperature for 10–15 min and the CO₂ evolution had subsided, the evolved CO₂ was collected in a gas bulb at liquid nitrogen temperature and purified on a high vacuum manifold for analysis by mass spectrometry. The results are given in Table V. A similar reaction of 0.040 g (1.82 mmol) of *cis*-4-*tert*-butylcyclohexyl chloroformate-¹⁸O with 0.070 g (2.04 mmol) of silver hexafluoroantimonate in 1.5 ml of acetic acid gave the mass spectral analysis for the evolved CO₂ in Table V. A blank reaction is also reported in Table V.

Reactions of *N*-(*cis*- and -*trans*-4-*tert*-Butylcyclohexyl)sulfinylamines with Nitrosyl Hexafluoroantimonate in Acetic Acid. A solution of nitrosyl hexafluoroantimonate, 0.232 g (0.870 mmol), in 3.0 ml of acetic acid was added to *N*-(*trans*-4-*tert*-butylcyclohexyl)sulfinylamine, 0.114 g (0.568 mmol), and the reaction was allowed to proceed at ambient temperature for 1.5 hr. Quenching and work-up as described for the chloroformate reactions led to the acetate products described in the text. Similarly, reaction of 0.0480 g (0.239 mmol) of *N*-(*cis*-4-*tert*-butylcyclohexyl)sulfinylamine and 0.0772 g (0.290 mmol) of nitrosyl hexafluoroantimonate in 1.5 ml of acetic acid gave the acetate products described in the text. Unsuccessful attempts were made to increase the yields of olefinic products from the *trans*-*N*-sulfinylamine by carrying out the reaction with a deficiency of nitrosyl salt, by inverse addition, and by rapid quenching. These attempts did not affect the ratios of the acetates or produce olefinic products.

A control reaction revealed that 4-*tert*-butylcyclohexene was not stable to the reaction conditions.⁷⁷

threo- and *erythro*-3-phenyl-2-butanol were prepared and purified by vacuum distillation.⁴³ The *threo* isomer had the expected nmr spectrum⁵⁸ and its isomeric purity was assigned as better than 99.8% by glpc analysis (column E, 120°). Under these conditions 0.2% of the *erythro* isomer could be detected. The *erythro* isomer had the expected nmr spectrum⁵⁸ and its isomeric purity was established by glpc (column F, 130°) as 99.8% *erythro* and less than 0.2% *threo* alcohol.

threo-3-Phenyl-2-butyl chloroformate (**17**) was prepared in 96% yield from phosgene and *threo*-3-phenyl-2-butanol in ether: ν (neat) 1773 cm^{−1} (C=O); nmr δ 7.17 (s, 5 H), 5.06 (quintet, *J* = 6.3 Hz, 1 H), 2.99 (quintet, *J* = 6.8 Hz, 1 H), overlapping doublets at 1.29 (*J* = 7.0 Hz, 3 H) and 1.21 (*J* = 6.2 Hz, 3 H). At a spectrum amplitude ten times that of the normal spectrum, absorptions corresponding to the δ 3.74 quintet of the starting alcohol were observed and corresponded to an alcohol impurity of ca. 3% (mol %). A small portion of the sample was evacuated (0.01 Torr) at ambient temperature for 10 hr and submitted for analysis.⁷³

erythro-3-Phenyl-2-butyl chloroformate (**18**) was prepared in 91%

yield from *erythro*-3-phenyl-2-butanol and phosgene. A portion of the sample was passed over Florex AA-LVM 60–90 mesh in pentane and the resulting solution was concentrated with a nitrogen stream and held under vacuum at 0.01 Torr for 80 min to give *erythro*-3-phenyl-2-butyl chloroformate:⁷³ ν (neat) 1774 cm^{−1} (C=O); nmr δ 7.17 (s, 5 H), 5.00 (doublet of quartets, *J* = 6.5 and 8 Hz, 1 H), 2.88 (broadened quintet, *J* = 7.3 Hz, 1 H), 1.32 (d, *J* = 7 Hz, 3 H), and 1.15 (d, *J* = 6.5 Hz, 3 H). At a spectrum amplitude 12.8 times that of the normal spectrum an integral ratio corresponding to 3.6% (mol %), starting alcohol was observed in the region δ 3.5–4.0.

threo- and *erythro*-3-phenyl-2-butyl chlorides were prepared from the reaction of thionyl chloride and a mixture of 23% *threo*- and 77% *erythro*-3-phenyl-2-butanol. Preparative glpc (column G, 170°) gave separation with the larger peak with shorter retention time assigned as the *erythro* isomer since the stereochemical course of the reaction has been demonstrated to give *threo* chloride **22** from *threo* alcohol and *erythro* chloride **23** from *erythro* alcohol.⁷⁸

threo-3-Phenyl-2-butyl chloride (**22**), a mixture of 97% *threo* and 3% *erythro* isomer, is a clear liquid:⁷⁹ nmr δ 7.14 (s, 5 H), 4.13 (doublet of quartets, *J* = 5.5 and 7 Hz, 1 H), 3.03 (broadened quintet, *J* = 6.5 Hz, 1 H), and 1.35 (broadened doublet, *J* = 6.5 Hz, 6 H).

erythro-3-Phenyl-2-butyl chloride (**23**) is a clear liquid:⁷³ nmr δ 7.13 (s, 5 H), 4.01 (doublet of quartets, *J* = 6.5 and 7 Hz, 1 H), 2.82 (broadened quintet, *J* = 7.3 Hz, 1 H), and overlapping doublets with equal coupling constants at 1.40 (*J* = 6.5 Hz, 3 H), and 1.29 (*J* = 6.5 Hz, 3 H).

3-Phenyl-2-butanone-1,1,1,3-*d*₄ was prepared by repetitive base-catalyzed exchange of 3-phenyl-2-butanone with deuterium oxide catalyzed by sodium methoxide. Vacuum distillation gave 3-phenyl-2-butanone-1,1,1,3-*d*₄: δ 7.18 (s, 5 H), 3.54 (s, dioxane impurity ca. 2.1 mol %), 1.89 (quintet, *J* = 2.2 Hz, 1.8% relative to intensity of δ 1.32, s), and 1.32 (s, 3 H). No absorption for the benzylic proton was observed even at a spectrum amplitude ten times that of the normal spectrum. From the proton nmr spectrum the 3-phenyl-1-butanone-1,1,1,3-*d*₄ is estimated to be better than 97% isotopically pure. Mass spectral analysis shows an ion at *m/e* 151 which would correspond to 7.7% product with only three deuteriums. This result is in conflict with the nmr data, which are considered more reliable in the absence of detailed data concerning the fragmentation of 3-phenyl-2-butanone-1,1,1,3-*d*₄.

threo-3-Phenyl-2-butanol-1,1,1,3-*d*₄ was prepared by repetitive reduction of 3-phenyl-2-butanone-1,1,1,3-*d*₄ in ether with LiAlH₄ at 0° to give 84% of crude product which gave an nmr spectrum consistent with a mixture of the expected *threo* and *erythro* deuterium substituted alcohols. A portion of the crude alcohol mixture was treated with phthalic anhydride and pyridine to give 31% of colorless crystalline phthalate:⁴³ mp 129.5–130.5°; nmr δ 12.3 (broad s, 1 H), 7.1–8.0 (complex multiplet, 9 H), 5.36 (broadened s, 1 H), and 1.15 (broadened s, 3 H). Hydrolysis of *threo*-3-phenyl-2-butyl-1,1,1,3-*d*₄ acid phthalate with aqueous NaOH at 100–118° for 12 hr followed by distillation under vacuum gives 62% of a colorless liquid, which by glpc contains less than 0.1% isomeric *erythro* material. The nmr spectrum of 3-phenyl-2-butanol-1,1,1,3-*d*₄ is consistent with the assigned structure: ¹H nmr δ 7.17 (s, 5 H), 3.80 (s, 1 H), 2.15 (broad s, 1 H), and 1.20 (s, 3 H); ²H nmr (15.4 MHz, HA-100) δ −4.84 and −6.48 (ratio 0.20 ± 0.03:1.00). In the ¹H spectrum the exact ratios of the 3.80 and 2.15 absorptions relative to the 1.20 absorption were 30 ± 2 and 26 ± 2:100.

threo-3-Phenyl-2-butyl-1,1,1,3-*d*₄ chloroformate (**17-d**₄) was prepared from 152 mg (0.99 mmol) of *threo*-3-phenyl-2-butanol-1,1,1,3-*d*₄ and phosgene by the same procedure used for preparation of **17**. After isolation the product was placed under vacuum at 0.01 Torr for 1.5 hr to give 87% of **17-d**₄: ¹H nmr δ 7.19 (s, 5 H), 5.05 (s, 1 H), and 1.30 (s, 3 H); ²H nmr δ −4.26 and −6.10 (ratio 0.25 ± 0.05:1.00). The exact ratio of proton absorption intensities for 5.05:1.30 absorptions was 0.26 ± 0.01:1.00.

threo- and *erythro*-3-phenyl-2-butyl acetates²³ (**19** and **20**), 2-methyl-2-phenylpropyl acetate²³ (**21**), *cis*-2-phenyl-2-butene^{33,80} (**24**), *trans*-2-phenyl-2-butene^{33,80} (**25**), 2-methyl-2-phenyl-1-pro-

(78) D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 332 (1953).

(79) The analysis obtained for carbon was 0.34 high and for chlorine 0.31 low.

(80) M. Barbioux, N. Defay, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belg.*, **73**, 716 (1964).

penes⁸¹ (26), 2-phenyl-1-butene (28), and 2-phenyl-2-butyl acetate⁸² (29) were prepared and identified by standard procedures.⁷⁷

3-Methyl-2-phenyl-1-penten-4-one (27) was isolated and characterized from reaction of *cis*- and *trans*-2-phenyl-2-butene and 2-phenyl-1-butene (ca. an 8:1:2 mixture of isomers) and 0.4 M silver hexafluoroantimonate in acetic acid with gaseous HCl. The reaction was allowed to stir at room temperature for 12 hr before it was poured into water and extracted with pentane. Washing and concentration of the pentane layer gave a yellow oil which was purified by preparative glpc (column H, 145°). No yield was determined for the reaction. 3-Methyl-2-phenyl-1-penten-4-one (27) is a clear liquid:⁷³ ν (CCl₄) 1720 cm⁻¹; nmr δ 7.28 (s, 5 H), 5.40 (broad s, 1 H), 5.10 (broad s, 1 H), 3.59 (quartet, $J = 7$ Hz, 1 H), 2.04 (s, 3 H), and 1.27 (d, $J = 7$ Hz, 3 H); and mass spectrum m/e (rel intensity) 174 (8.3), 159 (24.7), 132 (6.3), 131 (18.1), 130 (13.6), 129 (8.8), 117 (8.9), 116 (6.4), 115 (12.4), 103 (5.9), 91 (23.9), 77 (10.8), 51 (6.9), and 43 (100.0).

Reactions of *threo*- and *erythro*-3-Phenyl-2-butyl Chloroformates and Chlorides with Silver Hexafluoroantimonate in Acetic Acid. After a solution of silver hexafluoroantimonate in acetic acid had been mixed with a solution of the chloroformate in acetic acid or with the neat chloride, solutions ca. 0.3 M in chloroformate and ca. 0.4 M in chloride and equimolar in silver salt were obtained and allowed to stir at ambient temperature. After 1 hr the reaction was quenched by the addition of pentane and water. Extraction with pentane and water was followed by glpc analysis (column F, 130°) with the addition of biphenyl as an internal standard. For analysis of the olefinic products, it was necessary in some cases to concentrate the sample under a slow stream of nitrogen to no less than 20% of the original volume. The yield of silver chloride was determined gravimetrically by nitric acid reprecipitation of the solids soluble in aqueous ammonia.

A solution of 42.15 mg (0.198 mmol) of 17 in 0.125 ml of acetic acid was added to 0.50 ml of 0.400 M silver hexafluoroantimonate in the same solvent to provide the yields shown in Table VI. A small amount of an unidentified material with a retention time and area similar to those of 25 was observed but is not included in the table. The pentane solution of the products was concentrated and the structures of the major products were verified by nmr analysis of the fractions collected from preparative glpc (column I, 145°). The fractions gave, in order of increasing retention time, nmr data consistent with the following compounds: 24, with ca. 20% 26; 22; 21 and 19 in ca. 2:1 ratio; and no erythro acetate was observed.

A solution of 40.04 mg (0.192 mmol) of 18 in 0.125 ml of acetic acid was allowed to react with 0.5 ml of 0.400 M silver hexafluoroantimonate. After concentration with a nitrogen stream to ca. half the original volume, glpc analysis of the pentane solution gave the yields shown in Table VI. A small amount of an unidentified material with retention time and area similar to those of 25 was noted. The structures of the major products were verified by nmr analysis of the fractions collected from preparative glpc (column I, 145°). The fractions gave, in order of increasing retention time, nmr data consistent with the following: 24; 23; and ca. an 8:1:1 mixture of 20:19:21.

The reaction with 33.41 mg (0.198 mmol) of 23 and 0.50 ml of 0.400 M silver hexafluoroantimonate in acetic acid for 1 hr gave the products indicated in Table VI. After glpc analysis the mixture was concentrated under reduced pressure and gave 52.0 mg of colorless oil, 95% of the amount of material expected from the glpc analysis. Nmr analysis showed that the mixture was quantitatively in agreement with the results which would be expected for a mixture of biphenyl, 20, 24, and 23, with the structures and relative amounts determined above.

The reaction of 21.4 mg (0.127 mmol) of 22 and 0.5 ml of 0.400 M silver hexafluoroantimonate in acetic acid for 1 hr gave the products shown in Table VI. Unreacted chloride amounted to 54 ± 3%. After determination of the yields, the pentane solution was concentrated under reduced pressure to give a mixture of biphenyl, 19, 24, and 22. The nmr spectrum of the concentrate was consistent with the glpc yields, the structures assigned by glpc retention times, and the presence of residual pentane.

A solution of 17 in acetic acid was allowed to stand at ambient temperature for 30 min. Extractive product isolation with pentane gave a 94% recovery of material which had ir and nmr spectra identical with those of the starting chloroformate.

General Procedure for Control Experiments for the Stability of the Products of the Reactions of the 3-Phenyl-2-butyl Chloroformates and the 3-Phenyl-2-butyl Chlorides. The control experiments were performed in the same fashion as the reaction of 17 in that the product being tested was added to the solution of the silver salt and a solution of chloroformate. Product stability control experiments were carried out with 19-29.⁷⁷

The Reaction of 17-*d*₄ with Silver Hexafluoroantimonate in Acetic Acid. The reaction of 17-*d*₄ was carried out with 84.0 mg (0.388 mmol) of the chloroformate and 1 ml of 0.4 M silver salt solution in acetic acid in the same fashion as the reaction of 17, except that no biphenyl was added. The pentane solution of the products was concentrated and mixtures of products were collected from preparative glpc (column I, 145°), and each of the collected fractions was analyzed by proton and deuterium nmr spectroscopy.

The first fraction collected was a mixture of deuterium-substituted 2-methyl-1-phenyl-1-propenes and *cis*-2-phenyl-2-butenes: nmr δ 7.17 (m, 4.5 H), 6.62 (s, 0.17 H), 5.75 (s, 0.30 H), and 2.00 (d, $J = 1.3$ Hz), 1.87 (s), and 1.82 (s) with the intensities assigned relative to 3.00 for peaks in the region 1.82 to 2.00; nmr analysis (100 MHz) gives relative intensities for signals at δ 2.00 and 1.87 + 1.82 of ca. 1.0:0.87 and δ 6.62:5.75 of ca. 0.55:1.00; and ²H nmr δ -1.10 (s, 0.12), -1.25 (s, 0.35), and -5.61 (s, 3.0), and with acetone-*d*₆ lock δ -1.10 (s, 0.47) and -1.25 (s, 1.0). The small sample size and use of deuteriochloroform lock cause drift in the base line in the vinyl deuterium region which makes the ratio with acetone-*d*₆ lock a better ratio of the vinyl deuteriums. No absorptions for protons at C-4 of *cis*-2-phenyl-2-butene were observed. The ratio of the vinyl protons for 26-*d*₃ at δ 6.62 to the vinyl protons for 24-*d*₃ at 5.75 is 0.56:1 (average of 60 and 100 MHz ratios), and the similar ratio for compounds 26-*d*₄ to 24-*d*₄ is 0.47:1, as determined by deuterium nmr (acetone-*d*₆ lock); these data are consistent with a 1:2 ratio for the downfield vinyl to upfield vinyl ratio in both proton and deuterium nmr spectra. The total vinyl to methyl ratio, for signals at δ 6.62 and 5.75:2.00 and 1.87 and 1.82 in the proton nmr spectrum, with the 2.00 absorption assigned to 24-*d*₃ and 24-*d*₄ and the 1.87 and 1.82 absorptions assigned to 26-*d*₃ and 26-*d*₄, is 0.47:3 for both proton and deuterium nmr. The intensity ratios allow the calculation of the ratios of compounds 24-*d*₃, 24-*d*₄, 26-*d*₃, and 26-*d*₄. For 26-*d*₃:24-*d*₃ and 26-*d*₄:24-*d*₄, there is ca. a 1:2 ratio calculated from the vinyl proton ratio and for the ratios of 26-*d*₃ + 24-*d*₃:26-*d*₄ + 26-*d*₄ + 24-*d*₃ + 24-*d*₄ and 26-*d*₄ + 24-*d*₃:26-*d*₃ + 26-*d*₄ + 24-*d*₃ + 24-*d*₄ calculated from the vinyl to methyl ratios in the proton and deuterium nmr the ratios are also ca. 1:2. The ratios show 26-*d*₃ + 24-*d*₃ \cong 26-*d*₄ \cong 24-*d*₄. Since the ratios of 26-*d*₃:24-*d*₃ and 26-*d*₄:24-*d*₄ are 1:2, the ratios of 26-*d*₃:26-*d*₄:24-*d*₃:24-*d*₄ are 1:1:2.2. The ratios of the relative intensities for the methyl protons in the 100-MHz spectrum are inconsistent with this analysis as a ratio of the 2.00:1.87 + 1.82 absorptions is 1:0.87, instead of the expected 1:0.5. A reliable ratio is difficult to obtain as the absorptions are poorly resolved and under these conditions the 1:0.87 ratio may have large errors associated with the determination. The ratios assigned for compounds 24-*d*₃, 24-*d*₄, 26-*d*₃, and 24-*d*₄ are approximate and reflect the origins of these olefins even if large limits of error are assumed.

The second fraction was a mixture of deuterium-substituted *threo*-3-phenyl-2-butyl chlorides: nmr ¹H δ 7.18 (s, 5.3), 4.15 (s, 0.55), 3.04 (s, 0.33), and 1.35 (s, 3.0) and ²H δ -3.22 (s, 0.50), -4.26 (s, 0.59), and -5.95 (s, 3.0). The proton absorptions for 22-*ta* are 7.18, 4.15, and 1.35, while 22-*tb* gives absorptions at 7.18, 3.04, and 1.35. The percentage of each compound calculated from the proton and deuterium methine absorptions is 54% 22-*ta*: and 46% 22-*tb* from the deuterium nmr data and 63% 22-*ta* and 37% 22-*tb* from the proton nmr data. These data are consistent with ca. a 3:2 mixture of 22-*ta*:22-*tb*.

The third fraction was a mixture of deuterium-substituted acetates: 2-methyl-1-phenylpropyl acetate (21-*d*₄), *threo*- and *erythro*-3-phenyl-2-butyl acetates (19-*ta*, 19-*tb*, 20-*ea*, and 20-*eb*), and a trace amount of *threo*-3-phenyl-2-butyl chloride (22-*tb*): nmr (220 MHz with a sweep from δ 0.61-5.15 and a spectrum amplitude to make the peaks of interest as large as possible, the integrals are assigned values relative to the δ 1.22 absorptions as 100) δ 5.04 (s, 30), 4.99 (s, 6), 3.01 (s, <3), 2.88 (s, 14), 2.78 (s, 3), 1.95 and 1.82 (singlets superimposed upon a multiplet, offscale), 1.40 (s, 6), 1.22 (s, 100) 1.08 (s, 34), 1.00 (s, 23), 0.93 (d, $J = 7$ Hz, 95) and 0.76 (d, $J = 7$ Hz, 95) and ²H δ -1.95 (s, 0.50), -4.51 (s, 0.34), and -6.49 (s, 3.0). The assignment of the proton chemical shifts relative to tetramethylsilane was made by comparison to a spectrum with a 2500-Hz sweep width. The assignment of the resonances is

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(82) D. J. Cram, *J. Amer. Chem. Soc.*, **74**, 2137 (1952).

made by comparison of the chemical shifts to the chemical shifts of the authentic protonated compounds.

The 2-methyl-1-phenylpropyl acetate **21-d₄** was assigned as a 1:1 mixture of diastereomers by the observed doublets of equal intensity at δ 0.93 and 0.76 and the multiplet in the range of *ca.* δ 1.9. The absorption at δ 5.40 for the benzylic proton of 2-methyl-1-phenylpropyl acetate was not observed, which confirms that only acetate **21-d₄**, and no other isomer with the same carbon skeleton, is present.

The *erythro*-3-phenyl-2-butyl acetates **20a** and **20b** give absorptions at δ 4.99, 2.78, 1.22, and 1.00. The 1.22 absorption is coincident with a methyl absorption from the *threo* acetate **19a** and the intensity for the *erythro* acetate **20a** which occurs at 4.99. With this analysis the ratios of methine intensities and methyl intensities for **20a**:**20b** are 2:1 and 1.3:1, which gives an average of 1.7:1 for the ratio **20a**:**20b**.

The *threo*-3-phenyl-2-butyl acetates **19a** and **19b** give absorptions at δ 5.04, 2.88, 1.22, and 1.08. The ratios for the methine and methyl resonances for **19a**:**19b** are 2.1:1 and 2.4:1, with the ratios of methyl determined after subtraction of the contribution from the *erythro* acetate **20a** to the absorption at 1.22. The average value for the ratio of **19a**:**19b** is 2.3:1.

Another component in the third fraction is *threo*-3-phenyl-2-butyl chloride **22b**, which gave absorptions at δ 3.01 and 1.40. No

other absorptions for 3-phenyl-2-butyl chlorides were observed and chloride **22b** was found in trace amounts only.

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Supplementary Material Available. The details of the experiments for preparing and identifying **7**, **8**, **11**, and **13** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-2494.

Solvolysis of Tertiary Tricyclo[3.3.0.0^{3,7}]octyl *p*-Nitrobenzoates¹

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Abstract; Solvolysis rates in 90:10 acetone–water have been measured for the following tertiary *p*-nitrobenzoates of the 2-tricyclo[3.3.0.0^{3,7}]octyl system: methyl, phenyl, *p*-anisyl, and *p*-trifluoromethylphenyl. From considerations of the rates and products of these reactions, it was concluded that all of them react *via* classical ions which may subsequently undergo skeletal rearrangements. Earlier estimates of the anchimeric assistance in the secondary system are shown to have been in error by a factor of 10⁴–10⁶.

Evaluation of the importance of anchimeric assistance has relied heavily on the use of semi-empirical calculations² and/or rate comparisons involving "model" systems. Interestingly, relatively little discussion of what constitutes a good "model" has appeared in the literature,³ but it seems generally agreed that a gross structural similarity is important. Thus, differences in rate that might be caused by angle strain, steric effects, torsional strains, and solvent participation might be minimized.⁴

Despite these limitations, the use of model systems has proven to be valuable. For example, the solvolytic behavior of *anti*-7-norbornenyl systems is suitably modeled by the corresponding saturated analogs as

shown by the work of Gassman and Fentiman.⁵ These workers demonstrated that participation can be revealed by comparisons of the relative responses of the solvolysis rates to electron demand at the reaction site. Similarly, the relatively strong participation attributable to α -cyclopropyl rings has been demonstrated by the use of isopropyl systems as models.⁶ On the other hand, comparisons of the *exo*–*endo* rate ratios of tertiary 2-norbornyl derivatives failed to reveal significant σ participation in the secondary derivatives.⁷

While there is little controversy with regard to the importance of participation in the first two examples discussed above, considerable doubt surrounds the interpretation of the rate product data for the *exo*-2-norbornyl system and other systems for which σ participation has been proposed.⁸ The present research

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