The Reactions of Chloroformates with Silver Fluoro Salts

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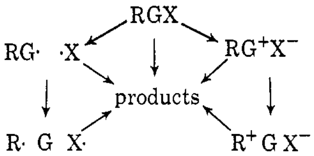
Abstract: The reactions of cyclohexyl, *n*-propyl, 1-apocamphyl, and phenyl chloroformates with silver tetrafluoroborate and silver hexafluoroantimonate give products formally derived from carboxylium and carbonium ions. The presence of the base, tetramethylurea, is required in the first two cases to eliminate the possibility that the observed products arise from transient olefin. The hypothesis that the processes involved in product formation may be similar to reactions believed to involve diazonium ions is suggested by the relatively high yields of isopropyl products and cyclopropane from *n*-propyl chloroformate and is supported in detail for the fraction of reaction of 1-apocamphyl chloroformate leading to cationic aromatic substitution at the bridgehead position.

A family of reactive intermediates formally derived from RGX can be imagined in which G and X are leaving groups and G is stable and nonnucleophilic. Conversions of RGX to products may proceed directly



or by ionic or radical intermediates.

Deaminative reactions of amines under diazotization conditions have generally been discussed in terms of such processes. Ionic pathways usually are favored for alkylamines, and the diazonium ion **1** is a frequently implicated intermediate.[1,2] Isocarboxonium ions **2**, suggested as intermediates in the reactions of alkoxides

$[\mathrm{RN}\equiv\mathrm{N}:]^+$ **1** $\quad[\mathrm{R\ddot{O}}\text{---}\mathrm{C}:]^+$ **2** $\quad[\mathrm{RO}\text{---}\mathrm{C}\equiv\mathrm{O}]^+$ **3**

with halocarbenes, also may be accommodated in this scheme and the similarity of **1** and **2** has been noted.[3] We have recently reported reactions which may involve carboxylium ions **3**, another member of this hypothetical family.[4,5]

Reactions considered to involve the diazonium ion (**1**) proceed with relatively low energies of activation to give products derived from cationic precursors.[6] The rapid rate of reaction is attributed to an exothermic loss of nitrogen such that the transition state for ionization has relatively little positive charge on carbon.[1,7] It is on the similarity of carbon dioxide and nitrogen as leaving groups that the prospective parallel between reactions which could involve carboxylium ions **3** and those which are believed to involve diazonium ions **1** is based. There is considerable evidence that the loss of carbon dioxide can provide a driving force for many reactions.[8] The present work was undertaken to determine if reaction of chloroformates with nonnucleophilic silver salts, a reaction which could produce carboxylium ions,[9] would give products characteristic of a cationic species at a rate appreciably faster than that of the corresponding halide.[4,10]

Carboxylium ions have occasionally been suggested as one of a number of alternative intermediates in the reactions of chloroformates.[11] These include solvolyses,[12] rearrangements to alkyl chloride and carbon di-

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(1) H. E. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, New York, N. Y., 1961; R. A. More O'Ferrall, *Advan. Phys. Org. Chem.*, **5**, 331 (1967); J. H. Ridd, *Quart. Rev.* (London), 15, 418 (1961); R. J. Baumgarten, *J. Chem. Ed.*, **43**, 398 (1966).

(2) The details of deamination reactions are a matter of considerable continuing interest; ionic pathways: E. R. Stedronsky, J. Gal, R. A. More O'Ferrall, and S. I. Miller, *J. Amer. Chem. Soc.*, 90, 993 (1968); E. H. White and C. A. Ellinger, *ibid.*, 89, 165 (1967); J. R. Mohrig and K. Keegstra, *ibid.*, 89, 5492 (1967); J. Bayless, A. T. Jurewicz, and L. Friedman, *ibid.*, 90, 4466 (1968); radical pathways: J. F. Bunnett and H. Takayama, *J. Org. Chem.*, 33, 1924 (1968); A. Lewin and T. Cohen, *ibid.*, 32, 3844 (1967), and references cited therein.

(3) P. S. Skell and I. Starer, *J. Amer. Chem. Soc.*, 81, 4117 (1959); J. Hine, E. L. Pollitzer, and H. Wagner, *ibid.*, 75, 5607 (1953); P. S. Skell and D. H. Reichenbacher, *ibid.*, 90, 2309 (1968), and references cited therein.

(4) Preliminary reports have appeared: P. Beak and R. J. Trancik, *ibid.*, 90, 2714 (1968); P. Beak, R. J. Trancik, J. B. Mooberry, and P. Y. Johnson, *ibid.*, 88, 4288 (1966).

(5) Other species which could be formal members of this group can be envisioned; *cf., e.g.*, G. A. Olah, N. Friedman, J. M. Bolinger, and J. Lukas, *ibid.*, 88, 5328 (1966).

(6) The significance of a comparison of the rates of deamination with other reactions involving the formation of carbonium ions is indirect because different rate-limiting steps are involved and different reaction conditions are common. However, the rate of ionization of 1 is clearly rapid relative to the ionization of halides or esters in those cases in which amides are smoothly deaminated while the corresponding halides or esters are stable.

(7) R. Huisgen and H. Reimlinger, *Ann.*, **599**, 183 (1956); R. Huisgen and C. Rüchardt, *ibid.*, 601, 1 (1956); A. Streitwieser, Jr., *J. Org. Chem.*, 22, 861 (1957); G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

(8) Examples include promotion to an electronically excited state: F. M. Capra, Y. C. Chang, and V. P. Francois, *Chem. Commun.*, 22 (1968); T. A. Hopkins, H. H. Seliger, E. H. White, and M. M. Cass, *J. Amer. Chem. Soc.*, 89, 7148 (1967); M. M. Rauhut, L. J. Bollyby, B. G. Roberts, M. Loy, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and R. A. Clarke, *ibid.*, 89, 6515 (1967); formation of strained double bonds: E. J. Corey and R. A. Winter, *ibid.*, 85, 2677 (1963); formation of strained rings: H. J. Bestman, H. Hortung, and T. Denzel, *Tetrahedron Lett.*, 359 (1966); other reactions: L. Wei and D. S. Tarbell, *J. Org. Chem.*, 33, 1884 (1968); M. S. Newman, N. Gill, and B. Darré, *ibid.*, 31, 2713 (1966); C. Rüchardt and H. Schwarzer, *Ber.*, **99**, 1861 (1966); R. Huisgen and H. Gotthart, *ibid.*, 101, 1059 (1968); D. H. R. Barton, B. J. Garner, and R. H. Wightman, *J. Chem. Soc.*, 1855 (1964); S. L. Johnson and K. A. Rumon, *J. Amer. Chem. Soc.*, 87, 4782 (1965); J. H. Howe and C. R. Morris, *J. Org. Chem.*, 27, 1901 (1962); L. A. Paquette, T. J. Barton, and N. Horton, *Tetrahedron Lett.*, 5039 (1967).

(9) G. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Barker, *J. Amer. Chem. Soc.*, 84, 2733 (1962), references cited therein and subsequent work.

(10) D. N. Kevill and F. L. Weitl, *ibid.*, **90**, 6416 (1968), have subsequently used this reaction to promote ionization and nitrobenzene arylation of 1-adamantyl chloroformate.

(11) For a review of the chemistry of chloroformates see M. Matzner, R. P. Kurkjy, and R. J. Culter, *Chem. Rev.*, 64, 645 (1964).

(12) F. W. Crunden and R. J. Hudson, *J. Chem. Soc.*, 3748 (1961); M. Green and R. J. Hudson, *ibid.*, 1076 (1962); H. Minato, *Bull. Chem. Soc. Jap.*, 37, 316 (1966); A. Kivinen, *Acta Chem. Scand.*, **19**, 845 (1965).

Table I. Reactions of Cyclohexyl Chloroformate (**4**) and Cyclohexyl Chloride (**5**) with Silver Tetrafluoroborate in Chlorobenzene at Ambient Temperature

Reactant(s)	Cyclohexylchlorobenzenes				Cyclohexene	Cyclohexyl fluoride	Cyclohexyl chloride
	%	*ortho*	*meta*	*para*			
4	81	39	6	55	<5	<5	<5
5	80	39	5	56	<5	<5	<5
4 + TMU[a] (2 equiv)[b]	0.5	42	10	48	27	48	13
5 + TMU[a] (2 equiv)[c]					22	30	38
4 + TMU[a] (4 equiv)[d]	0.3				40	31	18

[a] Tetramethylurea. [b] 79% silver chloride, 85% carbon dioxide. [c] 43% silver chloride. [d] 76% silver chloride.

oxide,[13] Friedel–Crafts reactions,[14] and reactions with silver nitrate.[15] The latter reactions are considered to involve acyl nitrates leading to the observed nitrate esters from alkyl chloroformates and nitrophenols from aryl chloroformates. A correspondence between products obtained in thermal decompositions of alkyl chloroformates and deamination of amines has been noted recently.[16] Carboxylium ions were named by Crawford and Raap and postulated as intermediates in the hydrolysis of some N,N′-dicarbalkoxy-N,N′-dialkoxyhydrazines.[17] The species **3** was once suggested as an intermediate in the oxidative decarboxylation of acid anhydrides by pyridine N-oxide.[18] Acylium ions, which have been isolated and characterized,[9] provide a formal analogy for carboxylium ions.

Results and Discussion

Cyclohexyl and *n*-Propyl Chloroformates. Reactions of cyclohexyl chloroformate and *n*-propyl chloroformate in chlorobenzene with silver tetrafluoroborate and silver hexafluoroantimonate give silver chloride and carbon dioxide in yields of 50–100% shortly after being mixed. The reactants are mixed at ambient temperature but the reactions are exothermic and an increase in temperature of *ca.* 10° occurs.

Reaction of cyclohexyl chloroformate (**4**) in chlorobenzene gives an 81% yield of cyclohexylchlorobenzene isomers in an *ortho*:*meta*:*para* ratio of 39:6:55 with less than 5% each of cyclohexene, cyclohexyl fluoride, and cyclohexyl chloride produced. The same isomers in the same amounts are produced by the reaction of cyclohexyl chloride (**5**) with silver tetrafluoroborate in chlorobenzene. These and related results are summarized in Table I. Although cyclohexene is not observed as a product, it is possible that the alkylated products are formed by arylation of transient olefin catalyzed by the HBF_4 or HF–BF_3 produced in the reaction. When a 1:4 ratio of **4** and **5** is allowed to react with silver tetrafluoroborate in chlorobenzene in the presence of a tenfold excess of cyclohexene, a 284% yield (based on the sum of **4** and **5** as 100%) of cyclohexylchlorobenzene isomers is produced. This indication that all of the alkylated isomers might not be primary products of the reactions is supported by reactions carried out in the presence of the base tetramethylurea.[19,20]

Reaction of cyclohexyl chloroformate in chlorobenzene with silver tetrafluoroborate in the presence of 2 equiv of tetramethylurea gives 0.5% of the cyclohexylchlorobenzene isomers, 27% cyclohexene, 48% cyclohexyl fluoride, and 13% cyclohexyl chloride (Table I). Under the same conditions cyclohexyl chloride gave the olefin and fluoride in 22 and 30% yields, along with 43% silver chloride, and cyclohexyl fluoride gave 7% cyclohexene under these conditions. Reaction of chloroformate **4** in the presence of 1 equiv of cyclohexene gave the same products as in its absence but the yield of cyclohexyl fluoride was reduced to 38%. Chloroformate **4** and chloride **5** were stable to tetramethylurea in the absence of silver tetrafluoroborate. The involvement of tetramethylurea in product partitioning is shown by the reaction of cyclohexyl chloroformate in the presence of 4 equiv of tetramethylurea to give 40% cyclohexene, 31% cyclohexyl fluoride, and 18% cyclohexyl chloride.

The reactions of *n*-propyl chloroformate (**6**) and *n*-propyl chloride (**7**) with silver fluorate salts in chlorobenzene at ambient temperature are summarized in Table II. In the absence of added base, **6** and **7** give the same ratio of *o*- and *p*-isopropylchlorobenzenes, but the former reaction gives 56% of the isomers and 84% silver chloride and the latter gives 6% of the isomers and 13% silver chloride. Under these conditions **6** also gave an 11% yield of diisopropylchlorobenzenes. Volatile products from the reaction of **6** are listed in Table II.

The presence of tetramethylurea again has a pronounced influence on the course of the reaction. Reaction of **6** with silver tetrafluoroborate in the presence of 2 equiv of the base yields only 0.6% alkylated isomers. With silver hexafluoroantimonate under the same conditions for 1 hr, **6** gives propene as the major product with lesser amounts of isopropylchlorobenzenes, *n*-propylchlorobenzenes, isopropyl chloride, isopropyl fluoride, *n*-propyl chloride, *n*-propyl fluoride, and cyclopropane (Table II). Silver chloride and carbon dioxide were obtained in 50 and 95% yields, respectively. Infrared analysis of the reaction mixture after 1 hr showed that no more than 2% *n*-propyl chloroformate could be

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[13] (a) SNi: E. S. Lewis and W. C. Herndon, *J. Amer. Chem. Soc.*, **83**, 1961 (1961); K. L. Oliver and W. G. Young, *ibid.*, **81**, 5811 (1959); K. B. Wiberg and T. M. Shryne, *ibid.*, **77**, 2774 (1955); (b) displacements: D. N. Kevill, G. H. Johnson, and W. A. Neubert, *Tetrahedron Lett.*, 3727 (1966); K. W. Buck and H. B. Foster, *J. Chem. Soc.*, 2217 (1963); S. Nakanishi, T. C. Meyers, and E. V. Jensen, *J. Amer. Chem. Soc.*, **77**, 5003 (1955); (c) heat of reaction: G. Olofson, *Acta Chem. Scand.*, **21**, 1114 (1967).

[14] Aryl chloroformates give the expected aryl ester and alkyl chloroformates give the alkylated products resulting from loss of carbon dioxide: W. H. Coppock, *J. Org. Chem.*, **22**, 325 (1957); C. Friedel and J. M. Crafts, *Compt. Rend.*, **84**, 1450 (1877); E. J. Bowden, *J. Amer. Chem. Soc.*, **60**, 645 (1938); F. A. Drahowzal, "Friedel–Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1964, p 644; Vol. I, 1963, p 122.

[15] R. Boschan, *J. Amer. Chem. Soc.*, **81**, 3341 (1959); G. A. Mortimer, *J. Org. Chem.*, **27**, 1876 (1962); D. N. Kevill and G. H. Johnson, *Chem. Commun.*, 235 (1966); D. N. Kevill and G. H. Johnson, *J. Amer. Chem. Soc.*, **87**, 928 (1965); M. J. Zabik and R. D. Schuetz, *J. Org. Chem.*, **32**, 300 (1967); V. A. Pattison, *ibid.*, **31**, 954 (1966).

[16] D. W. Clinch and H. R. Hudson, *Chem. Commun.*, 925 (1968).

[17] R. J. Crawford and R. Raap, *J. Org. Chem.*, **28**, 2419 (1963).

[18] C. Rüchardt and O. Krätz, *Tetrahedron Lett.*, 5915 (1966); T. Koenig, *ibid.*, 2751 (1967); T. Cohen, I. H. Song, J. H. Fager, and G. L. Deets, *J. Amer. Chem. Soc.*, **89**, 4968 (1967).

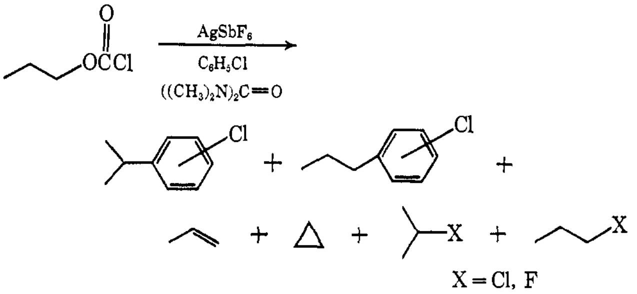
[19] M. S. Newman and L. K. Lala, *Tetrahedron Lett.*, 3267 (1967).

[20] The previously noted similarity in products from the reactions of chloroformates and chlorides[4] has significance only in that the olefins which could be producing the alkylchlorobenzene isomers as secondary products are probably produced by ionic processes.

Table II. Reactions of *n*-Propyl Chloroformate (**6**) and *n*-Propyl Chloride (**7**) with Silver Fluorate Salts in Chlorobenzene at Ambient Temperature

	%						
Reactants	Isopropyl-chloro-benzenes		*n*-Propyl-chloro benzenes	Propene	Isopropyl halide	*n*-Propyl halide	Cyclopropane
6, $AgBF_4$	56[a]		Trace	0.5[b]	RCl 0.2[b] RF 1.2[b]	RCl 13.0 RF 4.5[b]	<0.25
7, $AgBF_4$	6[c]						
6, $AgBF_4$, TMU[d]		0.6[e]					
6, $AgSbF_6$, TMU[d]	5.6[f]		2.4[f]	47.5	RCl 11.7 RF 3.3[b]	RCl 13.0 RF 0.7[b]	3.9
6, $AgSbF_6$, TMU[d,g]		1.4			RCl 16.3 RF 1.4[b]	RCl 10.7 RF 0.4[b]	3.4

[a] An *ortho*:*para* ratio of 47:53, 11% diisopropylchlorobenzene isomers is also formed. [b] Yields are not corrected for differences in thermal conductivity with the internal standards *trans*-2-butene and cyclohexane. [c] An *ortho*:*para* ratio of 48:52, 13% silver chloride is formed. [d] 2 equiv of tetramethylurea; reaction time 1 hr. [e] The isomers appear to be a mixture of isopropyl- and *n*-propylchlorobenzenes by retention time comparison with authentic compounds. [f] The *ortho*:*meta*:*para* ratios are: for isopropylchlorobenzene 52:7:41; for *n*-propylchlorobenzene 47:23:30. [g] Reaction was carried out in the presence of a 1.5–3.0-fold excess of propene.



present. The reactions of *n*-propyl chloride and isopropyl chloride with silver hexafluoroantimonate in the presence of tetramethylurea for 1 hr give 1 and 24% yields of silver chloride, respectively. Some of the propene and isopropyl products observed in the reaction of **6** probably arise from initially formed isopropyl chloride. The high *meta* ratio in the formation of the *n*-propylchlorobenzene isomers is interesting and will bear further investigation. Reaction of **6** in the presence of a 1.5–3.0-fold excess of propene leads to the same products as in its absence but with a decrease in the yields of alkylated chlorobenzenes and an increase in isopropyl chloride (Table II).

Comparison of the products formed in these reactions with those produced by deamination of *n*-propylamine under the same conditions could be most informative. The recently discovered reaction of isocyanates or sulfinylamines with nitrosating agents[5] seemed to offer an appropriate method. Unfortunately, the nitrosating agents react with tetramethylurea under our reaction conditions. Comparison of the reactions in the absence of base could be misleading since the products might arise from secondary reactions. The studies with added base emphasize the importance of establishing olefin stability in reactions involving formation of acid.[21]

Reactions of cyclohexyl chloroformate (**4**) and *n*-propyl chloroformate (**6**) with silver tetrafluoroborate and silver hexafluoroantimonate in chlorobenzene at ambient temperature appear to proceed with rate acceleration relative to the corresponding chloride and to give products expected from a cationic precursor. The rearranged, cyclized, and solvent-alkylated products, olefins, and fluorides[5,9] have precedent in carbonium ion reactions. The formation of cyclopropane and of large amounts of isopropyl products from *n*-propyl precursors appears to be characteristic of reactions involving diazonium[1,7,24,25] or isocarboxonium[6,25] ions. This result suggests that the proposed parallel between these ions and the carboxylium ion is at least useful. However, in view of our failure to find suitable conditions for directly comparing deaminations and dehalodecarboxylations, this correspondence is at best indicative.

1-Chloroformylapocamphane. The inertness of the bridgehead position of bicyclo[2.2.1]heptanes to carbonium ion formation is a reference point in the understanding of carbonium ion structure and has served as a prototype for structure–reactivity relationships.[26] The inactivity of 1-chloroapocamphane (**8**) toward silver nitrate[27] at high temperatures as opposed to the reactivity of 1-aminoapocamphane (**9**) to deamination by

[21] To determine if olefins are stable under deaminative conditions, the reaction of N-*t*-butylsulfinylamine with nitrosyl hexafluoroantimonate in nitromethane–benzene was carried out according to the method of Olah, *et al.*,[5] in the presence of *ca.* 1 equiv of isobutylene. This gave 74% *t*-butylbenzene and 85% *p*-di-*t*-butylbenzene based on starting sulfinylamine. In the absence of isobutylene the yields of the alkylated products are 25% *t*-butylbenzene and 10% *p*-di-*t*-butylbenzene.[5] Apparently some of the alkylated products can be produced from transient olefin. For some substrates comparisons of deamination and Friedel–Crafts alkylations[22,23] could be misleading if an appreciable amount of the alkylated products arises from olefin.

[22] G. A. Olah, N. A. Overchuk, and J. C. Lapierre, *J. Amer. Chem. Soc.*, 87, 5785 (1965).

[23] A. T. Jurewicz, J. H. Bayless, and L. Friedman, *ibid.*, 87, 5788 (1965).

[24] F. C. Whitmore and R. S. Thorpe, *ibid.*, **63**, 1118 (1941).

[25] The formation of cyclopropanes has been reported: (a) deaminations: A. T. Jurewicz and L. Friedman, *ibid.*, **89**, 149 (1967); M. S. Silver, *ibid.*, 82, 2971 (1960); P. S. Skell and I. Starer, *ibid.*, 82, 2971 (1960); J. H. Bayless, F. Mendicino, and L. Friedman, *ibid.*, 87, 5790 (1965); R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *ibid.*, 89, 1442 (1967); W. G. Dauben and P. Laug, *Tetrahedron*, 20, 1259 (1964); O. E. Edwards and M. Lesage, *Can. J. Chem.*, 41, 1592 (1963); C. C. Lee and J. E. Kruger, *Tetrahedron*, 23, 2539 (1967); G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *J. Amer. Chem. Soc.*, 87, 4394 (1965); A. A. Aboderin and R. L. Baird, *ibid.*, 86, 2301 (1964); J. D. Petke and J. L. Whitten, *ibid.*, 90, 3338 (1967); (b) deoxidation: P. S. Skell and I. Starer, *ibid.*, 84, 3962 (1962); (c) solvolysis: G. Solladie, M. Muskatirovic, and H. S. Mosher, *Chem. Commun.*, 809 (1968); G. M. Fraser and H. M. R. Hoffmann, *ibid.*, 561 (1967); S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, 87, 376 (1965); (d) after condensation of the products from the gas-phase decomposition of neopentyl chloroformate.[13a]

[26] (a) P. D. Bartlett and L. H. Knox, *ibid.*, 61, 3184 (1939); (b) G. J. Gleicher and P. von R. Schleyer, *ibid.*, 89, 582 (1967); (c) R. C. Fort and P. von R. Schleyer, *Advan. Alicyclic Chem.*, 1, 284 (1966), and references cited therein.

[27] Ionization can be forced at the bridgehead position. (a) 4-Chlorocamphane gives 59% silver chloride on heating at 205° for 19.5 hr: W. von E. Doering and E. F. Schoenewaldt, *J. Amer. Chem. Soc.*, 73, 2333 (1951). (b) The reaction of 1-chloronorbornane with SbF_5 in SO_2 gives 1- and 2-norboranols in varying proportions depending on the temperature: P. von R. Schleyer, W. E. Watts, R. C. Fort, M. B. Comisarow, and G. A. Olah, *ibid.*, 86, 5679 (1964).

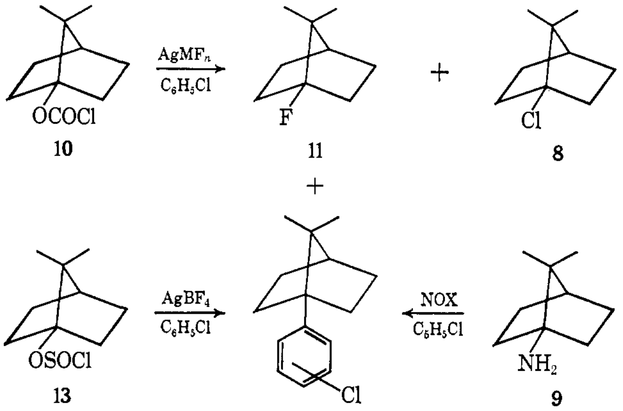
Table III. Reactions of 1-Chloroformylapocamphane (**10**), 1-Chlorosulfinylapocamphane (**13**), and 1-Aminoapocamphane (**9**) in Chlorobenzene at Ambient Temperature[a]

Reactants	% Alkylation	*ortho*	*meta*	*para*	**11**	**8**
10 + $AgBF_4$	24	42	31	27	60	10
10 + $AgSbF_6$	81	39	35	26	<5	17
10 + $AgBF_4$[b] (TMU,[c] 2 equiv)	12	33	35	32	82	15
10 + $AgSbF_6$[b] (TMU,[c] 2 equiv)	36	36	35	29	32	16
9 + NOCl	15	41	30	29		29
9 + $NOBF_4$	9	39	31	30		
13[d] + $AgBF_4$	19	41	31	28	58	<5

[a] Yields are determined by glpc and have an estimated error of ±3%. [b] The error in these experiments is estimated as ±6%. [c] Tetramethylurea. [d] Contained *ca.* 25% diapocamphanyl sulfite.

nitrosyl chloride[26a] at −10° provides a dramatic example of the rate acceleration which can be observed in comparing deaminations and ionizations of halides.[6] If the low activation energy for the loss of nitrogen from diazonium ions is paralleled by the loss of carbon dioxide from a carboxylium ion or its potential precursor, 1-chloroformylapocamphane (**10**) should exhibit bridgehead reactivity.

Reaction of **10** with silver tetrafluoroborate in chlorobenzene at room temperature for 8 hr gives 92% silver chloride, 99% carbon dioxide, 60% 1-fluoroapocamphane[5,9] (**11**), 24% isomers of 1-chlorophenylapocamphane **12** in an *ortho*:*meta*:*para* ratio of 42:31:27, and 10% 1-chloroapocamphane (**8**) (Table III). Assignments of structures to **11** and **12** are made on the basis of analytical, nmr, infrared, and mass spectral data. The gross structure of **12** is established by dechlorination in 98% yield to 1-phenylapocamphane[28] and ozonolysis of that compound to 1-apocamphanecarboxylic acid in 30% yield. The structural assignments to the positional isomers are made on the basis of infrared, nmr, and glpc data. The reactivity of **10** provides evidence that the formal analogy between **1** and **3** is significant.



12, *ortho* 40 ± 3%

meta 32 ± 3%

para 28 ± 3%

Control experiments established that the *meta* isomer of **12** and the *ortho* and *para* isomers of **12** are not significantly interconverted in the presence of the reaction of **10** with silver tetrafluoroborate. 1-Chloroformylapocamphane (**10**) is stable in chlorobenzene containing excess boron trifluoride at room temperature although partial conversion to **8** and **12** occurs on heating at 50–60° for 1–4 hr.[12,29] 1-Chloroapocamphane (**8**) is stable to boron trifluoride and silver tetrafluoroborate at room temperature for 15 hr.

Reaction of 1-chloroformylapocamphane (**10**) with silver hexafluoroantimonate in chlorobenzene at ambient temperature gives an 81% yield of the isomers of 1-chlorophenylapocamphane (**12**) in the same ratio, within experimental error, as obtained previously (Table III). Reduction in the amount of fluoride produced with hexafluoroantimonate as the counterion instead of tetrafluoroborate is consistent with previous observations.[9] This and analogous reactions may be synthetically useful for achieving substitution in reasonable yields at positions of low incipient carbonium ion stability.

Reactions of **10** in chlorobenzene in the presence of 2 equiv of tetramethylurea with silver tetrafluoroborate and silver hexafluoroantimonate to give **8**, **11**, and **12** are summarized in Table III. The added base causes an increase in the amount of fluoride, as observed heretofore, but does not appear to affect the isomer distribution of the 1-chlorophenylapocamphanes.

The amine, 1-aminoapocamphane (**9**), reacts with nitrosyl chloride or nitrosonium tetrafluoroborate in chlorobenzene to give essentially the same ratio of isomers of **12** as was obtained from **10** in yields of 15 and 9%, respectively (Table III).[30,31] Reaction of 1-chlorosulfinylapocamphane (**13**) with silver tetrafluoroborate also gives the same ratio of isomers of **12** within experimental error in 19% yield, along with 58% of **11** (Table III).

The common ratio of 1-chlorophenylapocamphane isomers in these experiments indicates that the fraction of reaction leading to alkylated products from the chloroformate **10**, the chlorosulfite 13, and the amine **9** involves a common intermediate.

The ratio of isomers of **12** obtained in the above reactions is consistent with the intermediacy of either a reac-

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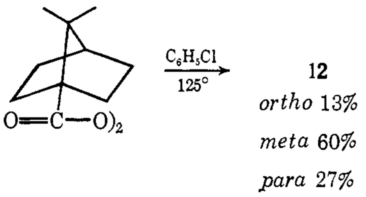
(28) D. I. Davies and C. Waring, *Chem. Commun.*, 263 (1965).

(29) Catalyzed and thermal rearrangements of fluoroformates to fluorides and carbon dioxide have been reported: S. Nakanishi, T. C. Meyers, and E. V. Jensen, *J. Amer. Chem. Soc.*, 77, 3099 (1955); K. O. Christe and A. E. Pavlath, *J. Org. Chem.*, 30, 3170 (1965); G. A. Olah and S. J. Kuhn, *ibid.*, 21, 1319 (1956); G. A. Olah and D. Kreienbühl, *ibid.*, **32**, 1614 (1967).

(30) Alkylations of aromatics by amines under diazotization conditions have been reported.[22,23]

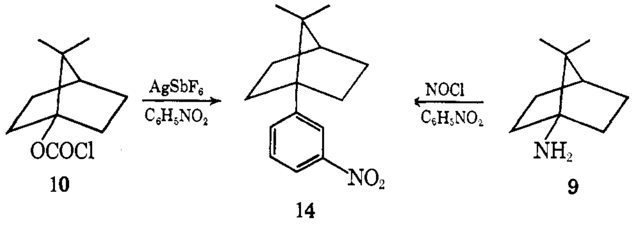
(31) Deamination of 1-aminonorbornane *via* the N-nitroamide and carbamate to give ester and 1-phenylnorbornane in benzene and 1-chloronorbornane in chlorinated solvents has recently been reported by E. H. White, H. P. Tiwari, and M. T. Todd, *J. Amer. Chem. Soc.*, 90, 4735 (1968). Radicals were ruled out as intermediates in these substitutions because the expected radical products norbornane and dimerized solvent were not observed.

tive and unselective cation[31] or a radical.[32,33] The positional selectivity of the radical was assessed by its presumed production in the decomposition of 1-apocamphane acyl peroxide at 125° in chlorobenzene.[34,35] This reaction gave a 23% yield of isomers of **12** in an *ortho*:*meta*:*para* ratio of 13:60:27.[36] The *ortho*:*meta* ratio of 13:60 shows that the species involved in the alkylation of chlorobenzene in the acyl peroxide decomposition at 125° is more selective than the species giving an *ortho*:*meta* ratio of 40:32 in the alkylations of chlorobenzene from **9**, **10**, and **13** at ambient temperature. Since selectivity would be expected to increase with decreasing temperature[37] if it is presumed that a free 1-apocamphyl radical is the species which attacks chlorobenzene in the peroxide decomposition, this radical is clearly not involved in the alkylations of chlorobenzene starting from **9**, **10**, and **13**.[38] On the other hand, the assumptions that the intermediate in the peroxide decomposition is truly free of the circumstances attendant to its formation or that ionic species which might be present in peroxide decompositions[39] would not react with solvent might be questioned.[40]



The position of alkylation of nitrobenzene appears to depend on the nature of the attacking species.[32] Radicals substitute predominantly at the *ortho* and *para* positions while cations form mainly *meta* products.[42] For example, alkylation of nitrobenzene by methyl radicals gives the nitrotoluenes in an *ortho*:*meta*:*para* ratio of 65:6:28; on the other hand, the nitration of nitrobenzene gives dinitrobenzenes in an *ortho*:*meta*:*para* ratio of 8:90:2.[43]

Reaction of 1-chloroformylapocamphane (**10**) with silver hexafluoroantimonate at ambient temperature in nitrobenzene gave a 24% yield of 1-*m*-nitrophenylapocamphane (**14**)[44] and 16% of 1-chloroapocamphane (**8**). *meta* substitution was also observed in 47% yield at 125° and in 4% yield upon reaction of apocamphylamine **9** with nitrosyl chloride at ambient temperature. The structural assignment to **14** rests on analytical and spectral data. The formation of the *meta* isomer **14** is diagnostic of attack on nitrobenzene by a cationic species.



These results strongly suggest that alkylations of the aromatic solvents by the chloroformate **10**, the amine **9**, and the sulfinyl chloride **13** proceed by a cationic species. Apparently the driving force provided by the loss of carbon dioxide, nitrogen, and sulfur dioxide is sufficient to allow the development of positive character at the bridgehead of the bicyclo[2.2.1] system. The novel alkylation of nitrobenzene[10] and the high yield of *meta* isomer in the alkylation of chlorobenzene might suggest an unusually reactive species. However, the extent of cationic character at the bridgehead carbon in the transition state for loss of the stable nonucleophilic leaving group or developed subsequently in other species cannot be decided with the present data.[45,47]

Although the alkylations of 1-aminoapocamphane (**9**), 1-chloroformylapocamphane (**10**), and 1-chlorosulfinylapocamphane (**13**) seem to involve a common cationic intermediate, it does not necessarily follow that this intermediate is a free bridgehead apocamphanyl carbonium ion. For example, reaction with the aromatic substrate could occur by front-side displacements to give chloronium ions,[31,48] π complexes, or equilibrating σ complexes[49] such that the common alkylated products could result from partitioning after the leaving group has been displaced.

Phenyl Chloroformate. The stability of aryldiazonium salts relative to alkyldiazonium ions suggested

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(32) The intermediacy of a radical in the deamination of a perchlorohomocubane bridgehead amine has been reported by K. V. Scherer, Jr., and R. S. Lunt, III, *J. Amer. Chem. Soc.*, 88, 2860 (1966).

(33) J. R. Shelton and C. W. Uzelmeier, *ibid.*, 88, 5222 (1966).

(34) M. S. Kharasch, F. Engelmann, and W. H. Urry, *ibid.*, **65**, 2428 (1943).

(35) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 332–387.

(36) The *ortho* compound appears to be produced in lower yield than expected. Cyclohexylchlorobenzenes are formed in 46% yield from the reaction of cyclohexane in chlorobenzene in the presence of di-*t*-butyl peroxide in an *ortho*:*meta*:*para* ratio of 54:34:12. The low *ortho* yield might be rationalized in terms of the steric requirements of the apocamphyl radical. Alternatively, the isomer assignments (see Experimental Section) might be questioned. It is clear that different ratios of 1-apocamphylchlorobenzenes are observed from the peroxide decomposition and the reaction of 10 with silver fluoro salts.

(37) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p 124.

(38) Reaction of the chloroformate 10 with silver tetrafluoroborate at 125° gave a 21% yield of 1-(chlorophenyl)apocamphane isomers, 12, in an *ortho*:*meta*:*para* ratio of 35:32:33. This is close to the results observed at ambient temperature. It is possible, however, that some equilibration of the products could have occurred under these conditions.

(39) F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *J. Amer. Chem. Soc.*, **86**, 2080 (1964).

(40) Reactions of 1-apocamphanecarboxylic acid with lead tetraacetate[28,41] at 125° in chlorobenzene gives 12 in an *ortho*:*meta*:*para* ratio of 40:44:16. The fact that this ratio is different from that produced in the peroxide decomposition or the chloroformate reaction suggests that the species produced in at least one of these cases is not free from the circumstances attendant to its formation or that substitution occurs directly without production of a free intermediate.

(41) J. Kochi, J. Bacha, and T. Bethea, *J. Amer. Chem. Soc.*, **89**, 6538 (1967), and references cited therein.

(42) B. R. Cowley, R. O. C. Norman, and W. A. Waters, cited by G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford, England, 1960, p 106; see also p 68 for phenylation.

(43) G. Olah and S. J. Kuhn, "Friedel–Crafts and Related Reactions," Vol. III, G. Olah, Ed., Interscience Publishers, New York, N. Y., 1964, p 1467; see also pp 1362, 1548 for sulfonation and chlorination. Alkylation of nitrobenzene does not seem to have been observed under Friedel–Crafts conditions: *ibid.*, Vol. I, 1963, p 34.

(44) We estimate that 3% of the *ortho* and *para* isomers of 1-nitrophenylapocamphane would have been detected. Attempts to obtain alkylation products by decomposition of 1-apocamphane acyl peroxide in nitrobenzene were not successful.

(45) Estimates of differences between planar and nonplanar tertiary carbonium ions favor the former by 13–25 kcal/mol.[26b,46]

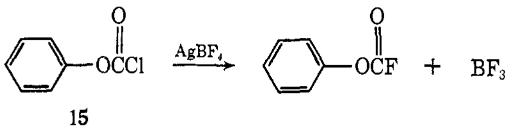
(46) R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964).

(47) Schleyer, *et al.*,[27b] have reported isomerization of a 1-norbornyl cation to a 2-norbornyl cation. In view of the high material balance, 94% for the reaction of 13 and silver fluoroborate, it does not appear that a rearrangement process competes effectively with the substitution reactions under the present conditions.

(48) P. Kovacic and J. J. Hiller, *J. Org. Chem.*, 30, 1581 (1965).

(49) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, 84, 1688 (1962); ref 43, Vol. I, 1963, pp 921–926.

that investigation of arylcarboxylium ions might be fruitful.[29] Reaction of phenyl chloroformate (**15**) with silver tetrafluoroborate in refluxing chlorobenzene for 2 hr to give boron trifluoride and phenyl fluoroformate has been reported[4] and the details are given in the Experimental Section.



15

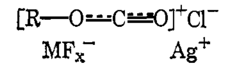
The formation of phenyl fluoroformate has precedent in the reactions of acylium ions.[5,9] Reaction of **15** with silver hexafluoroantimonate in toluene in the presence of tetramethylurea gave a 98% yield of silver chloride and an 88% yield of phenyl N,N-dimethylcarbamate.[49a] The carbamate could arise *via* the fluoroformate or by attack of tetramethylurea on an intermediate carboxylium ion.

The few per cent of carbon dioxide detected in the reaction of **15** with silver tetrafluoroborate was equivalent to a blank. In a series of experiments designed to promote cleavage of the phenyl oxygen bond, the reactions of **15** with silver hexafluoroantimonate, of phenyl chloroglyoxalate[50] with silver tetrafluoroborate and hexafluoroantimonate, and of phenyl chlorosulfite with silver tetrafluoroborate in toluene were investigated. With the tetrafluoroborate, 90–100% silver chloride was produced but no significant amounts of carbon dioxide were detected. The expected products of phenyl oxygen cleavage, biphenyls and fluorobenzene, were not found from any reactions. Phenols and carbonates, produced during the work-up and containing the aryl-oxygen bond intact, were found.

Reaction Pathway. The reactions of chloroformates with silver salts of nonnucleophilic anions in aromatic solvents yield products expected from cationic precursors. Alkyl chloroformates give dehalodecarboxylated products with a rate acceleration relative to the corresponding halide, suggesting that the loss of carbon dioxide provides a driving force for ionization similar to that ascribed to the loss of nitrogen from diazonium ions.

The formulation of the diazonium ion (**1**), the isocarboxonium (**2**), and the carboxylium ion (**3**) as reaction intermediates stresses the potential analogy among these species. However, the reactivity which can be attributed to these hypothetical species may also be assigned to activated complexes in which the loss of the stable nonnucleophilic species is concerted with other bond making or breaking events.

A simple rationale for the present results may be formulated in terms of **16**. The observed products may be accounted for by the loss of carbon dioxide and the precipitation of silver chloride[51] along with (1) donation of fluoride from the polyfluoroanion to give alkyl fluoride, (2) the loss of a proton to give olefin or cyclopropane, (3) hydride transfer to give rearranged products, and (4) alkylation of the aromatic solvent. Acyl fluoride could result from substitution of fluoride for chloride. The formation of product chloride could involve the loss of carbon dioxide from **16** and the formation of a carbon-chlorine bond.[52]



$$\underset{MF_x^-}{[R{-}O}{\cdots}\underset{Ag^+}{C{\equiv}O]^+Cl^-}$$

16

The latter possibility suggests that an alkyl chloride, even in the presence of a reacting system, might not serve as a suitable control reaction for chloride produced by the silver-catalyzed rearrangement of a chloroformate, since the chloride produced from the chloroformate might be formed in an ion aggregate close to the silver ion with a dispensation for further reaction. It is probable that these reactions in aromatic solvents, like the reactions of other halides with silver salts, involve ion aggregates.[53] The scheme involving **16** can, of course, be elaborated to include subspecies and intermediates. The effect of tetramethylurea on the course of the reaction is of interest. The details of these reactions will require further investigation. Meaningful comparisons with other reactions would best be made in the same solvent, with the same base and counterion, and with variation only in the nature of the nonnucleophilic leaving group.

The formal analogy linking the reactions of chloroformates and nonnucleophilic silver salts with the deaminations of amines should prove useful. A new and convenient entry to species previously observed in deamination reactions may be available. The reaction may be used to generate reactive cations in the presence of a nonnucleophilic counterion and to achieve substitutions at positions of low incipient cationic stability.

Experimental Section[54]

Materials. The commercially available solvents and reactants were purified by distillation and characterized by established physical constants and spectral data. Silver tetrafluoroborate, silver hexafluoroantimonate, nitrosyl tetrafluoroborate, and nitrosyl hexafluoroantimonate obtained from the Ozark-Mahoning Co. were dried at 25° for a minimum of 3 days at 0.05 mm over phosphorus pentoxide. A silver determination (Ni(CN)$_4^{2-}$ titration) showed the fluoroborate and hexafluoroantimonate salts to be 99.5 and 100%, respectively. Florex AA-LVM 60–90 mesh, a neutral Florisil obtained from the Floridin Company, St. Louis,

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[49a] Note Added in Proof. For an analogous reaction see G. M. Coppinger, *J. Amer. Chem. Soc.*, **76**, 1372 (1954).

[50] S. J. Rhodes and R. Michel, *ibid.*, **85**, 585 (1963).

[51] Silver chloride is calculated to be *ca.* 30% ionic from the values of L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

[52] P. G. Gassman and R. Cryberg (*J. Amer. Chem. Soc.*, **90**, 1355 (1968)) have recently reported silver ion catalysis of a chlorine rearrangement.

[53] Y. Pocker and D. N. Kevill, *ibid.*, **87**, 4760, 4771, 4778, 5060 (1965); G. S. Hammond, W. D. Emmons, C. O. Parker, B. M. Graybill, J. H. Waters, and M. F. Hawthorne, *Tetrahedron, Suppl.*, 1, 177 (1963); D. N. Kevill and V. V. Likhite, *Chem. Commun.*, 247 (1967); D. J. Pasto and K. Garves, *J. Org. Chem.*, **32**, 778 (1967); G. D. Parfitt, A. L. Smith, and A. G. Walton, *J. Phys. Chem.*, **69**, 661 (1965); G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Amer. Chem. Soc.*, **82**, 704 (1960); F. M. Battson and C. A. Kraus, *ibid.*, **56**, 2017 (1934); D. W. A. Sharp and A. G. Sharp, *J. Chem. Soc.*, 1855 (1956).

[54] Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrometer or a Perkin-Elmer Infracord with 10% carbon tetrachloride solutions unless otherwise noted. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates A-60 spectrometer with 5–20% carbon tetrachloride solutions unless otherwise noted and are reported in δ, parts per million (ppm), relative to the internal standard, tetramethylsilane. The mass spectra were determined by Mr. J. Wrona on an Atlas CH4 mass spectrometer. Microanalyses were performed by Mr. J. Nemeth and his associates. Melting points were determined with a Büchi apparatus and are uncorrected. Glpc was performed on an Aerograph Model A-90-P instrument with a thermal conductivity detector and on an Aerograph Model A-600-B "Hy-fi" with a flame ionization detector. Yields (±3%) determined by glpc are corrected for the differences in thermal conductivity between the internal standards and the products. Separations were achieved by preparative glpc.

Mo., was invaluable in the chromatographic purification of alkyl chloroformates.

General Procedure for the Preparation of Chloroformates. A diethyl ether solution of the alcohol was added dropwise to a cold five- to tenfold excess of phosgene in diethyl ether. After warming overnight to ambient temperature under a positive nitrogen flow, the reaction mixture was washed with 5% aqueous sodium bicarbonate and dried ($MgSO_4$), and the solvent was evaporated to the crude product.

Cyclohexyl chloroformate[55] was prepared in 82% yield from cyclohexanol. *n*-Propyl chloroformate and phenyl chloroformate were obtained from Eastman Organic Chemicals. *n*-Propyl and isopropyl fluorides were prepared by the method of Edgell and Parts.[56] 1-Apocamphane acyl peroxide was prepared by the method of Kharasch, *et al.*[34] 1-Aminoapocamphane was prepared by the reaction of 1-apocamphanecarboxylic acid with hydrazoic acid as reported by Kursanov and Vitt.[57] The physical properties and ir and nmr spectra of these compounds were consistent with the established structures.

1-Apocamphanol was prepared by direct oxidation of 1-apocamphanecarboxylic acid[57] by the method of Luong.[58] To a solution of the acid, 4.00 g (0.024 mol), at −10° in 25 ml of concentrated sulfuric acid, 5.0 ml (0.024 mol) of 30% hydrogen peroxide was added at a rate such that the reaction temperature did not exceed 2°. The mixture was stirred for 8 hr at room temperature, poured onto ice, and worked up by extraction with hexane to give 2.13 g (0.015 mol; 63%) of 1-apocamphanol, mp 161–163° (sealed tube; lit.[26a] mp 154°). The infrared, nmr, and mass spectra were consistent with the assigned structure.

1-Chloroformylapocamphane (10) was prepared by addition of an equimolar amount of *n*-butyllithium and 1-apocamphanol in dry tetrahydrofuran to a fourfold excess of phosgene in tetrahydrofuran. Extraction with hexane and subsequent elution from a Florex column with distilled pentane afforded 50% of pure 1-chloroformylapocamphane, mp 65–66°; ir 1780, 1155, 844, 828, and 687 cm^{-1}; δ 1.04 (s, 6, $\mathrm{C}(\mathrm{C}H_3)_2$) and 0.90–2.50 (broad, 9); mass spectrum (70 eV) ($M\cdot^+$).

Anal. Calcd for $C_{10}H_{15}O_2Cl$: C, 59.25; H, 7.46; Cl, 17.49. Found: C, 59.55; H, 7.52; Cl, 17.15.

1-Chlorosulfinylapocamphane (13) was prepared by reaction of 1-apocamphanol and a tenfold excess of thionyl chloride at room temperature. The crude material obtained on evaporation of the excess thionyl chloride contained *ca.* 25% 1-apocamphane disulfite: ir 1220, 1370 (d), 990, and 853 cm^{-1}; nmr δ 1.09 (s, $\mathrm{C}(\mathrm{C}H_3)_2$ of **13**) and 1.02 (s, $C(CH_3)_2$ of disulfite).

1-Apocamphane disulfite and thionyl chloride are apparently in equilibrium with 1-chlorosulfinylapocamphane.[59] A sample of pure dialkyl sulfite, allowed to stand overnight in an excess of thionyl chloride, gave a mixture containing 74% chlorosulfite **13** and 26% dialkyl sulfite.

General Procedure for the Reaction of Chloroformates with Silver Salts. A solution of the chloroformate was added to a 5% excess of the silver salt in chlorobenzene or nitrobenzene at ambient temperature. Reaction mixtures were 0.5–1.0 *M* in chloroformate. The initially homogeneous solutions became warm as the precipitation of silver chloride and evolution of carbon dioxide proceeded rapidly. The amount of carbon dioxide produced was determined gravimetrically as the acid-soluble material, barium carbonate, produced in three barium hydroxide traps. The amount of silver chloride produced was determined gravimetrically as the ammonium hydroxide soluble material. Reaction times of 8 hr were used initially but times as short as 20 min give the same products. The separated products were identified by spectral and chemical criteria (*vide infra*).

For the reactions in the presence of tetramethylurea, the indicated excess of this compound was added before the chloroformate and removed after reaction by extraction with 5% aqueous hydrochloric acid. Carbon dioxide was determined directly by absorption on Ascarite.

Reaction of Cyclohexyl Chloroformate. The yield of the cyclohexylchlorobenzene isomers was determined by glpc analysis with a 5 ft × 0.25 in. 20% Apiezon L column at 190° and 1,2,4,5-tetrachlorobenzene as the internal standard. Preparative glpc with a 3 ft × $^3/_8$ in. 20% Apiezon L column at 190° gave the separated compounds. *ortho* isomer: $n^{29}\mathrm{D}$ 1.5420 ($n^{29}\mathrm{D}$ lit.[60] 1.5429); ir (CS_2) 745 cm^{-1};[61] nmr δ 1.59 ($(-\mathrm{C}H_2)_5-$), 3.00 (m, $\mathrm{C}H\mathrm{Ar}$), and 7.14 (m, $\mathrm{Ar}H$). *para* isomer: $n^{29}\mathrm{D}$ 1.5367 ($n^{28}\mathrm{D}$ lit.[62] 1.5386); ir (CS_2) 817 cm^{-1};[61] nmr δ 1.55 (m, 10, $(-\mathrm{C}H_2)_5-$), 2.40 (m, $\mathrm{C}H\mathrm{Ar}$), and 7.22 (m, 4, $\mathrm{Ar}H$). *meta* isomer: ir (CS_2) 690 and 775 cm^{-1};[61] nmr δ 1.60 (m, 10, $-(\mathrm{C}H_2)_5-$), 2.40 (m, 1, $-\mathrm{C}H\mathrm{Ar}-$), and 7.10 (m, 4, $\mathrm{Ar}H$). The *ortho* and *para* isomers gave *o*- and *p*-chlorobenzoic acids, respectively, upon oxidation. The organic products from the reaction of **4** and silver tetrafluoroborate in the presence of 2 equiv of tetramethylurea (Table I) were analyzed by glpc with a 6 ft × 0.25 in. 20% Carbowax 20M column and compared with authentic materials by ir, nmr, and mass spectral criteria after collection. Microanalyses were also obtained on these products. Reaction of cyclohexyl chloroformate with silver tetrafluoroborate in the presence of 2 equiv of tetramethylurea and 1 equiv of cyclohexene under the same conditions gave 123% cyclohexene (based on the chloroformate as 100%), 38% cyclohexyl fluoride, 14% cyclohexyl chloride, and *ca.* 0.5% cyclohexylchlorobenzene isomers.

Reaction of *n*-Propyl Chloroformate. The yield of the isopropylchlorobenzene isomers was determined by glpc on the 5-ft Apiezon L column with 1,3,5-trimethylbenzene as the internal standard. The isomer mixture gave the correct microanalysis and the expected molecular ion at *m/e* 154 and 156 on mass spectral analysis. Preparative glpc gave the separated isomers. *ortho* isomer: ir (CS_2) 758 cm^{-1};[61] nmr δ 1.22 (d, 6, J = 14 Hz, $-\mathrm{CH}(\mathrm{C}H_3)_2$), 3.38 (septet, 1, J = 14 Hz, $-\mathrm{C}H(\mathrm{CH}_3)_2$), and 7.13 (m, 4, $\mathrm{Ar}H$). *para* isomer: ir (CS_2) 834 cm^{-1};[61] nmr δ 1.21 (d, 6, J = 14 Hz, $-\mathrm{CH}(\mathrm{CH}_3)_2$), 2.81 (septet, 1, J = 14 Hz, $-\mathrm{C}H(\mathrm{CH}_3)_2$), and 7.08 (m, 4, $\mathrm{Ar}H$). An 11% yield of diisopropylchlorobenzene isomers was determined by glpc on the 6-ft Carbowax 20M column with *o*-nitrotoluene as the internal standard. The isomer mixture was identified by ir, nmr, mass spectral, and analytical data.

The volatile products from the *n*-propyl chloroformate reaction were trapped after the effluent gases had passed through a 0° trap and an Ascarite trap. Glpc analysis was performed on the effluents and the reaction mixture with a 25 ft × 0.25 in. 20% dibenzyl ether column and a 12 ft × 0.25 in. 15% XF-1150 column with *trans*-2-butene and cyclohexane, respectively, as internal standards.

The *n*-propylchlorobenzene isomers (Table II) were analyzed by glpc with a 6 ft × $^1/_8$ in. 5% Apiezon L column in the Aerograph Model A-600-B "Hy-fi." Formation of these isomers was confirmed by mass spectral analysis, correct microanalysis, glpc comparison with authentic compounds, and nmr examination of the gross isomer mixture. The 100-MHz nmr spectrum clearly indicated the presence of *n*-propylchlorobenzenes. Propene was identified by comparison of a gas phase infrared spectrum with authentic material and by mass spectral analysis. Spectral evidence for the formation of cyclopropane was obtained by a 100-MHz nmr spectrum of the mixture of propene[63a] and cyclopropane:[63b] nmr (CCl_4) δ 5.83 (m, 1.0, $=\mathrm{C}H\mathrm{CH}_3$), 5.03 (m, 1.9, $\mathrm{C}H_2=$), 1.72 (m, 3.1, $=\mathrm{CHC}H_3$), and 0.21 (s, cyclopropane).

Reaction of 1-Chloroformylapocamphane. The mixture of 1-chlorophenylapocamphane isomers **12** was collected from preparative glpc on a 6 ft × $^3/_8$ in. Carbowax 20M column.

Anal. Calcd for $C_{15}H_{19}Cl$: C, 76.74; H, 8.16. Found: C, 76.49; H, 8.14.

Dechlorination of 1-chlorophenylapocamphane to 1-phenylapocamphane was accomplished by use of a procedure similar to that reported by Bruck.[64] The isomer mixture, 0.058 g of **12** (0.00025 mol) in 4 ml of THF, was allowed to react with *ca.* 3 mg of lithium metal and 60 μl of *t*-butyl alcohol under reflux for 1.5 hr.

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(55) J. A. Saunders, R. J. Slocombe, and E. E. Hardy, *J. Amer. Chem. Soc.*, 73, 3796 (1951).

(56) W. F. Edgell and L. Parts, *ibid.*, 77, 4899 (1955).

(57) D. N. Kursanov and S. V. Vitt, *J. Gen. Chem. USSR*, **25**, 2401 (1955).

(58) T. M. Luong and D. Lefort, *Bull. Soc. Chim. Fr.*, **29**, 827 (1962). We are grateful to Professor James A. Deyrup for bringing this procedure to our attention.

(59) Analogous equilibrium has been studied by W. E. Bissinger and F. E. Kung, *J. Amer. Chem. Soc.*, **69**, 2158 (1947).

(60) T. H. McGuine and M. F. Dull, *ibid.*, **69**, 1469 (1967).

(61) The usual correlations are *ortho* 735–770 cm^{-1}, *meta* 680–725 and 750–810 cm^{-1}: *para* 810–860 cm^{-1}: K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1964, pp 26–27; L. J. Bellamy, "The Infrared Spectrum of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 75–79. Other isomer assignments have been made on this spectral basis: G. A. Olah and N. A. Overchuk, *J. Amer. Chem. Soc.*, 87, 5786 (1965), footnote 33.

(62) H. A. Mayes and E. F. Turner, *ibid.*, 51, 500 (1929).

(63) (a) A. A. Bothner-By and C. Naar-Colin, *ibid.*, 83, 231 (1961); (b) K. B. Wiberg and B. J. Nist, *ibid.*, 83, 1226 (1961).

(64) P. Bruck, *Tetrahedron Lett.*, 4491 (1962).

The reaction was then stirred at room temperature for 114 hr and 2 mg of lithium metal and 25 μl of *t*-butyl alcohol were added every 24 hr. The reaction was worked up by dilution with water and extraction with ether. A glpc analysis performed with the 5-ft Apiezon L column and 1,2,4,5-tetrachlorobenzene as internal standard indicated a 98% yield of 1-phenylapocamphane. The product was isolated by preparative glpc and the infrared, nmr, mass spectra, and glpc retention times were identical with those obtained on the independently synthesized compound.[28]

Ozonolysis of 1-phenylapocamphane to 1-apocamphanecarboxylic acid (**17**) was accomplished by the procedure of Griffin and Veber.[65] 1-Phenylapocamphane, 0.10 g (0.0005 mol), in 6 ml of 90% acetic acid was subjected to ozonolysis for 4 hr at room temperature, after which 5 ml of 30% hydrogen peroxide was added and the solution was allowed to stand for 48 hr. After addition of palladium on carbon (10%) to decompose the excess peroxide, the mixture was filtered, acidified, and extracted with hexane. Isolation of the acidic product gave 0.025 g (0.0015 mol) of 1-apocamphanecarboxylic acid (30%). A melting point, ir, and mass spectral comparison with authentic material[57] established identity.

Preparative glpc of **12** gave two materials. The compound of shorter retention time is the *meta* isomer: ir (CCl_4) 1597, 1480, 1380 (d), and 698 cm^{-1} and (CS_2) 771 and 688 cm^{-1};[61] nmr δ 0.93 (s, 6, $C(CH_3)_2$), 1.00 to 2.55 (broad, 9), and 7.15 (m, 4, Ar*H*); mass spectrum *m/e* 234–236 (M·+). Glpc on a 150-ft BDS capillary column with flame ionization detection gave one peak.

The material of longer retention time is a mixture of *ortho* and *para* isomers: ir (CCl_4) 1385 (d), 828, and 712 cm^{-1} and (CS_2) 813[61] and 742[61] cm^{-1}; nmr δ 0.85 (s, 1, $C(CH_3)_2$), 1.29 (s, 1.4, $C(CH_3)_2$), 0.85–2.95 (broad, 3.3), and 7.15 (m, 1, Ar*H*); mass spectrum *m/e* 234–236 (M·+). Glpc analysis of the isomers with a BDS Golay capillary column at 165° showed that this material was two components in a 1.5:1 ratio consistent with the ratio of the two different methyl resonances in the nmr. The *ortho* compound is considered the major component on the basis of the downfield shift of the *gem*-dimethyl groups.[66] Several attempts to oxidize the isomers to chlorobenzoic acids failed because of oxidation of the aromatic ring. The dependence of the distinction between the *ortho* and *para* isomers on the basis of only the difference in chemical shift of the *gem*-dimethyl groups can be considered provisional; a change in the assignment would not affect the conclusions concerning the course of the reaction.

1-Fluoroapocamphane was purified by preparative glpc with the 3-ft Apiezon L column at 135°: ir 1450, 1370 (d), 1303, 1110, and 1050 cm^{-1}; nmr d 1.02 (s, 6, $C(CH_3)_2$) and 1.00–2.25 (broad, 9); fluorine nmr 11,015 cps (s, fluorotrichloromethane as the solvent and internal standard);[67] mass spectrum *m/e* 142 (M·+).

Anal. Calcd for $C_9H_{15}F$: C, 76.01; H, 10.64. Found: C, 75.74; H, 10.54.

1-Chloroapocamphane was identified by comparison of ir, nmr, and mass spectra with those of authentic material.[26a]

The yields of the 1-chlorophenylapocamphane isomers were determined by glpc on the 5-ft Apiezon L column with 1,2,4,5-tetrachlorobenzene as the internal standard. The isomer distributions were determined by nmr analysis by integration of the *gem*-dimethyl singlets at a sweep width of 100 cps, or by glpc analysis with a 150-ft BDS Golay capillary column. There was a maximum deviation of ±2% between the two methods of analysis.

Control experiments established that less than 10% of the *meta* isomer is converted to the combined *ortho–para* isomers and less than 30% of the latter is converted to the former in the presence of the reaction of **10** with silver tetrafluoroborate in chlorobenzene for 60 hr. In a separate experiment it was shown that less than 10% of the *ortho–para* isomers was converted to the *meta* isomer in the presence of reaction of *n*-propyl chloroformate with silver tetrafluoroborate in chlorobenzene.

When nitrobenzene was used as the solvent, analytical and preparative glpc with a 2.5 ft × 0.25 in. Apiezon L column at 230° with 4-chlorobiphenyl as the internal standard gave 1-*m*-nitrophenylapocamphane (**14**): ir (CS_2) 1340, 795 and 680[61] cm^{-1}; nmr δ 0.95 (s, 6, $C(CH_3)_2$), 1.00–2.40 (broad, 9), 7.34 (m, 2, ArH), and 7.92 (m, 2, Ar*H*);[68] mass spectrum *m/e* 245 (M·+).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.50; H, 7.92; N, 5.51.

Deamination of 1-Aminoapocamphane in Aromatic Solvents. The amine **9** was dissolved in the appropriate solvent and the nitrosating agent added at ambient temperature. Glpc analysis and separation of the reaction products reported were carried out as for the chloroformate.

The Thermal Decomposition of 1-Apocamphane Acyl Peroxide in Chlorobenzene. A mixture of 0.058 g (0.00017 mol) of 1-apocamphane acyl peroxide and 2.5 ml of chlorobenzene was heated for 20 hr at 125°. The glpc internal standard analysis, isolation, and acquisition of spectral data of the bridgehead alkylated chlorobenzene products were performed as above. An *ortho*:*meta*:*para* isomer ratio of 13:60:27 was observed.

The ester, 1-apocamphyl apocamphane-1-carboxylate, and the hydrocarbon, 1-apocamphylapocamphane, were formed in the reaction (18%, as a mixture) as reported[34] for the thermal decomposition of 1-apocamphane acyl peroxide in carbon tetrachloride.

Control experiments established that 1-chloroformylapocamphane was stable in chlorobenzene at 125° for 2.5 hr and in the presence of boron trifluoride at room temperature for 24 hr. Heating the latter solution to 60° for 4 hr gave *ca.* 8% 1-chloroapocamphane. Additional heating at 60° for 20 hr converted all the chloroformate to 48% bridgehead chloride and 18% 1-chlorophenylapocamphane isomers. Control experiments established that 1-chloroapocamphane was stable to silver tetrafluoroborate and to boron trifluoride in chlorobenzene at ambient temperature.

Reaction of Phenyl Chloroformate. The formation of silver chloride was slower than in the cases of alkyl chloroformates and was promoted by refluxing the reaction mixture for 1.5 hr. A 46% yield of phenyl fluoroformate, bp 143°, was obtained by careful distillation with a spinning-band column. The nmr spectrum was consistent with this assignment and the infrared spectrum was identical with that of authentic material.[69] In another run ethanol was added after formation of the silver chloride (obtained in 100% yield) and the reaction mixture was shown to contain 82% phenyl ethyl carbonate. This provides a better estimate of the actual yield of phenyl fluoroformate than does the isolated yield.

Glpc analysis of the reaction mixture under various conditions in attempts to find other possible products, fluorobenzene, phenyl ethyl ether, biphenyls, or aryl esters showed that less than 5% of each compound was present. Reaction of phenylchloroformate with silver hexafluoroantimonate in toluene in the presence of tetramethylurea (2 equiv) at 100° gave a 98% yield of silver chloride and an 82% yield of phenyl N,N-dimethylcarbamate, identified by glpc and by spectral comparison with authentic material. Phenyl chloroformate was shown to be stable to lithium fluoroborate and to ethanol in refluxing chlorobenzene.

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