Reactions of Apotricyclyl, Apocamphor, and Apobornenyl Chloroformates with Silver(I). Generation and Aromatic Substitution of a Bridgehead Radical and a Bridgehead Cation

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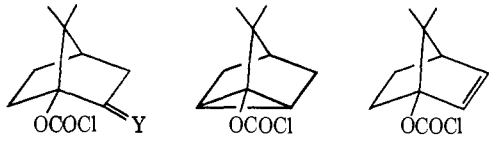
Abstract: Reactions of the bridgehead 1-chloroformyl group in apotricyclyl (**2**), apocamphor (**3**), and apobornenyl (**4**) systems with silver(I) are shown to involve an intermediate bridgehead radical, carboxylium ion, and cation, respectively, although it is suggested that the radical may arise from **2** *via* a cation. The reactions of 1-chloroformylapotricyclene (**2**) with silver tetrafluoroborate, of 1-aminoapotricyclene (**8**) with nitrosyl chloride, and of tricyclenic acid (**9**) with lead tetraacetate and thermolysis of 1-apotricyclene acyl peroxide (**10**) in chlorobenzene give 1-chlorophenylapotricyclene isomers (**7**) in a ratio which is characteristic of a radical intermediate. Treatment of 1-chloroformylapocamphor (**3**) with silver tetrafluoroborate yields 1-fluoroformylapocamphor (**11**), presumably *via* a carboxylium ion. The reactions of 1-chloroformylapobornylene (**4**) with silver hexafluoroantimonate and of 1-(*N*-benzoyl)aminoapobornylene with dinitrogen tetroxide in chlorobenzene give a ratio of 1-chlorophenylapobornylene isomers (**13**) characteristic of a cation which has essentially the same reactivity as the corresponding 1-apocamphyl cation. The high reactivity of the 1-apocamphyl cation is demonstrated by its unusually low substrate and positional selectivities in electrophilic aromatic substitutions which proceed *via* rate-limiting formation of a σ complex, at least for toluene and benzene. Chlorobenzene and nitrobenzene are also subject to electrophilic attack by the bridgehead cation, and nitrobenzene is found to be only about seven times less reactive than benzene in this substitution.

The ability of the chloroformate function to become a potent heterolytic leaving group on reaction with silver(I) provides a new method for the formation of cations at positions at which ionization is usually difficult.[1-3] In particular, aromatic substitution at the bridgehead position of 1-chloroformylapocamphane (**1**) has been shown to involve the bridgehead cation of this bicyclo[2.2.1]heptane.[3,4] We now report a study of 1-apocamphane bridgehead reactivity in systems in which the bridgehead is incorporated into a three-membered ring, adjacent to a carbonyl group, or adjacent to a carbon–carbon double bond. Specifically, the reactions of 1-chloroformylapotricyclene (**2**), -apocamphor (**3**), and -apobornene (**4**) with silver(I) in chlorobenzene



1, Y = H_2 **2** **4**
3, Y = O

have been studied and the structural changes in **2** and **3** found to have a significant effect on the course of the reactions. Positional and substrate selectivities in electrophilic aromatic substitutions by the 1-apocamphyl cation have also been investigated and found to be consistent with the high reactivity expected for a bridgehead cation from **1**.

(1) P. Beak, J. T. Adams, and J. A. Barron, *J. Amer. Chem. Soc.*, **96**, 2494 (1974), and references cited therein.
(2) D. N. Kevill, "The Chemistry of Acyl Halides," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 427–433.
(3) P. Beak, R. J. Trancik, and D. A. Simpson, *J. Amer. Chem. Soc.*, **91**, 5073 (1969).
(4) (a) For a general review of bridgehead reactivity, see R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicycl. Chem.*, **1**, 283 (1966); (b) for a recent review of bridgehead cations, see R. C. Fort, Jr., "Carbonium Ions," Vol. 4, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1973, p 1783.

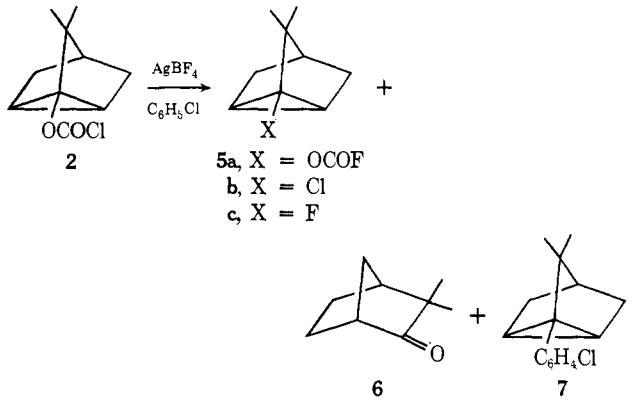
Results and Discussion

Syntheses. The sensitivity of the substituents in precursors to **2**, **3**, and **4** required protection of groups and modification of the procedures previously used for syntheses in this series,[3,5] as shown in Schemes I–III in the Experimental Section. The key features for each case are the stability of the lithium salt of a cyclopropanol[6] to ring opening[7] (step b, Scheme I), the mild hydrolysis of an ethylene ketal[8] with boron trichloride at −70° (step e, Scheme II) in a sequence required to prevent rearrangement,[9] and the stability of a primary benzamide to the excess methyllithium required for the elimination of a tosylhydrazone[10] (step b, Scheme III). The product structures are based on spectral and analytical properties, chemical precedent for the conversions, and, in the case of **4**, catalytic hydrogenation of the unsaturated alcohol to apocamphanol.

Apotricyclene Bridgehead Systems. The reaction of 1-chloroformylapotricyclene (**2**) with a slight excess of silver tetrafluoroborate in chlorobenzene at ambient temperature gives 63% carbon dioxide, 82% silver chloride, 17% 1-fluoroformylapotricyclene (**5a**), 7% 1-chloroapotricyclene (**5b**), 18% 1-fluoroapotricyclene (**5c**), 8% camphenilone (**6**), and 24% 1-chlorophenylapotricyclenes (**7**). The organic products were purified by preparative glpc and identified by ir, nmr, and mass spectral properties. The seven-line nmr pattern, which is particularly characteristic of apotricyclic systems,[11] is

(5) P. D. Bartlett and L. H. Knox, *J. Amer. Chem. Soc.*, **61**, 3184 (1939).
(6) C. H. DePuy and L. R. Mahoney, *J. Amer. Chem. Soc.*, **81**, 4891 (1959).
(7) P. Lipp and R. Padberg, *Ber.*, **54**, 1316 (1921).
(8) S. D. Gero, *Tetrahedron Lett.*, 591 (1966).
(9) A. Nickon, T. Nishida, and Y. Lin, *J. Amer. Chem. Soc.*, **91**, 6860 (1969); A. Nickon, T. Nishida, J. Frank, and R. Muneyuki, *J. Org. Chem.*, **36**, 1075 (1971); J. V. Paukstelis and D. N. Stephens, *Tetrahedron Lett.*, 3549 (1971).
(10) R. H. Shapiro and J. H. Duncan, *Org. Syn.*, **51**, 66 (1971).
(11) B. H. Jennings and G. B. Herschbach, *J. Org. Chem.*, **30**, 3902 (1965).

observed for **5a–c** and **7**. The fluoroformate **5a** was also characterized by analysis, the halides **5b** and **5c** by



2 **5a**, X = OCOF; **b**, X = Cl; **c**, X = F

6 **7**

high resolution mass spectrometry, and the ketone **6** by comparison with authentic material. The substitution products are precedented by similar products from 1-apocamphyl and phenyl chloroformates,[3] and the ketone **6** is presumed to arise from nucleophilic attack on the carbonyl by adventitious water followed by loss of carbon dioxide and ring opening of the resulting cyclopropanol.

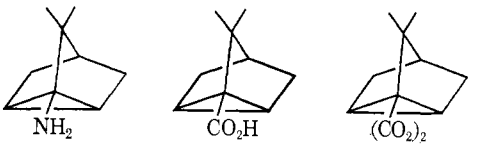
Although the chlorobenzene substitution products **7** have spectral and analytical properties consistent with those expected for a mixture of isomers, preparative glpc gives, as one component, a mixture of ortho and meta isomers, *7o* and *7m*, in which the ortho compound is predominant and, as a second component, a mixture containing some uncharacterized substitution products, in addition to the para isomer, *7p* + x. In further work (*vide infra*), the solvent substitution products were characterized by glpc directly from the reaction mixture by the ratios *7o*:*7m* and *7o*:*7m*:*7p* + x with the recognition that the latter ratio, although less soundly based, is useful for comparison of different reactions. These ratios are reported for the reaction of **2** and silver fluoroborate as the first case in Table I, although it should be noted that for this entry the ratios are apparently not those of the initially formed mixture. The instability of **7** to the reaction conditions was demonstrated in two ways. First, a mixture of *7o*:*7m*:*7p* + x of 57:31:12 (±2) in chlorobenzene is converted to a ratio of 71:24:5 (±2) in 60% yield, in the presence of ethyl chloroformate and silver tetrafluoroborate at ambient temperature. Secondly, the reaction of **2** with silver tetrafluoroborate in chlorobenzene, in the presence of 1 equiv of the base tetramethylurea,[3] yields 0.8% **7** in the ratio *7o*:*7m*:*7p* + x of 51:26:23, the second entry in Table I. Apparently, in the absence of base, some of the 1-chlorophenylapotricyclenes are partially destroyed and/or isomerized.

Table I. 1-Chloroapotricyclene Isomers from the Reactions of Functionally Substituted 1-Apotricyclenes in Chlorobenzene

Substrate	Reagent	*T*, deg	%	*7o*:*7m*[a]	*7o*:*7m*:*7p* + x[a]
2	$AgBF_4$	Ambient	24	3.6 ± 0.6	72:20:8 ± 2
2	$AgBF_4$, tetramethylurea	Ambient	0.8	2.0 ± 0.2	51:26:23 ± 2
8	NOCl	0	3	2.6 ± 0.3	59:23:18 ± 2
9	$Pb(OAc)_4$	130	26	1.8 ± 0.2	56:31:13 ± 2
10		125	42	1.4 ± 0.1	50:35:15 ± 2

[a] Errors are three times the standard deviations.

In order to compare the aryl substitution from **2** with those of other functionally substituted apotricyclenes, the reactions of 1-aminoapotricyclene (**8**) with nitrosyl chloride, of tricyclenic acid (**9**) with lead tetraacetate, and of 1-apotricyclene acyl peroxide (**10**) in chlorobenzene were investigated. The 1-chlorophenylapotricyclenes **7** were formed in each case in the yields and ratios given in Table I. A control experiment established that *7o* and *7m* were stable, within ±4%, in the presence of the thermolysis of **10**. Attempts at arylation of solvent nitrobenzene by reaction of **2** with silver tetrafluoroborate or reaction of **8** with nitrosyl chloride were not successful.



8 **9** **10**

The aryl substitutions by the 1-apotricyclenes **3**, **8**, **9**, and **10** on chlorobenzene appear, from the ratios of the positional isomers,[12] to arise from attack of a radical on the aromatic substrate. For comparison with the results reported in Table I, ortho:meta and ortho:meta:para ratios for the phenylation of chlorobenzene by different phenyl radical precursors at different temperatures are summarized in Table II. The values and ranges in the ratios of products in the two tables are comparable and provide support for the suggestion that the dechlorodecarboxylation of **2**, the deamination of **8**, the oxidative decarboxylation of **9**, and the thermolysis of **10** all produce the 1-apotricyclyl radical. While there is an analogy for radical formation in the latter three cases,[3,13–16] this appears to be the first case of radical formation in a silver(I)-promoted reaction of chloroformates.[17] The small differences in product ratios within Tables I and

(12) (a) G. H. Williams, *Chem. Soc. Spec. Publ.*, No. 24, 32 (1970); (b) H. I. M. Dov, G. Vernin, and J. Metzger, *Bull. Soc. Chim. Fr.*, 4604 (1971).

(13) K. V. Scherer, Jr., and R. S. Lunt, III, have reported that a radical is formed at the bridgehead on nitrosation of a perchlorohomocubylamine [*J. Amer. Chem. Soc.*, **88**, 2860 (1966)]. The formation of a bridgehead radical from **8** can be taken to suggest that radical formation in Scherer's case is not primarily due to destabilization of the incipient cation by the inductive effect of the chlorines but is an intrinsic effect to be expected at carbons which have a high degree of angle strain.

(14) For discussions of the formation of aryl radicals from arenediazonium ions, see (a) H. Zollinger, *Accounts Chem. Res.*, **6**, 335 (1973); (b) J. K. Kochi, "Oxidation-Reduction Reactions of Free Radicals," J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, p 591, and references cited therein.

(15) (a) R. A. Sheldon and J. K. Kochi, *Org. React.*, **19**, 279 (1972), present a convincing case for the intermediacy of radicals in lead tetraacetate oxidative decarboxylation of carboxylic acids. (b) Formation of a cyclopropyl radical and its attack on benzene by this process have been reported: T. Aratani, Y. Nakanisi, and H. Nozaki, *Tetrahedron Lett.*, 1809 (1969).

(16) The thermal decomposition of 1-apocamphane acyl peroxide *via* a radical is a classic case: (a) M. S. Kharasch, F. Engelmann, and W. H. Urry, *J. Amer. Chem. Soc.*, **65**, 2428 (1943); (b) ref 4a, pp 337–343; (c) D. F. DeTar and D. V. Wells, *J. Amer. Chem. Soc.*, **82**, 5839 (1960), and references cited therein.

(17) In terms of reactive intermediates, this is the first of the dehalodecarboxylations of haloformates which is similar to the dehalodecarboxylation of acyl hypohalides, well known as the Hunsdieker reaction; see C. V. Wilson, *Org. React.*, **9**, 332 (1957); K. Herwig and C. Rüchardt, *Chem. Ber.*, **105**, 363 (1972), and references cited therein.

Table II. Chlorodiphenyl Isomers from the Reactions of Different Phenyl Radical Precursors in Chlorobenzene

Substrate	T, deg	o:m	o:m:p	Ref
$C_6H_5NHNH_2$	0	2.9	65:22:13	*a*
$C_6H_5N_2^+BF_4^-$ [b]	10	2.3	59:25:16	*c*
$C_6H_5N(NO)COCH_3$	20	3.0	64:21:15	*d*
$(C_6H_5COO)_2$	80	2.1	55:26:19	*e*
$(C_6H_5CO_2)_2AgI$	130	2.5	60:24:16	*f*

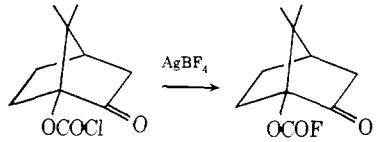
[a] R. L. Hardie and R. H. Thomson, *J. Chem. Soc.*, 2512 (1957). [b] The solvent is dimethyl sulfoxide. [c] M. Kobayashi, H. Minato, N. Kobori, and E. Yamada, *Bull. Chem. Soc. Jap.*, **43**, 1131 (1970). [d] M. J. Perkins, "Free Radicals," J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, p 261. [e] G. H. Williams, *Chem. Soc. Spec. Publ.*, **No. 24**, 32 (1970). [f] D. Bryce-Smith and P. Clark, *J. Chem. Soc.*, 2264 (1956).

II may result from differences in temperature or reflect small degrees of product instability, incursions of other substitution processes, or the possibility that radicals from the different precursors are not totally free.

The conclusions that the present aryl substitutions of 1-chloroformylapotricyclene (**2**) and 1-aminoapotricyclene (**8**) involve a bridgehead radical, whereas 1-chloroformylapocamphane (**1**) and 1-aminoapocamphane react *via* a bridgehead cation,[3] suggest that incorporation of the bridgehead of a bicyclo[2.2.1]heptane into a cyclopropane ring increases the energy of bridgehead cation to the point that it is either not formed or, if formed, does not have sufficient lifetime to alkylate the solvent.[18,19] Molecular mechanics calculations[20,21] suggest that angle strain is the dominant factor in the inhibition of ionization at the bridgehead of bicyclo[2.2.1]-heptanes, and such calculations support experimental demonstrations that this restraint is substantially reduced for bridgehead radicals.[4a,20,22] The possibility of ionization at the 1-position of apotricyclenes is suggested, however, by the fact that **8** reacts with nitrous acid in acetic acid to give 1-acetoxynortricyclene[23] and the report that 1-nortricyclyl triflate undergoes solvolysis in 60% aqueous ethanol, albeit at 186° and at a rate approximately four powers of ten less than that of 1-norbornyl triflate.[24,25]

Accordingly, the formation of silver chloride, carbon dioxide, **5b** and **5c**, as well as analogy,[3,23,24] may be taken to suggest that the 1-apotricyclene cation is formed in the reaction of **2** with silver tetrafluoroborate. The highly energetic cation,[27] however, is suggested to abstract an electron,[29] probably from the solvent, to form the radical which subsequently attacks chlorobenzene. Alternative schemes involving direct formation of the carbon radical from an alkoxy carbonyl radical and possibly silver(II) can be written, but the reluctance of most alkoxy carbonyl radicals to lose carbon dioxide[30] makes such possibilities less than attractive.

Apocamphor Bridgehead Systems. In the presence of silver tetrafluoroborate, 1-chloroformylapocamphor (**3**) reacts in chlorobenzene to give 97% silver chloride, 17% carbon dioxide, and 58% 1-fluoroformylapocamphor (**11**), identified by spectral and analytical criteria.



3 11

Attempts to definitively characterize other organic products were not successful. Apparently, in the case of **3**, the cation which would be produced on dechlorodecarboxylation is sufficiently destabilized by the inductive effect of the carbonyl group that loss of carbon dioxide is avoided, and fluoride ion replacement from tetrafluoroborate, with accompanying formation of boron trifluoride, is preferred. Such a process is also observed with phenyl chloroformate[3] and most reasonably involves an intermediate carboxylium ion. Precedent suggests, however, that ionization at this bridgehead position is possible under other conditions; 1-aminoapocamphor is reported to give low yields of bridgehead substitution on nitrosation,[31] and 1-amino-7-norbornanone is observed to give substitution of structurally maintained material as well as fragmentation product.[32]

Apobornylene Bridgehead Systems. Reaction of 1-chloroformylapobornylene (**4**) with silver hexafluoroantimonate at ambient temperatures, in chlorobenzene containing 1 equiv of added tetramethylurea,[3,33] gives 82% silver chloride, 99% carbon dioxide, 18% 1-chloroapobornylene (**12**), and 54% isomers of 1-chlorophenylapobornylenes (**13**). Assignment of structures to the positional isomers of **13** rests on spectral and analytical data and on hydrogenation to the 1-chlorophenylapo-

(18) For recent calculation and a summary of the evidence which suggests that the cyclopropyl cation is a high-energy species relative to the 2-propyl cation, see L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973).

(19) In most instances, attempted ionizations of cyclopropyl derivatives proceed *via* disrotatory ring opening to allylic systems. See, for example, C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972), and references cited therein. Such ring opening is clearly structurally inhibited in the apotricyclene system.

(20) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

(21) F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 12.

(22) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(23) (a) H. Hart and R. A. Martin, *Angew. Chem., Int. Ed. Engl.*, **82**, 6362 (1960); (b) P. Lipp and R. Padberg, *Ber.*, **54**, 1316 (1921), report the same reaction for 1-aminoapotricyclene.

(24) (a) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5386 (1969); (b) R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **92**, 3471 (1970). For this comparison, the value for 1-norbornyl triflate in 50% aqueous ethanol is extrapolated to 186° from data at lower temperature.

(25) It is interesting to note that 4-nortricyclyl triflate[24b] and 4-tricyclyl triflate[26] and not the 1-substituted isomers are apparently the least reactive tertiary alkyl systems studied as solvolyses.

(26) S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Amer. Chem. Soc.*, **94**, 4615 (1972).

(27) The strain energy for the 1-apotricyclyl cation can be calculated as *ca.* 31 kcal/mol on the basis of the solvolysis rates for the triflates,[24] a plot of strain energy *vs.* rates,[20,26] and a group contribution of 1 kcal/mol for the *gem*-dimethyl group.[26] Qualitatively, bond angle strain may be considered to increase the s character of the external bridgehead orbital,[28] an effect which would increase the energy of the bridgehead cation.

(28) G. C. Anderson and L. M. Stock, *J. Amer. Chem. Soc.*, **91**, 6804 (1969).

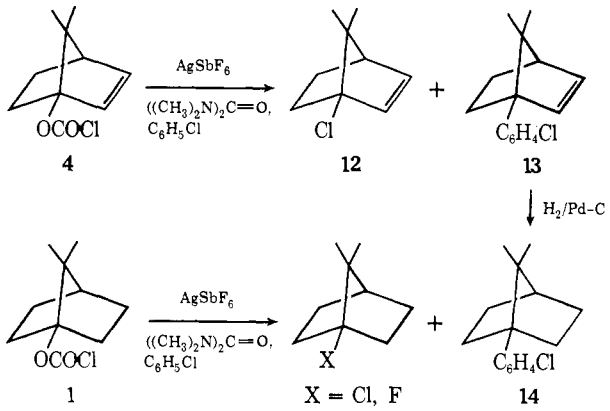
(29) (a) Electrochemical reduction of cations provides an analogy for this proposal: R. Breslow and W. Chu, *J. Amer. Chem. Soc.*, **95**, 411 (1973), and references cited therein. (b) The electron could possibly be provided by the solvent: J. K. Kochi, R. T. Tang, and T. Bernath, *ibid.*, **95**, 7114 (1973), and references cited therein.

(30) (a) H. G. Kuivila and E. J. Walsh, Jr., *J. Amer. Chem. Soc.*, **88**, 571 (1966); (b) P. Beak and S. W. Mojé, *J. Org. Chem.*, **39**, 1320 (1974), and references cited therein.

(31) M. Ishidate and A. Kawada, *Pharm. Bull.*, 4, 483 (1956); see also ref 9.

(32) D. E. Applequist and J. P. Kliemann, *J. Org. Chem.*, **26**, 2178 (1961).

(33) Tetramethylurea is present to prevent addition of acid to the double bond of the apobornylenes.



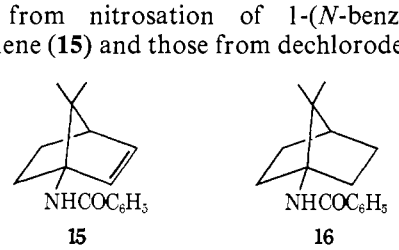
camphanes (**14**) of established structure. The mixture of isomers is separated by preparative glpc into the meta isomer, **13***m*, which was identified by oxidation to *m*-chlorobenzoic acid, and a mixture of ortho and para compounds, **13***o* and **13***p*, which gives *p*-chlorobenzoic acid on oxidation. The ratio of **13***o*:**13***m*:**13***p* is assigned on the basis of glpc and nmr data (Table III).

Table III. Arylation Product Yields and Isomer Distributions of 1-Chlorophenylapobornylenes (**13**) and 1-Chlorophenylapocamphanes (**14**) from the Reactions of Functionally Substituted 1-Apocamphanes and 1-Apobornylenes in Chlorobenzene

Substrate	Reagent (T, °C)	Product (%)[a]	Isomer ratios	
			Glpc[a]	Nmr[a]
4	$AgSbF_6$[b] (ambient)	**13** (54 ± 8)	**13***m*, 38 ± 3 **13***o* + **13***p*, 62 ± 3	**13***o*, 37 ± 3 **13***m*, 32 ± 3 **13***p*, 31 ± 3
15	N_2O_4[c] (0°)	**13** (4 ± 3)	**13***m*, 36 ± 6 **13***o* + **13***p*, 64 ± 6	**13***o*, 34 ± 2 **13***m*, 34 ± 2 **13***p*, 32 ± 2
1	$AgSbF_6$[b] (ambient)	**14** (60 ± 10)	**14***m*, 32 ± 3 **14***o* + **14***p*, 68 ± 3	**14***o*, 40 ± 3 **14***m*, 30 ± 3 **14***p*, 30 ± 3
16	N_2O_4[c] (0°)	**14** (17 ± 3)	**14***m*, 32 ± 5 **14***o* + **14***p*, 68 ± 5	**14***o*, 38 ± 2 **14***m*, 30 ± 2 **14***p*, 32 ± 2

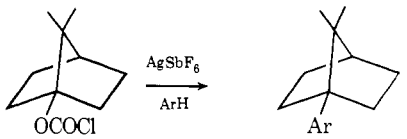
[a] Errors are three times the standard deviations. [b] One equivalent of tetramethylurea present. [c] Excess sodium acetate is present.

The yield and ratios of chlorobenzene substitution products from nitrosation of 1-(*N*-benzoyl)aminoapobornylene (**15**) and those from dechlorodecarboxylation of 1-chloroformylapocamphane (**1**), in the presence of tetramethylurea and nitrosation of 1-(*N*-benzoyl)-aminoapocamphane (**16**), are also given in Table III. Comparison of the isomer ratios in columns three and four of this table shows that all four compounds afford essentially the same isomer ratios within experimental error. In accordance with previous work, a highly reactive bridgehead 1-cation is considered to be a common intermediate[3,4b,34,35] for these substrates, and comparison of the apobornenyl and apocamphane substrates shows that the presence of the inductively electron-withdrawing double bond, which structurally cannot participate in the usual allylic stabilization,[36-38] does not significantly affect the isomer distribution.[39] On the other hand, the effect of such destabilization might be expected to have a greater influence on transition states leading to the reactive cation than on reactions of the cation. In any case, the reactions of the apobornylenes provide further support for the suggested analogy between dehalodecarboxylations and deaminations.[1,3]



Apocamphane Bridgehead Electrophilic Aromatic Substitutions. The isomer ratios from the reaction of **1**, **4**, **15**, and **16** with chlorobenzene, as well as the novel alkylation of nitrobenzene by **1**[3,40] and a recent study by White, *et al.*,[35b] of norbornyl and apocamphyl systems suggest that bridgehead cations of bicyclo[2.2.1]heptane are highly reactive. We have probed this reactivity by a study of the substrate and positional selectivity of the 1-apocamphyl cation in electrophilic aromatic substitution.[41,42]

Reactions of 1-chloroformylapocamphane (**1**) with silver hexafluoroantimonate at ambient temperature in toluene, benzene, chlorobenzene, and nitrobenzene as pure or mixed solvents give the corresponding bridgehead substitution products **14***o*, **14***m*, **14***p*, **17***o*, **17***m*,



14, Ar = C_6H_4Cl
17, Ar = $C_6H_4CH_3$
18, Ar = C_6H_5
19, Ar = *m*-$C_6H_5NO_2$

(34) E. H. White and D. J. Woodcock, "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, London, 1968, pp 440–461.

(35) (a) E. H. White, T. T. Ryan, and K. W. Field, *J. Amer. Chem. Soc.*, **94**, 1360 (1972); (b) E. H. White, R. H. McGirk, C. F. Aufdermarsh, Jr., H. P. Tiwari, and M. J. Todd, *ibid.*, **95**, 8107 (1973), have recently extended their earlier studies of amide nitrosation to the generation of 1-norbornyl and 1-apocamphyl cations and noted the high reactivity of these species toward alkylation, ether cleavage, and chloride and hydride abstraction from solvent.

(36) (a) B. R. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970), have determined a σ_I for a double bond to be +0.09 from a study of 2-methyleneadamantyl tosylate; (b) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

(37) J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, S. J. Wagner, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

(38) For a related bridgehead substitution, see J. Meinwald and D. Putzig, *J. Org. Chem.*, **35**, 1891 (1970).

(39) Moreover, the yields of carbon dioxide are 97% (for **1**) and 99% (for **4**), and the fraction of reaction giving bridgehead substitution is 75% (for **1**) and 72% (for **4**), suggesting similar fractionation of the initial ion pair toward such substitution.

(40) D. Kevill and F. L. Weitl, *J. Amer. Chem. Soc.*, **90**, 6416 (1968), have reported alkylation of nitrobenzene by 1-chloroformyladamantane and silver(I).

(41) Electrophilic aromatic alkylation by chloroformates is a well-known reaction: (a) F. A. Drahowzal, "Friedel–Crafts and Related Reactions," G. A. Olah, Ed., Interscience, New York, N. Y., 1965: Vol. I, p 122; Vol. II, p 644; for silver-induced reactions, see (b) ref 2; (c) D. N. Kevill, W. Reis, and J. B. Kevill, *Tetrahedron Lett.*, 957 (1972); (d) P. Beak, J. T. Adams, P. D. Klein, P. A. Szczepanik, D. A. Simpson, and S. G. Smith, *J. Amer. Chem. Soc.*, **95**, 6027 (1973), and references cited therein.

(42) Cogent criticism of indiscriminate correlations of reactivity and selectivity has been made by D. S. Kemp and M. L. Casey, *J. Amer. Chem. Soc.*, **95**, 6670 (1973). For the present case, decreased differentiation between competing pathways follows if the energy differences of comparable transition states for the competing processes are substantially less than energy differences of the reactants compared. The energy of the 1-apocamphyl cation has been estimated as more than 20 kcal/mol above that of an unstrained tertiary cation, while the different transition states for substitution are, from product distributions, within a few kcal/mol of one another.

17*p*, **18**, and **19** in yields of 50–70%, as compiled in Table IV, along with 1-chloroapocamphane in yields of 37–48%. The isomers of **17** were separated by preparative glpc and identified by ir and nmr spectral criteria. Control experiments established that 3 and 7% isomerization of **17***o* and **17***p* to **17***m* could occur in toluene and benzene–toluene but that the isomers of **17** are stable to within ±3% otherwise. Accordingly, the ratio of isomers produced in the alkylation of toluene by the 1-apocamphyl cation is considered to be 23:46:31 (±3) **17***o*:**17***m*:**17***p*, a ratio which like that from 1-apocamphylation of chlorobenzene[3] suggests a very reactive cation.

Table IV. 1-Arylapocamphanes from the Reaction of 1-Chloroformylapocamphane with Silver Hexafluoroantimonate in Aromatic Solvents

Solvent[b]	Product, %[a] 14	17	18	19*m*
$C_6H_5CH_3$		52[c] ± 6		
C_6H_5Cl–$C_6H_5CH_3$	25 ± 2	28[d] ± 3		
C_6H_5Cl–C_6H_6	23 ± 4[e]		32 ± 3	
C_6H_5Cl–$C_6H_5NO_2$	61 ± 8			10 ± 3
C_6H_6–$C_6H_5CH_3$		21[f] ± 3	34 ± 5	
		20[g] ± 3	31 ± 2	
C_6H_6–$C_6H_5CH_3$[h]		34 ± 2	17 ± 2	
C_6H_6–$C_6H_5CH_3$[i]		29 ± 2	21 ± 2	

[a] Errors are three times the standard deviations. [b] Solvent mixtures are 1:1 (v/v) unless otherwise noted. [c] **17***o*:**17***m*:**17***p*, 23:42:35 (±3). [d] **17***o*:**17***m*:**17***p*, 17:50:33 (±3). [e] **14***o*:**14***m*:**14***p*, 36:33:31 (±2). [f] **17***o*:**17***m*:**17***p*, 24:45:31 (±3). [g] **17***o*:**17***m*:**17***p*, 21:48:31 (±3). [h] 3:1 (v/v) toluene:benzene. [i] 2:1 (v/v) toluene:benzene.

The product yields in Table IV are used in conjunction with the molar ratios of solvent pairs to calculate the relative solvent-pair reactivities summarized in Table V. The same reactivities are obtained for toluene to benzene ratios varying from 0.84 to 2.51, suggesting that the reactions have essentially the same order in aromatic substrate and that the values in Table V provide a meaningful measure of competition between the aromatics for the electrophile. A striking feature of the relative solvent pair reactivities is that benzene is more reactive than toluene, k_B/k_T = 1.28 ± 0.24 (from four values). The error limit, composed of a contribution of 0.03 from the least-squares analysis and the 0.21 average error of the values from the different experiments, suggests that the greater reactivity of benzene might be small, but it is, nonetheless, strikingly different from the values of k_B/k_T of 0.61 downward reported for isopropylation of toluene–benzene mixtures.[43] In fact, the k_B/k_T value for alkylation by the 1-apocamphyl cation is comparable to those reported for nitration of aromatics by nitronium salts in nitromethane.[45] On the other hand, Nakane has reported

Table V. Relative Solvent-Pair Reactivities for Reactions of 1-Chloroformylapocamphane with Silver Hexafluoroantimonate at Ambient Temperature in Aromatic Solvent Mixtures

Solvent A	Solvent B	B/A,[a] (*n*)	Alkyl A/alkyl B,[b] (*r*)	k_A/k_B,[c] (*rn*)
$C_6H_5CH_3$	C_6H_5Cl	1.16	1.12 ± 0.08	1.30 ± 0.19
C_6H_6	C_6H_5Cl	0.97	1.39 ± 0.10	1.35 ± 0.22
C_6H_5Cl	$C_6H_5NO_2$	0.89	6.1 ± 0.9	5.4 ± 1.4
C_6H_6	$C_6H_5CH_3$	0.84	1.62 ± 0.17	1.36 ± 0.29
C_6H_6	$C_6H_5CH_3$	0.84	1.55 ± 0.13	1.30 ± 0.25
C_6H_6	$C_6H_5CH_3$	2.51	0.50 ± 0.04	1.26 ± 0.14
C_6H_6	$C_6H_5CH_3$	1.68	0.72 ± 0.06	1.21 ± 0.17
C_6H_6	$C_6H_5CH_3$			1.31 ± 0.09[d]

[a] Mole ratios calculated from the volume compositions used with an estimated error of ±0.09 for all values. [b] From data in Table IV; all errors calculated by a differential propagation of errors treatment[e] of the equation r = alkyl A/alkyl B and use of standard deviations for the errors in alkyl A and alkyl B. [c] Relative reactivities; all errors calculated by a differential propagation of errors treatment[e] of the equation $k_A/k_B = rn$ and use of the indicated errors in r and n. [d] From the preceding four values; least-squares analysis from a plot of $1/n$ *vs.* r and definition of the line's origin as the point 0,0 for pure toluene gives k_B/k_T = 1.28 ± 0.03 standard deviation, where $r = 1.28(1/n)$. Inclusion of the point 0,0 but not defined as the origin give k_B/k_T = 1.31 ± 0.09 standard deviation, where $r = 1.31(1/n) - 0.02$. [e] D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill, New York, N. Y., 1967, pp 30–34.

k_B/k_T ratios in the range 1.43–1.79 for boron trifluoride catalyzed competitive ethylations and isopropylations of toluene–benzene mixtures in nonpolar solvents under homogeneous conditions,[44] and it is also reported[46] that k_B/k_T ratios of 1.11–1.67 are obtained for gas-phase isopropylation of toluene–benzene mixtures. In any event, it is clear that the 1-apocamphyl cation is not selective in electrophilic aromatic substitution with respect to either position or substrate. Such a result is reminiscent of Brown's[43b,47] original premise that high reactivity of the attacking species results in low selectivity between toluene and benzene.

On the basis of the experimental k_B/k_T ratio of 1.28 ± 0.24 and an average 1-tolylapocamphane isomer distribution of 23 ± 3%:46 ± 3%:31 ± 3% *o*:*m*:*p* from Table IV, the partial rate factors o_f, m_f, and p_f for apocamphylation of toluene are calculated[48] to be respectively 0.53 ± 0.17, 1.08 ± 0.26, and 1.45 ± 0.40. The reduced reactivity of toluene relative to benzene at the ortho position is almost balanced by increased reactivity of toluene at the meta and para positions. The selectivity factor S_f[43b,49] is calculated to be 0.127, appropriately low for a reactive electrophile, and the relationship $\log p_f = 1.28S_f$ shows only a slight deviation from Brown's relationship of $\log p_f = 1.31S_f$. The partial rate factors for 1-apocamphylation of chlorobenzene can be calculated from the chlorobenzene:benzene reactivity of 0.60 ± 0.10 (Table V) and the isomer distribution for **14** (Table IV) to be o_f:m_f:p_f 0.72 ± 0.17:0.54 ± 0.14:1.08 ± 0.29, revealing the para position of chlorobenzene to be of comparable reactivity to benzene in this case. In contrast, the corresponding values for ethylation of chlorobenzene are 0.27:0.10:

(43) With the exception of the work of Nakane[44] (*vide infra*), isopropylation appears to give the highest k_B/k_T rate ratios observed for Friedel–Crafts alkylation in solution: (a) C. H. Bamford and C. F. H. Tipper, "Comprehensive Chemical Kinetics," Elsevier, Amsterdam, 1972, pp 139–152; (b) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 35 (1963).

(44) R. Nakane, O. Kurihara, and A. Natsubori, *Advan. Phys. Org. Chem.*, **91**, 4528 (1969); R. Nakane, O. Kurihara, and A. Takematsu, *J. Org. Chem.*, **36**, 2753 (1971); A. Natsubori and R. Nakane, *ibid.*, **35**, 3372 (1970).

(45) G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, **84**, 3684 (1962).

(46) S. Takamuku, K. Iseda, and H. Sakurai, *J. Amer. Chem. Soc.*, **93**, 2420 (1971).

(47) H. C. Brown and K. L. Nelson, *J. Amer. Chem. Soc.*, **75**, 6292 (1953).

(48) L. M. Stock, "Aromatic Substitution Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1968.

(49) H. C. Brown and C. R. Smoot, *J. Amer. Chem. Soc.*, **78**, 6255 (1956).

0.54.[50] Comparison of the values of $k_B/k_{C_6H_5Cl}$ and $k_T/k_{C_6H_5Cl}$ of 1.35 ± 0.22 and 1.30 ± 0.19 to corresponding values for alkylation from the literature, which range from 2.1 to 30,[50,51] further supports a lack of substrate selectivity by the 1-apocamphyl cation. Finally, it should be noted that Table V provides a value of 7 ± 3 for $k_B/k_{C_6H_5NO_2}$ on 1-apocamphylation, apparently the first determination of this ratio for competitive alkylation.[52]

Reactions of 1-chloroformylapocamphane (**1**) and 1-chloroformylapobornylene (**4**) with silver hexafluoroantimonate in a 1:1 (v/v) mixutre of benzene and chlorobenzene containing 1 equiv of tetramethylurea[33] were compared and found to give benzene:chlorobenzene reactivities of 1.66 ± 0.29 and 1.56 ± 0.29, indicating again no pronounced effect on bridgehead reactivity of the bridgehead cation on introduction of the carbon–carbon double bond.

The 1-apocamphyl cation is characterized by a low positional and substrate selectivity in electrophilic aromatic substitution, and it appears to be the most reactive alkyl electrophile which has been studied in this regard. The close correspondence of 1-apocamphylation to the quantitative selectivity–reactivity relationships of Brown, *et al.*,[43b,48] strongly suggests that reaction of the 1-apocamphyl cation with benzene and toluene proceeds *via* rate-determining formation of a σ complex. It might have been expected that the 1-apocamphyl cation would have reacted *via* a rate-determining π complex in accord with suggestions made for other reactive electrophiles.[53] On the other hand, a recent critical analysis[54] suggests that σ-complex formation is the rate-determining transition state in most electrophilic aromatic substitutions.

It should be noted that the present results do not provide information about the role of silver(I), solvation or aggregation phenomena, or the possibilities of intermediate n complexes,[35b,41d] or ipso substitution.[55] More detailed study would no doubt show some of these effects to be operative. While the competitive experiments were carried out with solutions of the chloroformate and silver salts in the same solvent mixture to ensure that macroscopic encounter control would not obscure the results, the possibility of microscopic encounter control[54] is more difficult to assess. It is conceivable that differential complexation of silver(I) by the aromatic solvents could perturb the environment in which the cation is produced such that the 1-apocamphylation ratios reported herein are not accurate measures of competition for the cation. However, the relative reactivities measured by k_B/k_X for toluene, chlorobenzene, and nitrobenzene of 1.3, 1.4, and 7 are substantially different from the corresponding K_B/K_X ratio for silver complexation of 0.9, 3.5, and 13 for the same substrates.[56] Moreover, the above noted success with the selectivity correlation[43b,48] suggests, at least for benzene and toluene, that the same relative transition state energies of σ complexes are the determining factor in both substrate and positional selectivities.

Reaction Scheme. There is considerable precedent for the formation of reactive cations from the reactions of chloroformates and silver(I).[1-3] Although the effects of aggregation probably will prove important, the present results can be simply rationalized in terms of a scheme in which initial ionization produces a carboxylium ion pair, which can either be trapped by fluoride ion to give a fluoroformate or undergo loss of carbon dioxide to give a carbocation ion pair.[1] If the cation is sufficiently long-lived, it can react with the solvent, in

$$\mathrm{ROCOCl} \xrightarrow{\mathrm{Ag^+}} \mathrm{ROC^+O\ ClAg\ BF_4^-} \longrightarrow \mathrm{ROCOF} + \mathrm{BF_3}$$

$$\mathrm{RAr} \xleftarrow{\mathrm{ArH}} \mathrm{R^+} + \mathrm{CO_2} + \mathrm{BF_4^-} \xrightarrow{\mathrm{e^-}} \mathrm{R\cdot} \xrightarrow{\mathrm{ArH}} \mathrm{RAr}$$

the present case by electrophilic aromatic substitution, or provide halide products. If the cation is exceedingly reactive, it is postulated to abstract an electron to give a radical which can react with the solvent or conceivably give halide product. For the 1-apocamphyl cation, introduction of an adjacent carbon–carbon double bond has no observable effect on the formation or reaction of the cation, whereas inclusion of the bridgehead position in a three-membered ring provides a cation which is so unstable as to be a precursor to a radical, and introduction of a carbonyl group adjacent to the bridgehead position raises the energy of the transition state for carbocation formation to the point that carbon dioxide is not expelled.

Experimental Section[57]

Materials. Elution chromatography was carried out on Brinkmann 0.05- to 0.2-mm silica gel or Florex from the Floridin Co., St. Louis, Mo. Thin layer chromatography (tlc) was performed on Eastman silica gel coated strips, and components were visualized by staining with iodine. Preparative tlc was conducted using silica gel PF_{254}.

Tetrahydrofuran was distilled from lithium aluminum hydride or sodium benzophenone. Methylene chloride was dried over Drierite. The following materials were distilled at atmospheric pressure under nitrogen from calcium hydride: nitrobenzene, toluene, benzene, chlorobenzene, tetramethylurea.

Silver hexafluoroantimonate, obtained from the Ozark-Mahoning Co. and dried for 3 days at 0.07 mm over phosphorus pentoxide prior to use, gave acceptable (±0.3%) elemental analyses for silver and antimony. Silver tetrafluoroborate obtained from the Ozark-Mahoning Co. gave acceptable (±0.3%) elemental analysis for silver.

Gas–Liquid Phase Chromatography (glpc). Areas for product yields were measured by planimetry and corrected for differences in thermal conductivity between the substance of interest and added internal standard. The following columns were employed: 3 ft × 0.25 in. copper packed with 16% SE-30 on 60–80 mesh nonacid-washed Chromosorb P (column A); 5 ft × 0.25 in. stainless steel packed with 20% Apiezon L on 60–80 mesh firebrick (column B); 150 ft × 0.02 in. stainless steel butanediol succinate Golay capillary

(50) H. C. Brown and A. H. Neyens, *J. Amer. Chem. Soc.*, **84**, 1655 (1962).

(51) H. C. Brown and M. Grayson, *J. Amer. Chem. Soc.*, **75**, 6285 (1953); G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1695 (1962); G. A. Olah, S. H. Flood, and M. E. Moffatt, *ibid.*, **86**, 1065 (1964).

(52) L. Friedman and J. F. Chlebowski, *J. Org. Chem.*, **33**, 1633 (1968), have reported the results of substrate and positional competitive phenylations for nitrobenzene by phenyldiazonium ions which are considered to react, at least in part, *via* phenyl cations.

(53) G. A. Olah, *Accounts Chem. Res.*, 4, 240 (1971).

(54) P. Rys, P. Skrabal, and H. Zollinger, *Angew. Chem., Int. Ed. Engl.*, **11**, 874 (1972).

(55) R. C. Hahn and M. B. Groen, *J. Amer. Chem. Soc.*, **95**, 6128 (1973), and references cited therein.

(56) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 90. The values are for water at 25°, but the difference would probably be larger for nonpolar media: *ibid.*, p 87.

(57) Melting points are uncorrected. The nmr spectra were recorded by Mr. R. Thrift and associates, and chemical shifts are reported as δ (ppm) relative to tetramethylsilane as internal standard, unless otherwise noted. Mass spectra were recorded at 70 eV by Mr. J. C. Cook and associates, and peak intensities are relative to the base peak. Elemental analyses were performed at the University of Illinois Microanalytical Laboratory by Mr. J. Nemeth and associates.

column (column C); 5 ft × 0.25 in. aluminum packed with 20% Apiezon L on 60–80 mesh firebrick (column D); 2.5 ft × 0.25 in. aluminum packed with 20% Apiezon L on 60–80 mesh firebrick (column E).

Syntheses. 1-(*N*-Benzoyl)aminoapocamphane (16),[58,59] mp 111–113° (lit.[6] mp 112°), was prepared from 1-aminoapocamphane.

1-Aminoapocamphor hydrochloride,[58] prepared from 1-aminoapocamphor by reaction with hydrogen chloride gas in diethyl ether and purified by recrystallization from ethanol–ether, sublimes above 260°: $[\alpha]_0^{29}$ +48.8° (*c*, 1.6, H_2O); ir and nmr as expected.

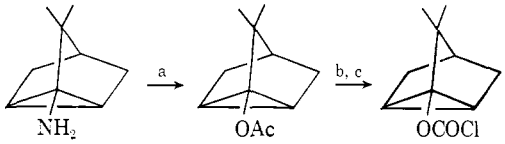
The preparation of 1-aminoapocamphor was based on a Curtius sequence as modified by Feller.[61] Reaction of the acid chloride (from 0.220 mol of ketopinic acid with excess thionyl chloride) in tetrahydrofuran with a chilled (−25°) solution of sodium azide (14.3 g, 0.220 mol) in 80 ml of water was stirred for 45 min at −25° and 30 min at 0° followed by addition to ice water and extractive work-up with benzene. After removal of most of the solvent by distillation, heating was continued for 1 hr, concentrated hydrochloric acid was added, and the two phase mixture was stirred at reflux for 3 hr. Extractive work-up with methylene chloride gave, after sublimation, 17. 5 g (52%) of 1-aminoapocamphor, mp (sealed tube) 196–197° (lit.[62] mp 194°); ir and nmr as expected.

1-Aminoapotricyclene hydrochloride[58] was prepared from tricyclenic acid[63] in 28% yield by the modified Curtius sequence described above. The material decomposed at *ca.* 220°; ir and nmr as expected.

1-Acetoxyapotricyclene[58,59] was prepared as a clear liquid in 61% yield from treatment of the amine hydrochloride in glacial acetic acid containing 8% acetic anhydride with a twofold excess of sodium nitrite according to a related procedure of Hart.[23a]

1-Chloroformylapotricyclene (2). A solution of 559 mg (3.10 mmol) of 1-acetoxyapotricyclene in 8 ml of tetrahydrofuran was treated with lithium aluminum hydride (0.318 *M*, 2.54 mmol) in tetrahydrofuran.[6] After agitation and standing for 15 min, the mixture was then added dropwise over 45 min under nitrogen with stirring to 5 ml (80 mmol) of neat phosgene at −75 to −70°. The mixture was stirred at this temperature for 2 hr, warmed to room temperature overnight, and worked up extractively with petroleum ether followed by chromatography on Florex to give 470 mg of a pale yellow liquid. This material was distilled to give 411 mg (66%) of **2** as a colorless liquid:[58] ir (film) 3070 (w, cyclopropyl CH), 1790 (s, ester C=O), 1145 (s) and 825 (s) cm^{-1}; nmr (CCl_4) 1.03 (s, 6, $C(CH_3)_2$), 1.55 (m, 1, H_4), 1.63 (q_{AB}, J_{AB} = 11 Hz, $\Delta\delta_{AB}$ = 0.80, 4, H_3 and H_5), and 1.81 (broad s, 2, H_2 and H_6); mass spectrum *m/e* 200 (M^+, 23) and 109 (100).

Scheme I



(a) $NaNO_2$, HOAc; (b) $LiAlH_4$; (c) $Cl_2C{=}O$

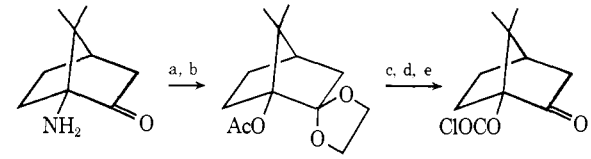
1-Apotricyclene Acyl Peroxide (10). Tricyclenic acid chloride, 532 mg (2.89 mmol), was added in 2 ml of ether to 112 mg (1.44 mmol) of sodium peroxide in 2 ml of ether.[64] After addition of 2 drops of water, the mixture was stirred at room temperature for 21.5 hr, one more drop of water being added after each of the first two 45-min intervals. The reaction mixture was taken up in ether and dried ($CaCl_2$); 290 mg of the 459 mg of a material remaining after evaporation of the solvent was chromatographed on silica gel to give 134 mg (45%) of **10** as a white solid which by iodometric titration was at least 96% pure:[58] ir (CCl_4) 3070 (vw, cyclopropyl CH), 1790 (m, C=O), and 1765 (s, C=O) cm^{-1}; nmr (CCl_4) 1.08 (s, 12, $C(CH_3)_2$), 1.49 (m, 2, H_4), 1.53 (q_{AB}, J_{AB} = 11 Hz, $\Delta\delta_{AB}$ = 0.56, 8, H_3 and H_5), and 1.96 (s, 4, H_2 and H_6); mass spectrum *m/e* 330 (M^+, 2) and 150 (100).

1-Acetoxyapocamphor ethylene ketal[58,59] was prepared in 54% yield from 1-aminoapocamphor by, first, reaction with ethylene glycol and *p*-toluenesulfonic acid in benzene and, second, deamination of the resulting aminoketal under the conditions used for 1-aminoapotricyclene (*vide infra*), bp 79–81° (0.18 mm).

1-Chloroformylapocamphor (3). Reduction of 1-acetoxyapocamphor ethylene ketal with lithium aluminum hydride in ether gave a colorless liquid which was converted to the chloroformate in 34% yield. To remove the ethylene ketal group, crude material (930 mg, 3.57 mmol) was dissolved in methylene chloride and treated with *ca.* 5 ml (6.75 g, 58 mmol) of boron trichloride at −75 to −70°.[8] The bath temperature was allowed to reach −20° after 4 hr and then recooled to −75 to −70° for 7 hr. After concentration under nitrogen, the mixture was diluted with petroleum ether and worked up extractively to give a yellow solid (769 mg) which was chromatographed on silica gel and further purified by two sublimations to afford 545 mg (71%) of colorless crystals of **3**: mp 92–93°; ir (CCl_4) 1790 (s, C=O), 1765 (s, C=O), 1140 (s), and 1130 (s) cm^{-1}; nmr (CCl_4) 1.02 (s, 3, CH_3), 1.15 (s, 3, CH_3) and 1.42–2.66 (m, 7, CH); mass spectrum *m/e* 216 (M^+, 26) and 67 (100); $[\alpha]^{26}D$ −41.3° (*c*, 1.5, $CHCl_3$).

Anal. Calcd for $C_{10}H_{13}O_3Cl$: C, 55.44; H, 6.05; Cl, 16.36. Found: C, 55.69; H, 6.02; Cl, 16.50.

Scheme II



(a)$HOCH_2CH_2OH$, TsOH; (b)$NaNO_2$, HOAc; (c) $LiAlH_4$; (d) $Cl_2C{=}O$; (e) BCl_3, −70°

1-(*N*-Benzoyl)aminoapobornylene (15). The benzamido ketone, prepared in 69% yield from the amino ketone and benzoyl chloride, was converted to the *p*-tosylhydrazone by reaction with *p*-toluenesulfonylhydrazide in 1% ethanolic hydrochloric acid, in quantitative yield. Treatment of the tosylhydrazone in tetrahydrofuran with a 2.5-fold excess of methyllithium in ether[10] followed, after 8.5 hr, by cautious dilution with water and extractive work-up with ether gave a semisolid residue. Chromatography on silica gel gave a solid which on recrystallization from hexane provided 48% of **15**: mp 98.5–101°; ir (CCl_4) 3380 (w), 3000 (w), 1670 (s, amide C=O), 1600 (w), 1585 (w), 1510 (s), and 1485 (s) cm^{-1}; nmr (CCl_4) 0.94–1.35 (m, 7, includes singlets at 0.94 and 0.97, $C(CH_3)_2$), 1.85 (m, 3), 2.29 (m, 1, H_4), 5.87 (AMX, 1, J_{AM} = 6 Hz, J_{MX} = Hz, $H_AC{=}C$), 7.24 (m, 3, Ar H), 6.22 (AMX, 1, J_{AM} = 6 Hz, J_{MX} = 1 Hz, H_M–C=C–), and 7.58 (m, 2, Ar H); mass spectrum *m/e* 241 (M^+, 21), 213 (M^+ − CO, 21), and 105 ($C_6H_5C{=}O$, 100).

Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.55; H, 7.91; N, 5.52.

1-Hydroxyapobornylene was prepared from 1-(*N*-benzoyl)-aminoapobornylene by reaction with a threefold excess of dinitrogen tetroxide and a sixfold excess of anhydrous sodium acetate in methylene chloride for 20 min at 0°.[34,35] Addition of water and extractive work-up of the methylene chloride, followed by chromatography on silica gel, gave an ester which was hydrolyzed in methanolic potassium hydroxide. Sublimation of the solid residue resulting from extractive work-up gave 50% of the desired alcohol: mp (sealed tube) 111–112°; ir (CCl_4) 3630 (w, OH), and 3070 (w) cm^{-1}; nmr (CCl_4) 0.86 (s, 6, $C(CH_3)_2$), 0.96–1.26 (m, 2), 1.74 (m, 3), 2.18 (m, 1, H_4), and 5.79 (m, 2, C=CH); mass spectrum *m/e* 138 (M^+, 24) and 123 ($M^+ - CH_3$, 100). Irradiation of H_4 (HR-220 spectrometer) resolved the 5.79 multiplet into 5.83 (AMX, 1, J_{AM} = 6 Hz, $H_AC{=}C$) and 5.92 (AMX, 1, J_{AM} = 6 Hz, J_{MX} = 3 Hz, $H_MC{=}C$). In benzene (TMS reference) the 0.86 singlet was resolved into equal intensity singlets at 0.80 and 0.95.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.13.

Catalytic hydrogenation (5% Pd/C) of 1-hydroxyapobornylene led to 1-apocamphanol (62%), mp (sealed tube 163–164° (lit.[7] mp

(58) Elementary analyses are within ±0.3%.[60]

(59) Ir, nmr, and mass spectral data are as expected.[60]

(60) Details of procedures, spectra, and analyses are available (B. R. Harris, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1974) from University Microfilms, Ann Arbor, Mich. 48106.

(61) W. Feller, Ph.D. Thesis, Johns Hopkins University, 1968. We are grateful to Professors B. Murr and A. Nickon for providing this procedure prior to publication.

(62) M. Ishidate and A. Kawada, *Pharm. Bull.*, **49**, 483 (1956).

(63) M. Hanack and H. Eggensperger, *Justus Liebigs Ann. Chem.*, **648**, 3 (1961).

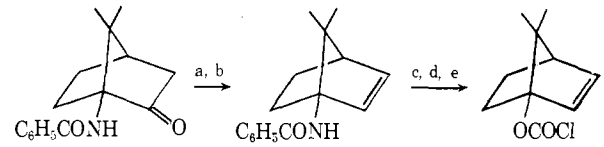
(64) H. Hart and D. P. Wyman, *J. Amer. Chem. Soc.*, **81**, 4891 (1959).

(sealed tube) 161–163°). The ir and nmr spectra of this material were identical with those of independently synthesized material.[3]

1-Chloroformylapobornylene (4) was prepared by reaction of the lithium salt of 1-hydroxyapobornylene and phosgene in tetrahydrofuran by the procedure previously described for 1-chloroformylapocamphane.[3] The compound was purified by chromatography on silica gel and distillation to afford 68% of **4**: ir (CCl_4) 1765 (s, ester C=O), 1155 (s), and 1140 (s) cm^{-1}; nmr (CCl_4) 0.99 [s, 6, $C(CH_3)_2$], 1.13 (m, 1), 1.77–1.94 (m, 3), 2.28 (m, 1, H_4), 5.98 (AMX, 1, J_{AM} = 6 Hz, J_{AX} = 3 Hz, H_AC=C), and 6.13 (AMX, 1, J_{AM} = 6 Hz, J_{MX} = 1.5 Hz, H_MC=C); mass spectrum *m/e* 200 (M^+, 48), 185 ($M^+ - CH_3$, 36), 172 ($M^+ - CO$, 33), 121 ($M^+ - OCOCl$, 39), and 105 (100).

Anal. Calcd for $C_{10}H_{13}O_2Cl$: C, 59.85; H, 6.53; Cl, 17.67. Found: C, 59.93; H, 6.59; Cl, 17.64.

Scheme III



(a) NH_2NHTs; (b) CH_3Li;

(c) N_2O_4; (d) KOH, CH_3OH; (e) Cl_2C=O

Product Studies. Reactions were conducted by addition of solutions of chloroformates dropwise to stirred solutions of the silver salts at ambient temperature under an atmosphere of dry nitrogen followed by stirring for 8 hr, unless otherwise noted. The carbon dioxide evolved was converted to barium carbonate by passage through saturated barium hydroxide solution. The barium carbonate yield was based on the amount of acid-soluble material. Silver chloride yields were determined as the ammonium hydroxide soluble material which could be precipitated by concentrated nitric acid. Solvent mixtures employed in the competitive solvent studies were prepared by prior mixing of equal volumes of each component, unless otherwise noted.

Reaction of 1-Chloroformylapotricyclene (2) with Silver Tetrafluoroborate in Chlorobenzene. To 112 mg (0.574 mmol) of silver tetrafluoroborate dissolved in 2 ml of chlorobenzene was added over 5 min at ambient temperature 108 mg (0.540 mmol) of **2** in 2 ml of chlorobenzene. Silver chloride formed immediately, and the reaction mixture was colorless immediately following addition. The rate of carbon dioxide evolution was visually slower than in the reactions of **1** and **4** (*vide infra*) but essentially ceased after 1 hr. Silver chloride was obtained in 82% yield; barium carbonate was obtained in 63% yield. A glpc analysis (235°, column B) indicated a 24% yield of arylation products of chlorobenzene **7** as two peaks in a 78:22 ratio. A glpc analysis (145°, column B) gave a 17% yield of 1-fluoroformylapotricyclene (**5a**), a 7% yield of 1-chloroapotricyclene (**5b**), and an 8% yield of camphenilone. A glpc analysis (110°, column A) gave an 18% yield of 1-fluoroapotricyclene (**5c**).

The arylation products were collected together on preparative glpc (235°, column B) and purified by distillation at 2.0 mm in a microsublimation apparatus: ir (film) 3050 (w), 1600 (w), 1575 (w), 900 (w), 890 (w), 870 (w), 815 (w), 785 (w), 750 (s), 735 (w), 720 (w), 700 (w), and 695 (w) cm^{-1}; nmr (CCl_4) 0.83 and 0.87 (both s, ratio 14:86 former:latter, $C(CH_3)_2$), 1.15–2.04 (m, CH), and 7.15 (m, ArH), the aliphatic region being 3.39 (calcd 3.25) times the area of the aromatic region; mass spectrum *m/e* 232 (M^+, 61), 217 ($M^+ - CH_3$, 16), and 189 ($M^+ - CH_3CHCH_3$, 100).

Anal. Calcd for $C_{15}H_{17}Cl$: C, 77.40; H, 7.36; Cl, 15.23. Found: C, 77.49; H, 7.51; Cl, 14.96.

1-Fluoroformylapotricyclene (5a) was collected by preparative glpc (145°, column B): ir (CCl_4) 3080 (vw), 1835 (s, ester C=O), 1270 (s), and 1235 (s) cm^{-1}; nmr (CCl_4) 1.02 (s, 6, $C(CH_3)_2$), 1.57 (m, 1, H_4), 1.61 (q_{AB}, J_{AB} = 11 Hz, $\Delta\delta_{AB}$ = 0.79, 4, H_3 and H_5), and 1.78 (s, 2, H_2 and H_6); mass spectrum *m/e* 184 (M^+, 13), 141 ($M^+ - CH_3CHCH_3$, 54), and 69 (100).

Anal. Calcd for $C_{10}H_{13}O_2F$: C, 65.20; H, 7.11. Found: C, 65.32; H, 7.13.

1-Chloroapotricyclene (5b) was collected by preparative glpc (145°, column B): ir (CCl_4) 3040 (w); nmr (CCl_4) 0.93 (s, 6, $C(CH_3)_2$), 1.44 (s, 2, H_2 and H_6), 1.53 (m, 1, H_4), and 1.56 (q_{AB}, J_{AB} = 11 Hz, $\Delta\delta_{AB}$ = 0.76, 4, H_3 and H_5); mass spectrum *m/e* 156 (M^+, 1), 113 ($M^+ - CH_3CHCH_3$, 5), and 28 (100); high resolution mass spectrum *m/e* 156.0706 (calcd for $C_9H_{13}Cl$, 156.0706). An analytic sample was not obtained.

Camphenilone (6), collected by preparative glpc (145°, column B), had a retention time and ir spectrum identical with those of authentic material synthesized from the potassium permanganate–potassium periodate oxidation[65] of ω-nitrocamphene.[63]

1-Fluoroapotricyclene (5c) was collected by preparative glpc (110°, column A): ir (CCl_4) 3020 (w) cm^{-1}; nmr (CCl_4) 1.03 (s, 6, $C(CH_3)_2$), 1.48 (s, 2, H_2 and H_6), 1.54 (q_{AB}, J_{AB} = 11 Hz, J_{HF} for portion partially buried under methyl singlet = 4 Hz, $\Delta\delta_{AB}$ = 0.80, 4, H_3 and H_5), and 1.58 (m, 1, H_4); mass spectrum *m/e* 140 (M^+, 7), 125 ($M^+ - CH_3$, 25), and 97 ($M^+ - CH_3CHCH_3$, 100); high resolution mass spectrum *m/e* 140.1001 (calcd for $C_9H_{13}F$, 140.1001). An analytical sample was not obtained.

The arylation mixture was resubjected to preparative glpc (235°, column B), with each peak being collected separately. The major peak (peak A) of shorter retention time proved by ir and nmr analysis to be predominantly 1-(*o*-chlorophenyl)apotricyclene (**7*o***) with a small amount of **7*m*** present: ir (film) 3040 (w), 1605 (w), 1575 (w), 900 (w), 875 (w), 840 (w), 790 (w, *m*), 755 (s, *o*), 735 (w, *o*), 725 (w, *o*), 705 (w, *m*), and 695 (w, *m*)[67] cm^{-1}; nmr (CCl_4) 0.87 (s, 6, $C(CH_3)_2$), 1.42 (s, 2, H_2 and H_6), 1.56 (m, 1, H_4), 1.61 (q_{AB}, J_{AB} = 11 Hz, $\Delta\delta_{AB}$ = 0.72, 4, H_3 and H_5), and 7.15 (nearly symmetrical 10-line m, 4, Ar H); mass spectrum *m/e* 232 (M^+, 66), 217 ($M^+ - CH_3$, 15), and 189 ($M^+ - CH_3CHCH_3$, 100).

Anal. Calcd for $C_{15}H_{17}Cl$: C, 77.40; H, 7.36; Cl, 15.23. Found: C, 77.34; H, 7.44; Cl, 15.20.

The minor peak (peak B) of longer retention time appeared to be a mixture by ir and nmr analyses of 1-(*p*-chlorophenyl)apotricyclene (**7*p***) and other chlorobenzene substitution material conforming to $C_{15}H_{17}Cl$: ir (CS_2) 3050 (w), 1090 (m), and 820 (m, para)[67] cm^{-1}; nmr (CCl_4) 0.83 (s of para isomer, $C(CH_3)_2$), 1.07–1.96 (m, CH, includes sharp, weak singlet at 1.37), and 7.15 (s superimposed on broad m, Ar H); relative areas of entire aliphatic, $C(CH_3)_2$, and CH regions to that of aromatic region were respectively 3.22 (3.33 calcd for 100% para isomer), 0.83 (1.5 calcd for 100% para isomer), and 2.4 (1.8 calcd for 100% para isomer); mass spectrum *m/e* 232 (M^+, 59), 217 ($M^+ - CH_3$, 26), 199 ($M^+ - CH_3CHCH_3$, 99.7), and 41 (100).

Flame ionization glpc analysis of the peak A component (160°, column C) indicated that it consisted of a major peak assigned to **7*o*** and a minor peak assigned to **7*m*** in a respective ratio of 92:8. Analysis of the peak B component under the same conditions shows a contaminant in the material designated as **7*p***. It is therefore possible to determine *o*:*m* isomer and *o*:*m*:*p* + x isomer ratios (Table I) by direct glpc analysis (160°, column C) of the reaction mixture before separation.

Treatment of 29 mg (0.149 mmol) of silver tetrafluoroborate dissolved in 1 ml of chlorobenzene with 28 mg (0.140 mmol) of **2** in 1 ml of chlorobenzene, followed by flame ionization glpc analysis as above, gives a **7*o***:**7*m***:**7*p*** + x ratio of 72 ± 2%:20 ± 2%:8 ± 2%.

Control Experiments.[60] A reaction of ethyl chloroformate with silver tetrafluoroborate in the presence of **7** shows that **7*o***:**7*m***:**7*p*** + x in a ratio of 57 ± 2%:31 ± 2%:12 ± 2% is converted to a ratio of 71 ± 2%:24 ± 2%:5 ± 2% in 60% yield, after 7 hr at ambient temperature. A reaction of **2** with silver tetrafluoroborate in chlorobenzene with tetramethylurea gives an 0.8% yield of **7** which consisted of a **7*o***:**7*m***:**7*p*** + x ratio of 51 ± 2%:26 ± 2%:23 ± 2%.

Reaction of 1-aminoapotricyclene (8) with nitrosyl chloride in chlorobenzene was achieved by treatment of a suspension of **8**·HCl with 1 equiv of calcium hydride, followed by addition of nitrosyl chloride and 21.5 hr at ambient temperature. Decarboxylation of tricyclenic acid (**9**) with lead tetraacetate in chlorobenzene at 130° was carried out by a procedure previously reported.[3]

Thermal decomposition of 1-apotricyclene acyl peroxide (10) in chlorobenzene was carried out at 125°. The product **7** was identified from each of the three preceding reactions in the yields and isomer ratios given in Table I by analytical and preparative glpc.[60]

(65) R. U. Lemieux and E. Von Rudloff, *Can. J. Chem.*, 33, 1701 (1955).

(66) The relative intensities of the bands assigned to the ortho and meta isomers,[67] which form the basis for the isomer assignments, are consistent with earlier assignments for the 1-chlorophenylapocamphanes[3] (*vide infra*), and the fact that *o*- and *m*-(*n*-propyl)chlorobenzene have similar extinction coefficients for these characteristic bands.

(67) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1964, p 60.

Preparative glpc provided material which had ir, nmr, and mass spectral properties similar to those of the products from **2**, except for differences in content of the meta isomer[68] in the peak A component and a lack of a weak nmr singlet at δ 1.37 in the peak B component.[60]

Reaction of 1-Chloroformylapocamphor (3) with Silver Tetrafluoroborate in Chlorobenzene. To 128 mg (0.656 mmol) of silver tetrafluoroborate dissolved in 8 ml of chlorobenzene was added, over 10 min, 121 mg (0.560 mmol) of **3** in 5 ml of chlorobenzene. Silver chloride was obtained in 97% yield; barium carbonate was obtained in 17% yield. The residue left after careful removal of the solvent was chromatographed on Florex to give 71 mg of white solid which afforded after sublimation 65 mg (58%) of pure 1-fluoroformylapocamphor (**11**) as a white solid, mp 138–138.5°: ir (CCl_4) 1840 (s, C=O) and 1170 (s) cm^{-1}; nmr (CCl_4) 1.06 (s, CH_3), 1.17 (s, 3, CH_3), 1.48–2.97 (m, 7, CH); ^{19}F nmr ($CFCl_3$ internal standard) -102 ppm (apparent t, $J = 20$ Hz); mass spectrum *m/e* 200 (M^+, 12) and 41 (100).

Anal. Calcd for $C_{10}H_{13}O_3F$: C, 59.99; H, 6.54. Found: C, 60.27; H, 6.51.

Reaction of 1-chloroformylapobornylene (4) with silver hexafluoroantimonate in chlorobenzene with added equimolar tetramethylurea was carried out with 0.530 mmol of **4** at ambient temperature. Silver chloride (82%) and barium carbonate (99%) were produced. Glpc analysis of the filtrate indicated 18% 1-chloroapobornylene (**12**) (100°, column D) and 54% of 1-chlorophenylapobornylene isomers (**13**) (230°, column D) in the ratio given in Table III.

In a preparative scale reaction the petroleum ether soluble residue was distilled at 0.50 mm to afford mixture **13**: ir (film) 1640 (vw), 1600 (w), 1570 (w), 825 (m), 780 (m), 755 (s), 745 (s), 725 (s), and 720 (s) cm^{-1}; nmr (CCl_4) 0.72–2.48 (m, 11, CH, includes five methyl singlets at 0.72 (*m*), 0.74 (*p*), 0.77 (*m*), 0.91 (*o*), and 0.95 (*o*)), 6.02 and 6.37 (m, 2.3, HC=CH), and 7.16 (m, 4.7 Ar H); assignments of methyl signals are based on the fact that, once separated, **13***m* shows resonances of equal intensity for the *gem*-dimethyl group as assigned and the fact that the resulting assignment of the ortho isomer to the two equal intensity signals at lower field is consistent with the 1-chlorophenylapocamphanes;[3] mass spectrum *m/e* 232 (M^+, 11), 217 ($M^+ - CH_3$, 10), and 28 (100).

Anal. Calcd for $C_{15}H_{17}Cl$: C, 77.45; H, 7.36; Cl, 15.19. Found: C, 77.49; H, 7.49; Cl, 15.11.

Glpc and nmr analysis gave the isomer ratios in Table III. The positional stability of these products to the reaction conditions is considered established by the previous control experiments on **14**.[3] The isomeric mixture was subjected to preparative glpc using column D at 230° and two peaks were collected. The peak of shorter retention time was assigned to the meta isomer (**13***m*): ir (film) 1600 (m), 1565 (m), 780 (s),[67] 745 (s), 720 (s), and 695 (s)[67] cm^{-1}; nmr (CCl_4) 0.74 and 0.78 (s, 6, $C(CH_3)_2$), 1.07–2.51 (m, 5, CH), 5.97 (AMX, 1, $J_{AM} = 6$ Hz, $J_{AX} = 1$ Hz, H_AC=C), 6.10 (AMX, 1, $J_{AM} = 6$ Hz, $J_{MX} = 3$ Hz, H_MC=C), 7.15 (m, 3, Ar H), and 7.24 (m, 1, Ar H). The peak of longer retention time is considered to be due to ortho and para isomers.

Catalytic hydrogenation (5% Pd/C) of the mixture of isomers led in 32% isolated yield to the saturated isomers **14** having a **14***o*:**14***m*:**14***p* ratio of 28:35:37 by integration of the *gem*-dimethyl singlets This ratio shows lower ortho and higher (meta + para) content than does the isomer distribution reported in Table III, suggestive of selective hydrogenation under the reaction conditions. The material was identical with an authentic sample[3] by glpc retention time and nmr and mass spectral criteria.

The very volatile bridgehead chloride **12** was purified by preparative glpc (105°, column D); ir (CCl_4) 3060 (w), 1630 (w), 1480 (s), 1320 (m), 1095 (m), and 980 (s) cm^{-1}; nmr (CCl_4) 0.91 and 0.94 (s, 6, $C(CH_3)_2$), 1.13–2.35 (m, 5, CH), 5.84 (AMX, 1, $J_{AM} = 6$ Hz, $J_{AX} = 1$ Hz, H_AC=C), and 5.96 (AMX, 1, $J_{AM} = 6$ Hz, $J_{MX} = 4$ Hz, H_MC=C); mass spectrum *m/e* 156 (M^+, 23) and 121 ($M^+ - Cl$, 100).

Anal. Calcd for $C_9H_{13}Cl$: C, 69.00; H, 8.37; Cl, 22.64. Found: C, 68.40; H, 8.26; Cl, 22.52.

Oxidation of 1-(*m*-Chlorophenyl)apobornylene (13*m*) to *m*-Chlorobenzoic Acid. A mixture of 38 mg (0.163 mmol) of **13***m*, 294 mg (0.987 mmol) of sodium dichromate, and 2 ml of 50% (w/w) sulfuric acid was heated at 115° for 19.5 hr. Dilution with water followed by extractive work-up, sublimation, and extraction provided 2 mg (8%) of a slightly impure sample of *m*-chlorobenzoic acid, mp 147–148°, mmp 149–150.5°; nmr ($CDCl_3$) and ir (KBr) spectra were virtually identical with those of authentic material. Less than 5% of *o*- and *p*-chlorobenzoic acids were present in the oxidation product.

Degradation of 1-((*o* + *p*)-Chlorophenyl)apobornylene to *p*-Chlorobenzoic Acid. A mixture of 15 mg (0.0647 mmol) of **13***o* and **13***p*, 116 mg (0.389 mmol) of sodium dichromate, and 1.5 ml of 50% sulfuric acid was heated for 14 hr at 110°. The same work-up as for the meta isomer afforded 3 mg (30%) of *p*-chlorobenzoic acid with nmr ($CDCl_3$) region and ir (KBr) spectra superimposable on those of authentic material. Apparently **13***o* does not undergo conversion to *o*-chlorobenzoic acid under these conditions.

Reactions of 1-(*N*-benzoyl)aminoapobornylene (15) and 1-(*N*-benzoyl)aminoapocamphane (16) with dinitrogen tetroxide in chlorobenzene were carried out as described for Scheme III. The products were separated from other material by passage through a silica gel column prior to glpc examination, which gave the results shown in Table III. Preparative glpc (235–240°, column D) and nmr analysis confirmed the isomer ratios.

Reaction of 1-chloroformylapocamphane with silver hexafluoroantimonate in chlorobenzene with added equimolar tetramethylurea was carried out as described[3] at ambient temperature with 0.495 mmol of **1** to give 77 and 97% yields of silver chloride and barium carbonate. Analysis by glpc (column D) at 230° indicated a 60% yield of 1-chlorophenylapocamphane isomers **14** with the isomer ratios (Table III) obtained by the combination of glpc and nmr methods as previously cited.[3] Other products, 1-chloroapocamphane (15%) and 1-fluoroapocamphane (14%), were also identified by glpc (column D) at 110°.

Reaction of 1 with Silver Hexafluoroantimonate in Toluene. To 184 mg (0.535 mmol) of silver hexafluoroantimonate dissolved in 3 ml of toluene was added, over 5 min, 101 mg (0.500 mmol) of **1** in 3 ml of toluene. Silver chloride was obtained in 35% yield. A glpc analysis of the filtrate (235°, column D) gave the yields of 1-tolylapocamphane isomers (**17**) in Table IV. A glpc analysis (125°, column D) gave a 48% yield of 1-chloroapocamphane with retention time and nmr spectrum of a subsequently collected sample identical with those of authentic material.[3]

From a larger scale reaction and preparative glpc (235°, column D), the three isomers of **17** were collected and purified by distillation: nmr (CCl_4) 0.87 (s, $C(CH_3)_2$), 0.89 (s, $C(CH_3)_2$), 1.27 (s, $C(CH_3)_2$), 1.19–2.22 (m, CH), 2.26, 2.28, and 2.40 (s, Ar CH_3), and 7.02 (m, Ar H), relative area of aliphatic to aromatic regions was 4.6 (calcd 4.5), relative *o*:*m*:*p* ratio by integration of the three *gem*-dimethyl singlets was 27 ± 3%:47 ± 3%:26 ± 3%; mass spectrum *m/e* 214 (M^+, 87), 199 ($M^+ - CH_3$, 20), 171 ($M^+ - CH_3CHCH_3$, 75), and 129 (100).[68]

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.71; H, 10.23.

The isomeric mixture was again subjected to preparative glpc with each peak collected separately. The peak of shortest retention time was identified as the meta isomer: ir (CS_2) 3040 (w), 875 (w), 775 (s), and 700 (s)[66,69] cm^{-1}; nmr (CCl_4) 0.88 (s, 6, $C(CH_3)_2$, 1.17–2.40 (m, 12, CH, includes singlet at 2.29, Ar CH_3), 6.89[69] (m, 1, Ar H), and 7.05[69] (m, 3, Ar H).

The peak of intermediate retention time was assigned to the para isomer: ir (CS_2) 3100 (w), 3030 (w), and 810 (s)[66] cm^{-1}; nmr (CCl_4) 0.86 (s, 6, $C(CH_3)_2$), 1.19–2.41 (m, 12, CH, includes singlet at 2.26, Ar CH_3), and 7.06[69] (AA'BB', 4, Ar H).

The peak of longest retention time was assigned to the ortho isomer: ir (CS_2) 3100 (w), 3040 (w), 750 (s),[66] and 725 (m)[66] cm^{-1}; nmr (CCl_4) 1.26 (s, 6, $C(CH_3)_2$), 1.18–2.18 (m, 9, CH), 2.41 (s, 3, Ar CH_3), 6.94[69] (m, 3, Ar H), and 7.33[69] (m, 1, Ar H).

Reactions of 1 with silver hexafluoroantimonate in mixed solvents were carried out as described heretofore by addition of the chloroformate dissolved in the solvent mixture to a solution of the silver salt in the same mixture. Yields of silver chloride and barium carbonate were determined gravimetrically, and yields of **14**,[3] **17**, **18**,[3] **19**[3] (Table IV), and 1-chloroapocamphane were determined by glpc.[60] Preparative glpc and nmr analyses confirm the identification of **18** and **19***m* based on correspondence of retention times with authentic material.

(68) Differences in isomer content in fractions, subjected to preparative glpc, appear to result from differences in collection efficiencies. The results of direct glpc on the reaction mixtures (Table I) show much less variation than do collected materials.

(69) The isomeric *tert*-butyltoluenes have the following characteristic absorptions: ir, meta, 775, 700 cm^{-1}; para, 810 cm^{-1}; ortho, 775, 725 cm^{-1} [M. J. Schlatter and R. D. Clark, *J. Amer. Chem. Soc.*, **75**, 361 (1953)]; nmr, Ar H, para, AA'BB'; meta, two signals, ratio 3:1 with the less intense at higher field; ortho, two signals, ratio 3:1 with the less intense at lower field. These patterns of chemical shifts are identical with the corresponding isomers of 17.

Control experiments on stabilities of the isomers of 17, carried out by subjecting **17***m* and **17***o* + **17***p* to the reaction of **1** with silver hexafluoroantimonate in toluene and benzene–toluene, showed that small amounts of isomerization of **17***o* and **17***p* could occur under those conditions.[60]

Reaction of 1 with silver hexafluoroantimonate in chlorobenzene–benzene with added tetramethylurea gave 71% silver chloride and 92% barium carbonate. Glpc analyses (column D, 220°) gave a 36% yield of **18**, a 21% yield of isomers of **14**, and (column A, 125°) a 20% yield of 1-chloroapocamphane.

Reaction of 4 with silver hexafluoroantimonate in chlorobenzene–benzene with added tetramethylurea gave 73% silver chloride and 89% barium carbonate. Glpc analyses (column B, 235°) indicated a 29% yield of 1-phenylapobornylene (**20**), an 18% yield of isomers of **13**, and (column B, 110°) a 33% yield of 1-chloroapobornylene.

Products **13** and **20** were collected by preparative glpc (column D, 235°), and the two peaks of longer retention time were proved to be isomers of **13** by the identity of their nmr spectrum with that of assigned material (*vide supra*). The component of shorter retention time was purified by distillation to give **20**: ir (film) 3050 (m), 1605 (w), 1580 (w), 760 (s), 740 (m), 720 (s), and 695 (s) cm^{-1}; nmr (CCl_4) 0.73 and 0.75 (both s, 6, $C(CH_3)_2$), 1.17 (m, 2, CH), 1.97–2.45 (m, 3, CH), 6.01 (AMX, J_{AM} = 6 Hz, J_{AX} = 1 Hz, 1, H_A–C=C), 6.08 (AMX, J_{AM} = 6 Hz, J_{MX} = 3 Hz, 1, H_MC=C), and 7.21 (m, 5, Ar H); mass spectrum *m/e* 198 (M^+, 38), 183 ($M^+ - CH_3$, 58), 155 ($M^+ - CH_3CHCH_3$, 97), and 91 (100).

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.56; H, 9.09.

The identity of 1-chloroapobornylene was established from the similarity of its nmr spectrum to the material from the chlorobenzene reaction above, after preparative glpc (120°, column D).

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Structural Studies on Nitrosobenzene and 2-Nitrosobenzoic Acid. Crystal and Molecular Structures of *cis*-Azobenzene Dioxide and *trans*-2,2′-Dicarboxyazobenzene Dioxide[1,2]

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Abstract: A spectroscopic and X-Ray structural study of crystalline nitrosobenzene and 2-nitrosobenzoic acid has been undertaken. A structure analysis of crystalline nitrosobenzene revealed that the familiar colorless crystals, which exist in two distinct habits, contained exclusively the *cis*-azobenzene dioxide (**3a**) molecule. This result was consistent with the infrared spectroscopic correlation proposed by Lüttke. An infrared examination of the melt of nitrosobenzene showed the presence of bands in the infrared indicative of the *trans*-azobenzene dioxide (**3b**) molecule. Attempts to obtain stable crystals of this dimer were unsuccessful. The crystals of **3a** are orthorhombic, a = 10.460 (3), b = 13.833 (3), c = 15.156 (5) Å, and there are eight molecules in the unit cell, space group *Pbcn*. The structure was refined to an R factor of 0.060 on 1084 nonzero reflections. The molecule has approximate C_2 symmetry; the N–N and N–O lengths are 1.321 (5) and 1.265 (4) Å (av). There is considerable out-of-plane distortion at nitrogen, resulting in C–N–N–C and O–N–N–O torsion angles of 18.0 and 3.9°. The X-ray analysis of crystalline 2-nitrosobenzoic acid showed that it exists in the crystal as *trans*-2,2′-dicarboxyazobenzene dioxide (**4**). This result was also consistent with Lüttke's correlation. The crystals are triclinic: a = 7.623 (4), b = 7.412 (4), c = 6.746 (4) Å; α = 115.14 (4), β = 106.66 (4), γ = 94.20 (4)°. This space group is $P\bar{1}$ with one molecule in the unit cell. The structure was refined to an R factor of 0.052 on 880 nonzero reflections. The dimer molecule has exact crystallographic C_i symmetry; the N–N and N–O lengths are 1.308 (3) and 1.267 (3) Å. In **4** there is much less out-of-plane distortion; the C–N–N–O torsion angle is 5.5°. The two C–O lengths are 1.301 (3) and 1.218 (3) Å and the C–C–O angles are 114.1 (2) and 122.5 (2)°. An analysis of corresponding published dimensions for aromatic carboxylic acids shows a wide range of values. There is a linear correlation between Δr (the difference in C–O lengths) and $\Delta\theta$ (the difference in C–C–O angles). It appears that there is essentially a continuum of these values among the published structures of aromatic carboxylic acids from completely ordered (with large values of Δr and $\Delta\theta$) to those that show statistical twofold disorder. The developed crystal faces exhibited by **3a** and **4** have been analyzed in terms of the molecular packing.

The range of structural behavior and the varied properties of aromatic *C*-nitroso compounds,[3–6] both in solution and in the crystalline state, provide a fruitful area for a combined crystallographic and chemical study.[7] Aromatic *C*-nitroso compounds can exist as blue or green colored monomers (**1**) or colorless dimers (**2**). In the dimeric state, cis (**2a**) and trans (**2b**) isomers are possible. As a general rule, but one with

(1) Taken from the Ph.D. thesis of David A. Dieterich, submitted to the University of Illinois, 1973, available from University Microfilms, Ann Arbor, Mich.

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