1,5-Hydride Shifts in Vinyl Cation Intermediates Produced upon the Acylation of Acetylenes

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Abstract: The acylation of alkynes with a variety of cyclohexanecarbonyl cations under nonnucleophilic conditions has been investigated. A facile intramolecular 1,5-hydride shift from the β-carbon of the acylating agent to the initially formed vinyl cation intermediate is a common feature of all these reactions. The subsequent reactions of the rearranged carbenium ion are sensitive to the structure of the acylating agent and one pathway available to this carbenium ion involves a 1,2-acyl migration. The utilization of this process is demonstrated in the synthesis of certain 1,2-adamantane systems.

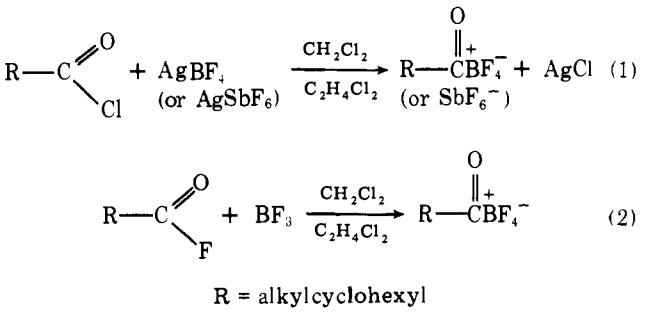
The present study reflects our continuing interest in the nature of the reactive vinyl cation intermediate produced upon the acylation of acetylenes under various weakly nucleophilic conditions. Our previous work has shown that the vinyl cation intermediate generated in this fashion can react with a variety of nucleophilic species, including aromatic substrates, and even with nucleophiles as weak as nitroalkanes.[2] This, along with other related studies,[3-7] provides rather conclusive evidence for the existence of reactive vinyl cation intermediates generated by certain electrophilic additions to the triple bond.[8,9]

Complementary to the above investigations, we have been examining the interaction of acyl cations with acetylenes in the nonpolar methylene chloride/1,2-dichloroethane solvent system at low temperatures. Our interest in pursuing reactions of this type stems from two initial and previously reported observations of this group.[10,11] First of all, it was noted that with branched acyclic acyl cations the addition to a variety of acetylenes proceeded as outlined in Scheme I to yield cyclopentenones.[10] The general reaction is illustrated for the formation of 1,2,4-trimethylcyclopentenone (**2**) from isobutyryl tetrafluoroborate (**1**) and dimethylacetylene. The formation of the cyclopentenones corresponds to substitution at the β position of the acyl side chain, and two conceivable pathways for the cyclization reaction of the initially formed vinyl cation intermediate are also suggested in Scheme I.

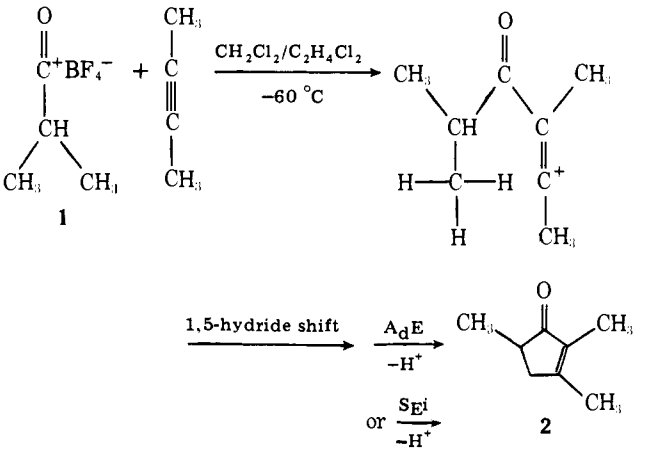
Secondly, it was noted that, in contrast to the acyclic acyl cations, a similar cyclization reaction was not observed with the cyclohexanecarbonyl cation **3**.[11] Instead the reaction proceeds with the production of the fluoroketone **4**, presumably formed by an intramolecular 1,5-hydride shift to the initially formed vinyl cation intermediate with subsequent capture by the tetrafluoroborate counteranion at the secondary carbenium ion stage as illustrated in Scheme II.[12]

Both the reactions shown in Schemes I and II seem to be rather novel and unusual and they serve as examples illustrating the diversity of the reaction course for the alkyne acylation, even with closely related acylium salts. These data prompted us to start a more detailed study of alkyne acylation with various acylium salts to obtain an insight into the factors affecting the reaction course and to evaluate the potential synthetic utility of the process.

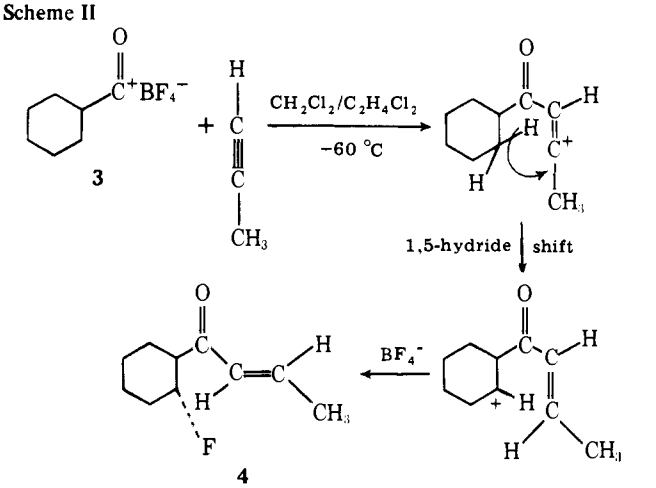
Here we wish to report our results on the acylation of methylacetylene with a series of alkyl substituted cyclohexanecarbonyl cations that demonstrate a number of reaction pathways available to the reactive vinyl cations formed under nonnucleophilic conditions. Furthermore, an example of the synthetic utility of this reaction is illustrated in the preparation of 1,2-adamantane derivatives.



Scheme I



Scheme II



Methods and Results

The acyl salts for the present investigation were generated by conventional methods as indicated in eq 1 and 2 (see Experimental Section for details). The acylation reactions were carried out by the addition of a methylene chloride solution of the acid halide to a stirred mixture of the silver salt and the

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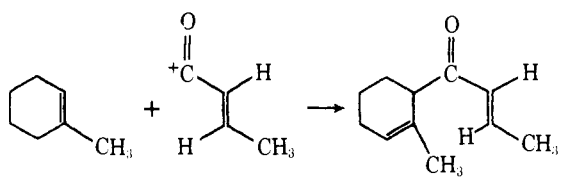
alkyne in a methylene chloride–dichloroethane solvent system at −60 to −20 °C, or alternatively by the introduction of the alkyne into a preformed solution of the acylium solvent system. The mixture was stirred vigorously at this temperature for 5–10 min and then decomposed by the addition of a dilute sodium bicarbonate solution and ethyl ether. Product separations were accomplished by preparative GLC and/or TLC and the reported yields were determined by analytical GLC on the initial reaction mixture by calibration using internal standards. The various cyclohexanecarbonyl cations that were used in this study, along with the resulting products, are listed in Table I. The structures of the products were established mainly by NMR (^{13}C and ^{1}H with appropriate spin decoupling experiments), together with IR, MS, UV, and, in certain cases, by independent syntheses. The products are divided into two categories, types A and B, for the sake of discussion. The basic ^{1}H NMR data for ketones of type A are listed in Table II and those for the minor products of type B are given in Table IV. The products obtained in adamantane series are given in Table V.

Structural Determinations

All the products of type A have in common the trans side chain fragment $-COCH_A{=}CH_BCH_3$ as is clearly evident by the ABX_3 in their ^{1}H NMR spectra (Table II). The presence of this residue is also apparent from MS with an intense peak at *m/e* 69 $(C_4H_5O)^+$. The structures of the ring portion of these products were established by a variety of techniques as discussed below.

For the fluoroketone **37**, the 1,2,6 positioning of the substituents is consistent with the ^{13}C, ^{19}F coupling values (^{13}C spectra: Table III) with $J_{C_1,F}$ = 17.4 cps, $J_{C_2,F}$ = 7.4 cps, $J_{C_3,F}$ = 1.7 cps, $J_{C_4,F}$ = 11.3 cps, and $J_{C_5,F}$ = 18 cps. The trans-anti-trans configuration is supported by the ^{1}H NMR data on proton coupling constants (determined at both 60 and 100 MHz with the aid of homo- and heteronuclear decoupling) with $J_{H_1,H_6} = J_{H_2,H_1} = J_{H_1,F} = J_{H_6,H_{5a}}$ = 10 cps, and $J_{H_6,H_{5e}}$ = 4 cps. The similarity of the corresponding coupling constants for the fluoroketones **4** and **7** permit one to assign the analogous configurations.

The structure of the dienone **17** was suggested by a ^{1}H



17

NMR spectral analysis, but the unexpected β,γ-ring double bond prompted us to confirm this assignment by an independent synthesis. This was done readily by the acylation of 1-methylcyclohexene with the crotonyl cation.[13]

The distinction between the dienones **23** and **27** is a subtle but very important one. The characterization of these ketones was accomplished by ^{13}C NMR, as well as high-resolution ^{1}H NMR with the aid of spin-decoupling and shift reagent studies. These detailed NMR studies enabled us to characterize and, hence, distinguish the allylic proton patterns in the isomeric ketones **23** and **27** and, hence, permitted an unambiguous assignment. The basic data are listed in Tables II and III.

The cyclopentene system **18** was synthesized independently by the acylation of ethylidenecyclopentane in the same manner already illustrated for the formation of **17**. The structure is further consistent with both the ^{1}H NMR (Table II) and ^{13}C NMR (Table III) patterns.

The close similarity in the ^{1}H NMR spectrum of the mixture of positional isomers **24a** and **24b** to the pattern in **18** helps the assignment here (Table II). Especially significant is the presence of the $-CH(CH_3)COR$ fragment as evidenced by the appearance of the methyl doublet δ 1.25, as well as a corresponding pair of quartets for the methine proton in the allylic region with a total intensity of one proton. The relative intensities of these latter two signals suggest equal amounts of the positional isomers, and this is further confirmed by GLC.

The spiroketone **28** was identified, in part, by a comparison with the ^{1}H NMR spectra of the closely related cyclopentanones (e.g., **2**[10]). Especially clear in the ^{1}H NMR and ^{13}C NMR spectra (Tables II and III) is the involvement of the methyl group in the cyclization process. The symmetry plane in **28** is further evidenced in the NMR data.

The products of type B, as shown in Table I, were identified by MS and ^{1}H NMR data. The acylium fragment, $C^+O{-}CH{=}CXCH_3$ with X = F or Cl, is readily observable in the mass spectrum. The structures of these β-halovinyl ketones are further consistent with the ^{1}H NMR spectra (Table IV). The details of the structural assignments for the adamantane derivatives **44–56** (Table V) will be published shortly.

Discussion

The nature of the products derived from the acylation reactions of the alkylcyclohexanecarbonyl cations listed in Table I fall into a somewhat regular, although in some cases unexpected, fashion. All of the reactions, first of all, yield minor amounts of *cis*- and *trans*-β-halovinyl ketones of type B as shown in Table I. These products are not only minor but are trivial in that they correspond to capture of the initially formed and reactive vinyl cation intermediate (B in Scheme III) by either the tetrafluoroborate counterion or by chloride abstraction from the solvent.[14] With the exception of the reaction with *cis*-4-*tert*-butylcyclohexanecarbonyl tetrafluoroborate (**10**), these β-haloketones are never the major products and are not discussed further.

The more interesting and major products in Table I are those of type A, all of which conceivably arise from an initial 1,5-intramolecular hydride shift to the carbenium ion center of the vinyl cation intermediate under these nonnucleophilic conditions (Scheme III). The net result of the hydride transfer is a syn addition of the acyl electrophile and hydride nucleophile to the triple bond.[11] The final products are derived from the ring carbenium ion resulting from the hydride transfer, and the reactions at this stage are dependent upon the location and the stereochemistry of the alkyl group on the cyclohexane ring.

The preference for formation of products of type A from the corresponding intermediate under these nonnucleophilic conditions suggests that the 1,5-intramolecular hydride shift

Scheme III

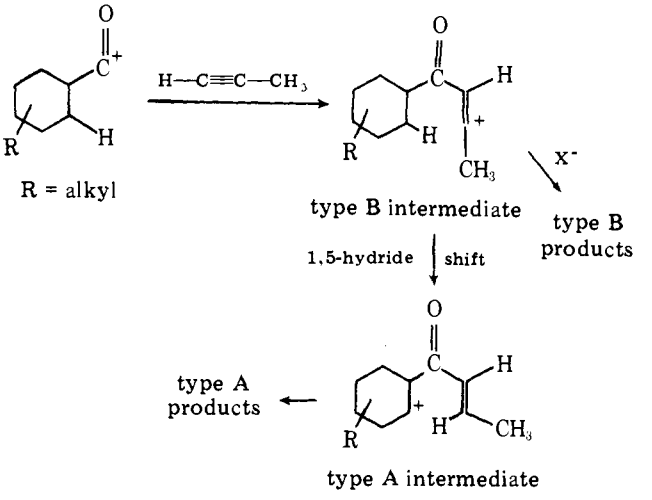


Table I. Products of the Addition of Alkylcyclohexanecarbonyl Tetrafluoroborates to Methylacetylene

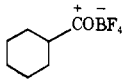
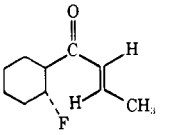
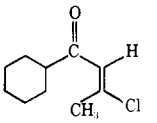
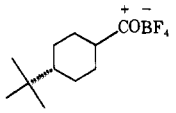
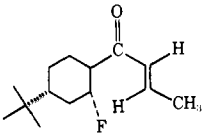
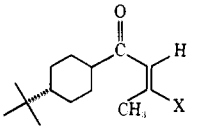
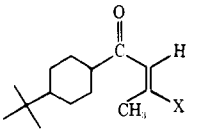
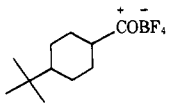
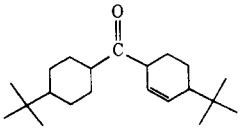
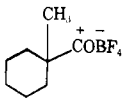
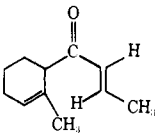
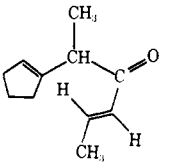
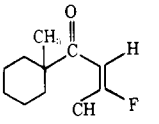
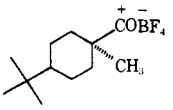
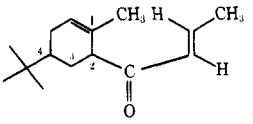
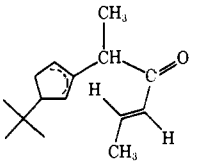
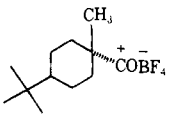
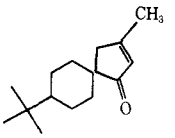
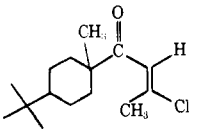
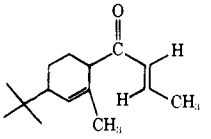
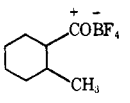
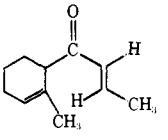
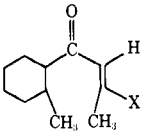
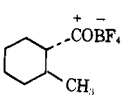
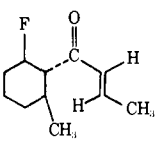
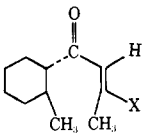
acyl salt	products of type A	products of type B
 **3**	 **4**, 35%	 **5**, 12%
 *trans*-**6**	 **7**, 35%	 **8**, X = F, 15% **9**, X = Cl, 15%  **11**, X = F, 15% **12**, X = Cl, 15%
 *cis*-**10**		 **13**, 25%
 **14**	 **17**, 40%  **18**, 20%	 **19**, 6%
 *cis*-**22**	 **23**, 25%	
	 **24a,b**, 25%	β-halo deriv not isolated
 *trans*-**26**	 **28**, 15% **24a,b**, 15%	 **29**, 15%
	 **27**, 15%	
 *cis*-**32**	 **17**, 40%	 **33**, X = F, 10% **34**, X = Cl, 10%
 *trans*-**36**	 **17**, 25% **37**, 15%	 **38**, X = F, 15% **39**, X = Cl, 10%

Table II. Pertinent ^{1}H NMR Data for Type A Ketones[a]

compd	$-COCH_A=CH_BCH_{3X}$ or $-CH_CCH_{3D}COCH_A=CH_BCH_{3X}$				other assignments on ring
	H_A	H_B	H_C	CH_{3X} and CH_{3D}	
17[b]	6.08 dq J_{AB} = 15.5 J_{AX} = 1.2	6.83 dq J_{BX} = 6.5		1.87 dd	3.07 m (H at C_1) 1.54 s (CH_3 at C_2) 5.55 m (H at C_3)
17-d_3 + d_4[c]	6.14 br s			1.87 d	5.55 m (ca. 0.15 H)
18[c]	6.1 dq J_{AB} = 15.5 J_{AX} = 1.2	6.85 dq J_{BX} = 6.5	3.37 q J = 7	1.89 dq 1.13 d	5.45 m (H at C_2)
18-d_3 + d_4[c]	6.1 s		1.14 s	1.89 d	5.45 m (31% D)
23[d]	6.07 dd J_{AB} = 15.5 J_{AX} = 1.2	6.83 dq J_{BX} = 6.5		1.87 dd	3.05 m (H at C_1) 1.52 s (CH_3 at C_2) 5.55 m (H at C_3) 0.86 s ($-C(CH_3)_3$)
24a,b[e]	6.07 dd J_{AB} = 15.5 J_{AX} = 1.2	6.77 dq J_{BX} = 6.5	3.18 and 3.22 (two isomers) J = 7	1.85 dd 1.25 d	5.41 m (H at C_2) 21. m (allylic protons)
27[f]	6.12 dd J_{AB} = 15.5 J_{AX} = 1.2	6.66 dq J_{BX} = 6.5		1.89 dd	5.55 br s (H and C_3) 2.95 d (H at C_1, J = 6) 0.91 s ($C(CH_3)_3$)
28[e]	5.8 m			2.13 d J = 1.2	2.5 broad s (2 H at C_7) 0.88 s ($C(CH_3)_3$)
37[c]	6.09 dd J_{AB} = 15.5 J_{AX} = 1.2	6.83 dq J_{BX} = 6.5		1.87 dd	2.5 m (H at C_1) 4.5 dm (H at C_6, J_{H_6F} = 49) 0.83 d (CH_3 at C_2, J = 7)
7[c]	6.09 dd J_{A_1B} = 15.5 J_{AX} = 1.2	6.85 dq J_{BX} = 6.5		1.88 dd	2.51 m (H at C_1, $J_{H_1H_2} = J_{H_1F}$ = 10) 4.5 dm (H at C_2, J_{HF} = 49) 0.91 s ($C(CH_3)_3$)

[a] J values in hertz. Chemical shifts in δ relative to $(CH_3)_4Si$. [b] 60 MHz. [c] 60 and 100 MHz. [d] 100 and 200 MHz. [e] 100 MHz. [f] 360 MHz.

Table III. ^{13}C NMR Data for Type A Ketones

compd	C_1	C_2	C_3	C_4	C_5	C_6	C=O	C_α	C_β	other assignments
17[a-c]	51.97	132.05	125.49	25.5	23.07	27.56	200.2	131.26	143.4	20.34 (CH_3 at C_2) 18.21 (CH_3 at C_β)
23[a-c]	54.4	130.96	126.1	26.96	43.47	28.28	208.53	129.56	142.98	21.25 (CH_3 at C_2) 18.21 (CH_3 at C_β) 32.24 and 27.26 ($C(CH_3)_3$)
27[a,b]	131.9	50.57	26.71	23.74	46.14	127.52	200.6	130.23	142.42	20.15 (CH_3 at C_1) 18.15 (CH_3 at C_β) 33.02 and 27.32 ($C(CH_3)_3$)
28[a,c,d]	50.0	34.6	24.6	48.0	24.6	34.6	192.5	128.8	176.2	46.2 (C_7) 19.3 (CH_3) 32.9 and 27.8 ($C(CH_3)_3$)
18[a,b]	143.34	126.95	33.27	23.43	32.54	47.23	200.17	12.86	142.31	18.15 and 14.93 (CH_3 signals)
7[a,d,e]	53.64 J = 19	93.55 J = 174.6	34.1 J = 17.7	41.5 J = 9.7	26.46	41.22 J = 8.7	200.24	132.79	143.46	18.69 (CH_3 at C_β) 28.09 and 32.8 ($C(CH_3)_3$)
37[a,d,e]	60.72 J = 17.6	35.4 J = 7.4	34.22 J = 1.7	36.08 J = 11.3	32.77 J = 18	94.76 J = 175	201.66	134.69	143.41	18.48 (CH_3 at C_β) 20.32 (CH_3 at C_2)

[a] J values in hertz. Obtained in $CDCl_3$ with chemical shifts reported in δ relative to the internal standard $(CH_3)_4Si$. [b] 15.08 MHz. [c] These assignments were aided by examining the relative sizes of pseudocontact shifts induced by $Eu(fod)_3$. [d] 25.2 MHz. [e] Obtained in C_6D_6 with chemical shifts reported in δ relative to the internal standard $(CH_3)_4Si$.

in the vinyl cation intermediate might be a general process.[15] Long-range hydride shifts of this magnitude in carbenium ion chemistry are observed only in select instances,[16,17] and, to our knowledge, have never been documented for a vinyl cation intermediate. In fact, even simple 1,2-hydride shifts, either to or across, in vinyl cations have been reported only in a few cases.[18] It behooved us, therefore, to examine this reaction in greater detail.

First of all, an unambiguous confirmation of the origin of the hydride shift comes from the examination of the products

Table IV. Pertinent ^{1}H NMR Data for Ketones of Type B[a]

compd[b]	$-COCH_A=CXCH_3$ where X = F or Cl		other assignments
	H_A	CH_3	
19	6.17 d, J = 20	2.34 d, J = 20	1.05 s (ring methyl)
23	6.54 m (small allylic coupling)	2.49 d, J = 1.2	0.87 s ($C(CH_3)_3$)
38	5.75 d, J = 20	2.22 d, J = 20	0.83 d (ring methyl) J = 7
39	6.33 m (small allylic coupling)	2.5 d, J = 1.2	0.84 d (ring methyl) J = 7
39a	5.33 s	2.0 s	0.84 d (ring methyl) J = 7
33	6.14 d, J = 20	2.41 d, J = 20	0.83 d (ring methyl) J = 7
34	6.41 m (small allylic coupling)	2.5 d, J = 1.2	0.84 d (ring methyl) J = 7
34a	5.34 s	1.97 s	0.84 d (ring methyl) J = 7
8	5.98, J = 20	2.3 d, J = 20	0.85 s ($C(CH_3)_3$)

[a] J values in hertz. [b] All spectra were obtained as CCl_4 solutions at 60 MHz. Chemical shifts are reported in δ relative to internal $(CH_3)_4$-Si.

Table V. ^{1}H NMR Data for Adamantane Derivatives[a]

compd[b]	$-COCH_A=CH_BR$	CHZ, where Z = F, Cl, or Ar	other assignments
44	6.40 d (H_A) J_{AB} = 15.5 6.85 dq (H_B) 1.87 q (CH_3) J = 7	4.87 dd J_{H_2F} = 49 J_{H_2,H_3} = 3	
45	6.34 d (H_A) J_{AB} = 15.5 6.81 dt (H_B)	4.8 dd J_{H_2F} = 49 $J_{H_2H_3}$ = 3	
46	6.38 d (H_A) J_{AB} = 15.5 6.87 dt (H_B)	4.87 dd J_{H_2F} = 49 $J_{H_2H_3}$ = 4	0.87 s ($C(CH_3)_3$)
47	6.23 d (H_A) J_{AB} = 15.5 6.77 d (H_B)	4.77 dd J_{H_2F} = 50 $J_{H_2H_3}$ = 3	
48		4.96 dd J_{H_2F} = 49 $J_{H_2H_3}$ = 3	7.32 m (C_6H_5 and H_A, H_B)
49	6.37 d (H_A) J_{AB} = 15.5 6.87 dq (H_B) 1.87 d (CH_3) J = 7	4.52 br s	
50	6.19 d (H_A) J_{AB} = 15.5 6.87 dq (H_B) 1.67 d (CH_3) J = 7	3.36 br s	7.02 br s ($-C_6H_5$)
51	6.26 d (H_A) J_{AB} = 15.5 6.34 dq (H_B) 1.72 d (CH_3) J = 7	3.5 and 3.37 br s (ortho and para isomers)	6.99 br s ($-C_6H_4-$) 2.22 and 2.32 s (CH_3-Ar)

[a] J values in hertz. [b] Chemical shifts are in δ relative to internal $(CH_3)_4Si$. All samples were CCl_4 solutions and spectra were obtained at both 60 and 100 MHz.

from the reaction of the acyl cation **14**-d_4 (Scheme IV). The products (**17** and **18**) derived from the type A intermediate (**15**-d_4) clearly have a deuterium (>95%, ^{1}H NMR, MS) at the β-vinylic position. This result must be considered as experimental proof of the proposed 1,5-intramolecular hydride shift mechanism for this and the other type A products.

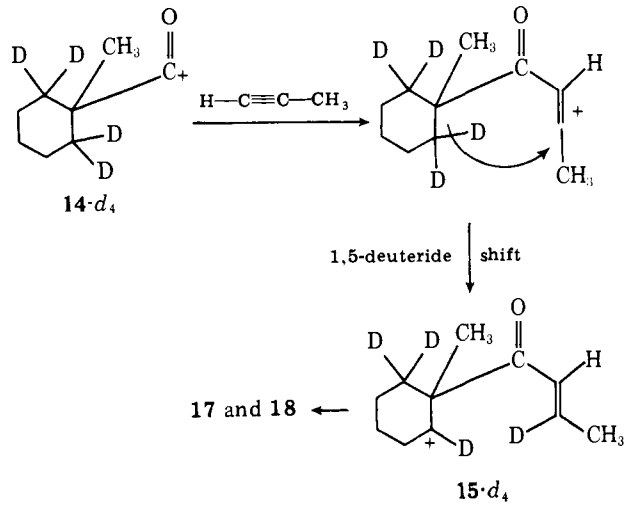
The subsequent reactions of the intermediates leading to type A products are very sensitive to the introduction of alkyl groups on the ring portion of the acylium ion. This aspect of the reaction is illustrated by the interesting and unexpected results observed in the acylations with the 1-methyl derivatives **14**, **22**, and **26**.

As shown in Table I, in the reaction of **14** the only products of type A were those derived from the secondary carbenium ion intermediate **15** (Scheme V), and no evidence could be found for the formation of the spiro substitution product **16**.

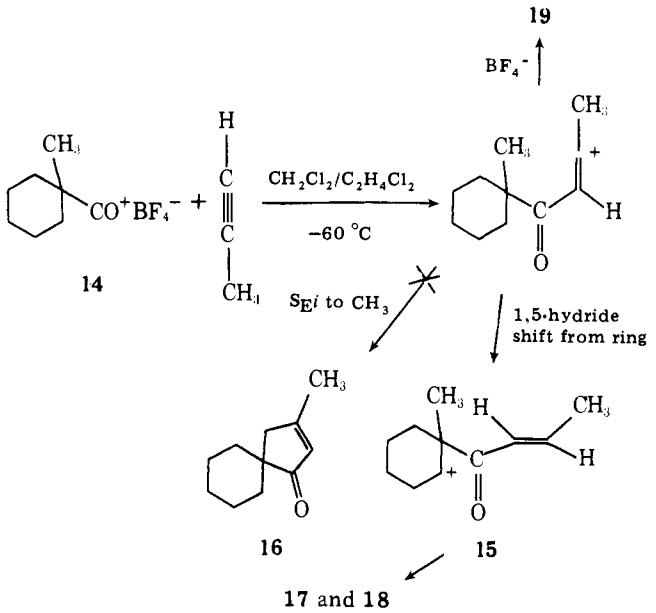
The subsequent reactions of the intermediate **15** lead to the two major products in this reaction, the dienones **17** and **18**, in a ratio of about 2:1. In the formation of the minor dienone **18** a ring contraction obviously has occurred and with the major dienone **17** it is interesting to note that the methyl group and the acyl fragment are no longer on the same carbon, and thus a rearrangement must have taken place here as well. There is no ambiguity as to the structural assignments for **17** and **18** which were established by spectral means as well as independent syntheses (see Methods and Results).

The simplest explanation to account for the formation of the dienones **17** and **18** is a competitive migration of bond a vs. bond b in the intermediate carbenium ion **15** as shown in Scheme VI. Migration of bond b corresponds to a ring contraction, and the route to the minor dienone **18** offers no surprises. The postulated migration of bond a, however, corresponds to a less common acyl shift. The possibility of, and migratory aptitude of, an acyl shift remains of general inter-

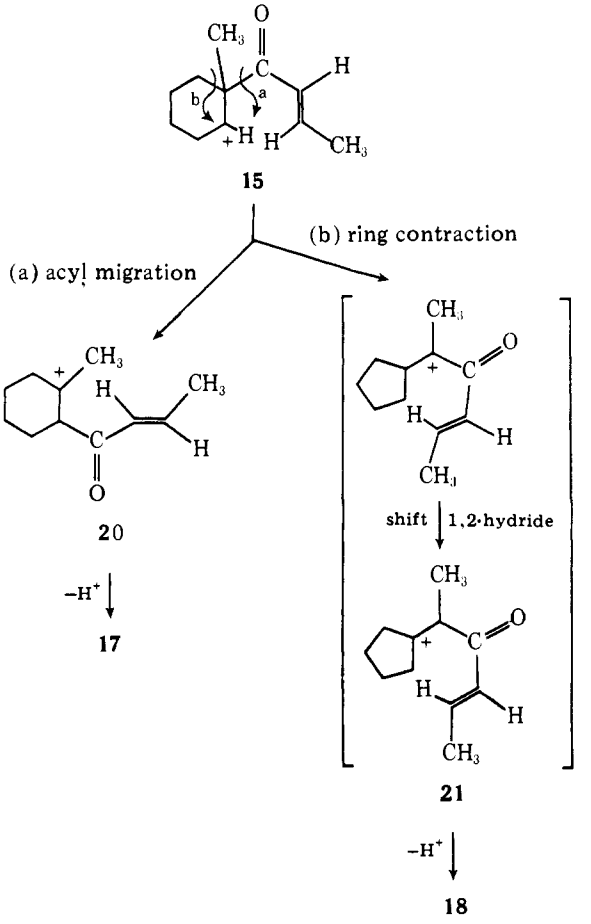
Scheme IV



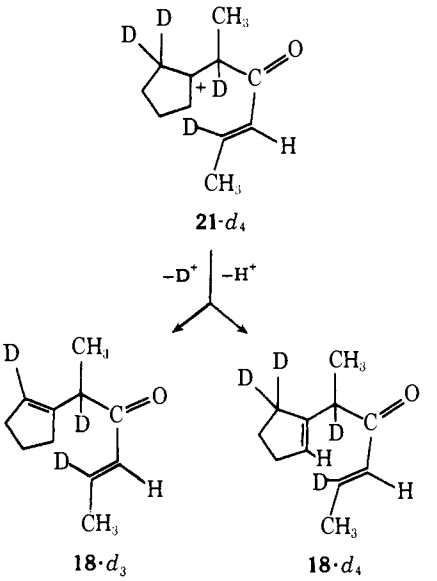
Scheme V



Scheme VI



Scheme VII



est,[19-24] and this reaction appeared to be well suited for testing the existence of an acyl migration as opposed to some combination of methyl and hydride shifts, which could also lead to the production of **17**.

In this regard it is very instructive to examine the deuterium distribution in the dienones **17** and **18** obtained upon the acylation of methylacetylene with 2,2,6,6-tetradeuterio-1-methylcyclohexanecarbonyl cation (**14**-d_4). The deuteriated ketone **18** obtained in this experiment consists of d_4 and d_3 products in a ratio of 61:39 (MS) with the deuterium labeling as shown in Scheme VII (^{1}H and ^{13}C NMR). This is an anticipated result if one considers the isotope effect for the ease of elimination of a proton vs. a deuteron from the intermediate **21**-d_4. As noted above, the absence of a proton at the β-vinyl carbon in the side chain of both **18** and **17** must be considered as unequivocal proof of the exclusive 1,5-intramolecular hydride shift in the formation of the intermediate **15** (1,5-deuteride shift for **15**-d_4).

In contrast to the d_4:d_3 ratio in **18**, where either a proton or deuteron can be lost in its formation, the d_4:d_3 ration in **17** is 20:80 and, hence, the letter must be formed by the *preferential* loss of a deuterium (Scheme VIII). The remaining deuteriums, furthermore, clearly can be shown to be distributed as anticipated for the acyl group migration mechanism via cation **20** and a partial ^{1}H NMR spectrum is shown in Figure 1. An alternate route for the formation of **17**, also shown in Scheme VIII, involving some combination of 1,2-methyl and hydride shifts seems improbable since in this case one would expect the preferential formation of **17**-d_4 containing no deuterium at the ring double bond.

At the same time, careful examination of the ^{1}H NMR spectrum for **17** (Figure 1) exhibits a small amount (less than 0.2 H) of the undeuteriated ring double bond. The MS spec-

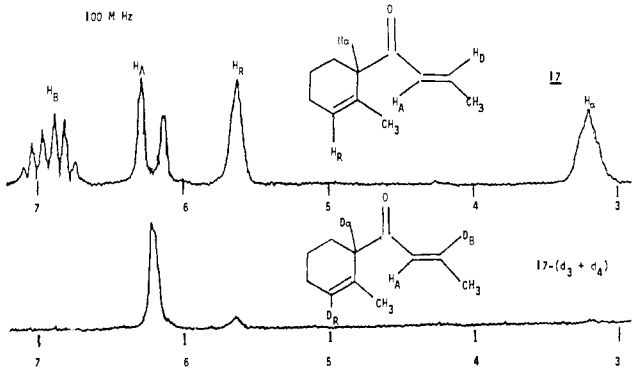
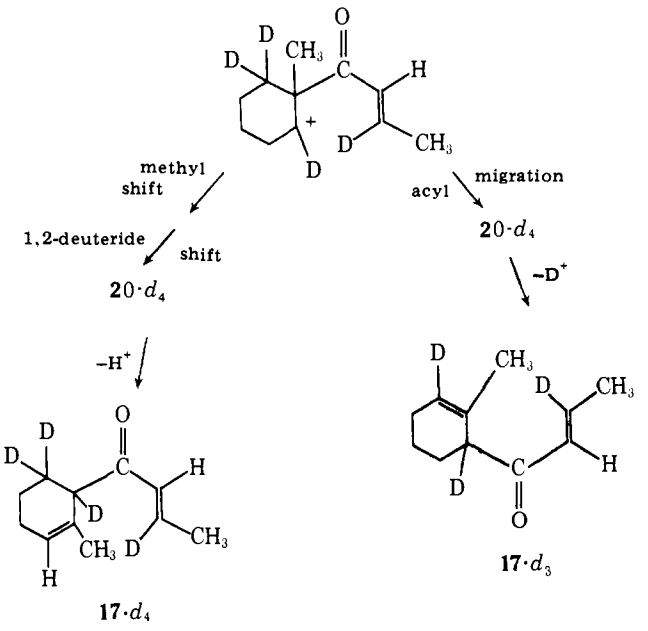


Figure 1. Partial ^1H NMR spectrum of dienone **17** and **17**-d_3 (spectrum obtained with deuterium decoupling).

Scheme VIII



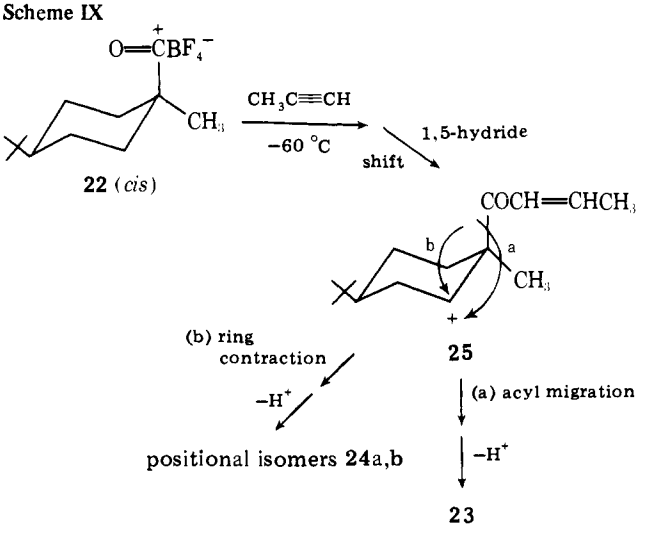
trum shows a similar excess of **17**-d_4, and along with the ^1H NMR analysis, suggests that a competitive pathway for the rearrangement process is conceivable. In fact, we have now shown that the competitive rearrangement pathways (vide infra) are sensitive to the geometry of the geminal substituents at the migratory origin.

It is impossible to state in this instance that in general the acyl group has a greater inherent propensity to migrate than a methyl group as there is a tremendous difference in the stability of the resulting cationic center (tertiary carbenium ion **20** vs. production of an intermediate with a cationic site adjacent to a carbonyl group). It is not unreasonable, however, that the acyl group should possess a satisfactory migratory aptitude, in spite of the unfavorable ground state polarization of the carbonyl group.[24]

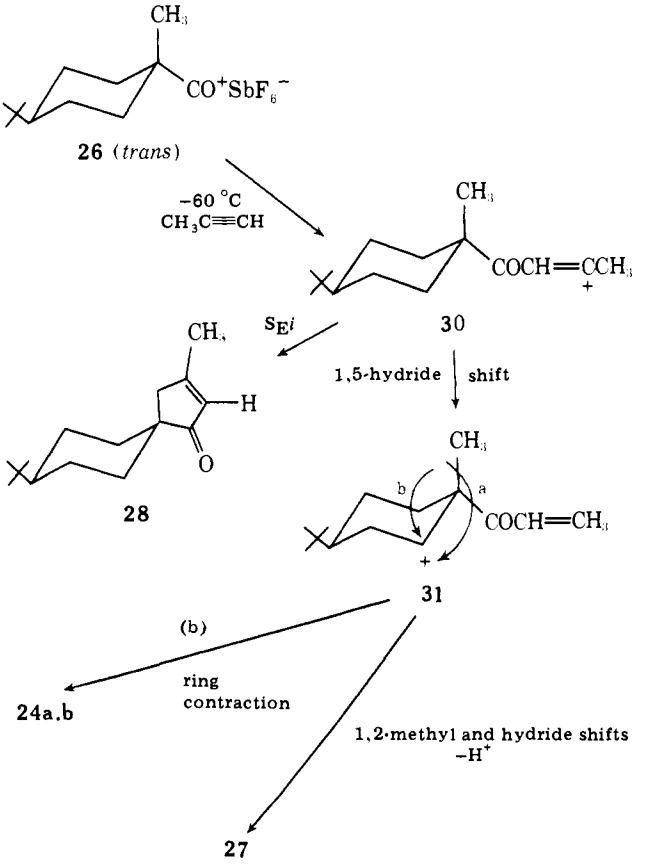
The acylium salts **22** and **26** seemed to be particularly suitable for the elucidation of the preferential pathways of 1,2 migrations, since in these cases the products of a 1,2-acyl shift and a 1,2-methyl shift must be positional isomers. In addition, one can take advantage of the locked conformation in **22** and **26** to determine the preferred stereochemical arrangement of the migrating substituent, whether acyl or methyl.

The results from the cis isomer **22** are remarkably similar to the reaction of 1-methylcyclohexanecarbonyl tetrafluoroborate **14**. Roughly equal amounts of the acyl shifted dienone **23**, corresponding to a path a from intermediate **25**, and the

Scheme IX



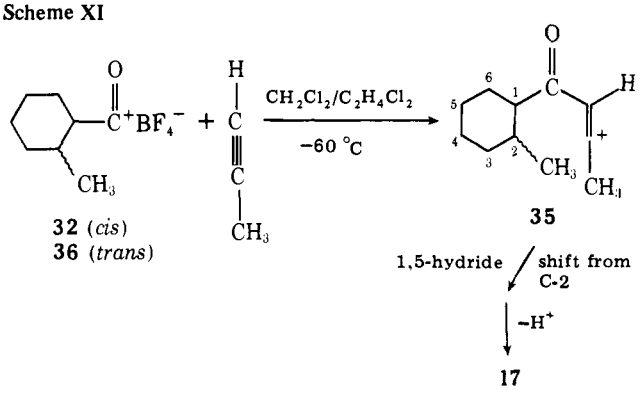
Scheme X



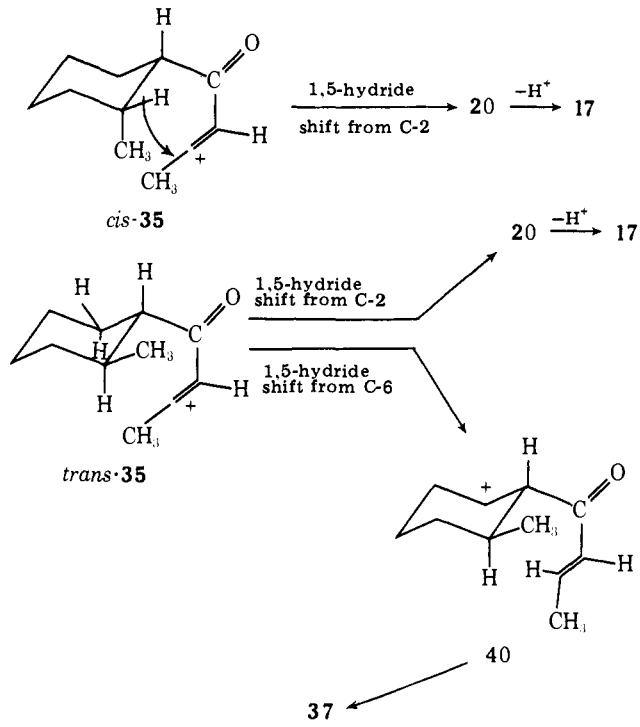
ring contraction dienones **24a,b**, corresponding to path b, are observed (Scheme IX).

The same mixture of ring contracted dienones **24a,b** have also been isolated from the mixture of products formed in the acylation with **26** (Scheme X). However, in this case none of the product **23** resulting from a 1,2-acyl shift could be detected, and instead the isomeric dienone **27** was isolated. The data on the structure of the latter demonstrated unequivocally that its formation is certainly owing to a 1,2-methyl shift, accompanied by the reverse 1,2-hydride shift in **31**, i.e., to the process which was ruled out as a possibility to account for the formation of dienone **17** (Scheme VIII). It appears that the absence of methyl shifted products in the reaction of **22** and the absence of acyl shifted products in the reaction of **26** illustrate the high preference for the migration of an axial substituent from the

Scheme XI



Scheme XII



migratory origin regardless of the nature of migratory group.

Several comments could be made on the possible steric course of the observed reactions. The fixed axial conformation of the acyl residue in **22** (and hence in the corresponding vinyl cation intermediate) allows only an equatorial C_2–H bond to take part in the 1,5-hydride shift process. The concerted removal of an *equatorial* hydride with concurrent contraction causes little surprise, since it is the anticipated pathway of this type of carbenium ion rearrangement.[20] However, in the formation of the dienone **23** resulting from an acyl shift, one can consider two extreme alternatives for the migration of the axial substituent. Thus, one can again postulate a process involving a concerted migration with the hydride transfer, or one can envisage a stepwise process involving the formation of the planar secondary carbenium ion **25** as a discrete intermediate. A concerted mechanism would not permit effective orbital overlap, and the second alternative appears more attractive. Certainly the geometry of the intermediate **25** has a more coplaner orientation of the axial C-acyl bond with the vacant p orbital at the carbenium ion center. This latter possibility also seems consistent with several recent observations,[25] including the concept of orbital control in the course of carbenium ion rearrangements as advanced by Brower and Hogeveen.[26]

The configuration of the trans isomer **26** permits the involvement of either an axial or equatorial hydride from C_2. Subsequent data (vide infra) suggest a pronounced preference for an equatorial hydride removal, and it seems reasonable to formulate a stepwise mechanism for the formation of the methyl shifted dienone **27**. The most unusual feature observed in the reaction of **26** was the isolation of the spiroketone **28**, a long sought-after product corresponding to an intramolecular cyclization of the type shown in Scheme I. It appears that the fixed equatorial disposition of the acyl fragment in **26** permits substitution at σ C–H bond of the methyl group to compete successfully with hydride transfer from a ring position in the vinyl cation intermediate **30**.

We further examined the reactions of *cis*- and *trans*-2-methylcyclohexanecarbonyl tetrafluoroborates, **32** and **36**, respectively, for two reasons. First of all, a 1,5-hydride shift originating from the tertiary ring carbon in **35** should produce the same intermediate **20**, resulting from an acyl migration in **14**. Secondly, the introduction of the 2-methyl substituent creates, of course, nonequivalent ring β positions, and thus offers the possibility of evaluating the difference in ease of hydride transfer from the secondary vs. the tertiary ring position. Any difference in reactivity presumably could be related, in part, to the ease of an equatorial vs. axial hydride transfer.

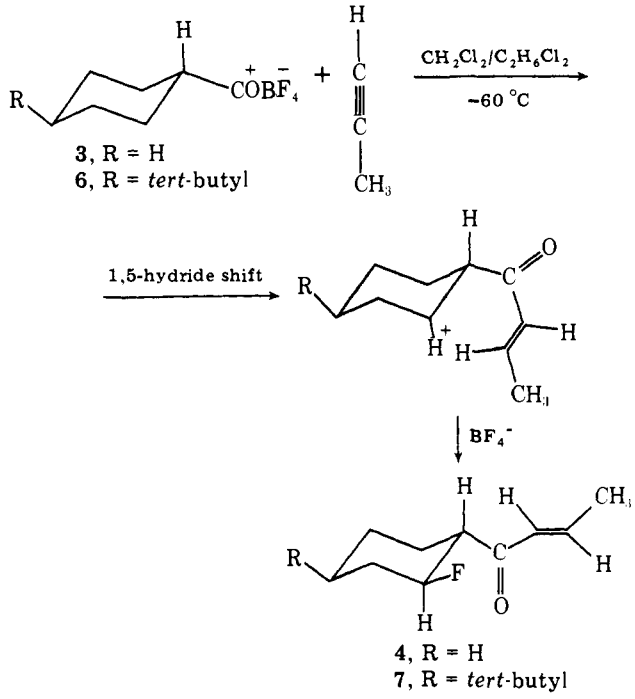
It was satisfying to note that the major product in the reaction of both isomers is, in fact, the dienone **17** (Scheme XI). Its formation corresponds to hydride transfer from the tetriary position in intermediate **35**, which produces the tertiary carbenium ion **20** and the latter, as noted in the reaction of **14**, leads to the dienone **17**.

It is interesting to note, however, that, whereas the cis isomer **32** leads only to the production of the dienone **17**, with the trans isomer **36**, a considerable amount of the fluoroketone **37** is formed. The formation of **37** suggests a competitive hydride transfer from the secondary carbon in the intermediate **35** to produce the secondary carbenium ion **40** for the trans isomer (Scheme XII). We interpret this result to suggest the preference for equatorial hydride transfer in this reaction, as equatorial hydride transfer from the secondary position apparently can compete with the axial hydride transfer from the tertiary position in the most stable conformation of the trans intermediate **33**. In the cis isomer of **35** only equatorial hydride transfer from the tetriary position could take place since in the alternative conformation (with axial orientation of acyl residue) the hydride removal from the tertiary position is sterically impossible.

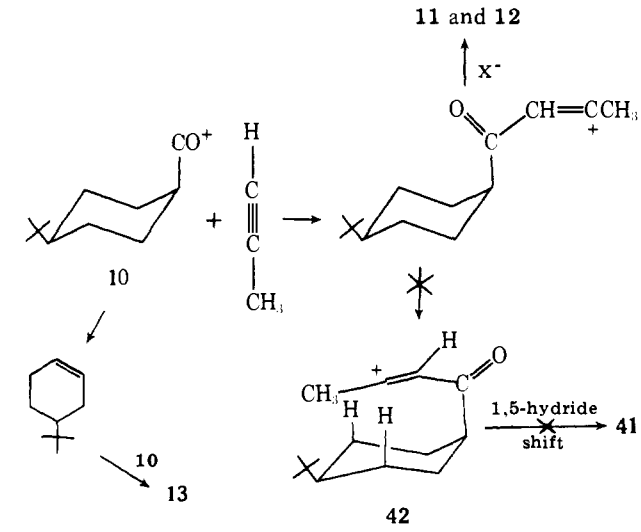
In the case of the acyl cation **3**, with no alkyl group on the ring, and **6**, with a 4-*trans*-*tert*-butyl group, the resulting secondary ring carbenium ion is trapped by the tetrafluoroborate counteranion to yield the fluoroketones **4** and **7**, respectively, of the configurations shown in Scheme XIII. Rather unexpectedly, no fused cyclopentenone analogues of **2** (Scheme I) have been detected in the reaction mixtures even by careful GC/MS analyses. Apparently with these reagents, and in fact with the majority of other cyclic acylium salts investigated in this study, the formation and the reaction of the secondary carbenium ion intermediate preempts the substitution reaction observed with acyclic acyl cations.[10] It seems that the S_Ei process in the reactions of **3** and its analogues is precluded both by the enhanced ring strain necessarily involved in the formation of the fused hydrindane system (see, however, reference 27) and by the greater stability and resulting lower activity of the secondary carbenium ion (as compared with incipient primary carbenium ion in Scheme I) enabling this intermediate to undergo a number of alternative reactions (vide supra).

The observation that the *cis*-4-*tert*-butylcyclohexanecarbonyl tetrafluoroborate (**10**) does not lead to any 1,5-hydride shifted product **42** is attributable to the severe steric interac-

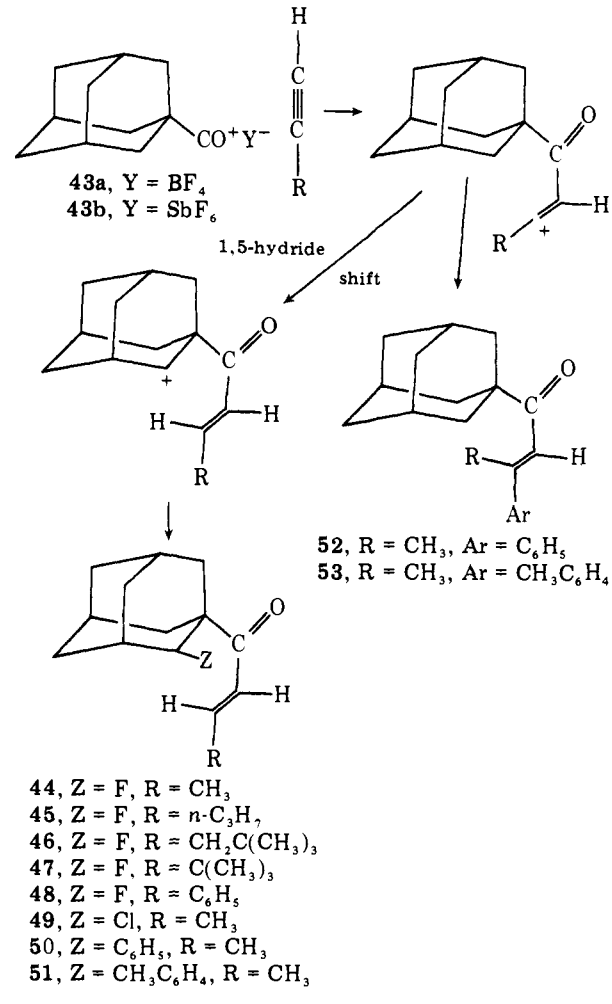
Scheme XIII



Scheme XIV



Scheme XV



tions, originating from the fixed axial orientation of the acyl fragment in **41** which prevent the approach of the vinyl carbenium center to the β-C-H bond. Owing to this interference, the main course of the reaction with **10** corresponds to the trapping of the vinyl cation intermediate with the external nucleophile and the formation of the β-haloketones **11** and **12** as shown in Scheme XIV. The ketone **13** is formed, presumably, by the acylation of 4-*tert*-butylcyclohexene produced by the partial decarbonylation of **10**.

A synthetic application of the observed, 1,5-intramolecular hydride shift appeared to be its utilization to introduce functionality into the saturated fragment of the acylating agent. The possibility of employing this process in a practical problem was illustrated by the synthesis of a series of 1,2-disubstituted adamantanes, obtained upon the acylation of several terminal alkynes with the acyl salts **43a** and **43b**. The results are summarized in Scheme XV and pertinent characterizing data are listed in Table V.

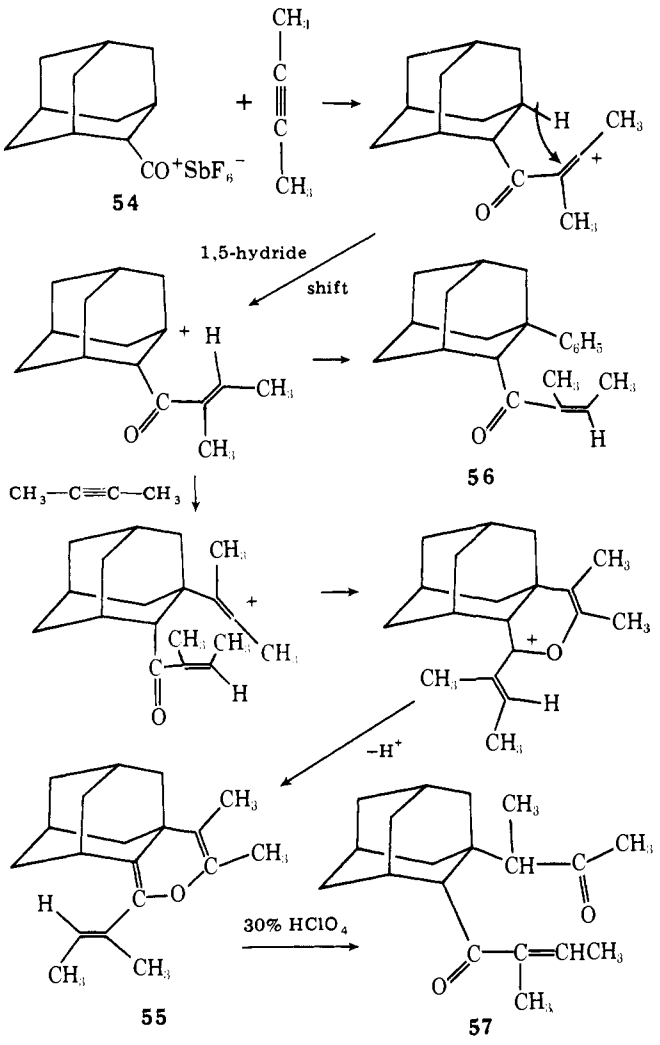
The 1,5-hydride shift process is characteristically effective in these adamantane reactions and leads to ketones of type A. Furthermore, even in those cases where the alkyne is pentyne or *tert*-butylacetylene, one does not observe the formation of elimination or rearranged products from the vinyl cation intermediate. The nature of the final product in these reactions depends upon the nature of the acyl salt (**43a** or **43b**) and upon the nature of nucleophilic species present in the reaction medium. Thus exclusive formation of the fluoroketones **44–48** results in the reaction of **43a** in CH_2Cl_2–$C_2H_4Cl_2$, whereas the chloro adduct **49** was formed when the reaction was carried out with **43b**.

When the acylation reaction was carried out with **43b** in CH_2Cl_2–$C_2H_4Cl_2$ containing aromatic nucleophiles (C_6H_6 or $C_6H_5CH_3$), the major products were 2-aryl derivatives of adamantane (**50** and **51**). In this case the formation of the β-aryl vinyl ketones **52** and **53** was also observed.

The hydride shift process appears equally effective with acyl salts derived from 2-adamantanecarboxylic acid. However, in this case, the tertiary carbenium ion resulting from the 1,5-hydride shift readily reacts with a second molecule of the alkyne. A major final product upon the interaction of 2-butyne with **54** is the pyran derivative of adamantane **55** (50%) (Scheme XVI). The structure of **55** is in agreement with its spectral characteristics and consistent with the perchloric acid catalyzed conversion to the diketone **57**. However, if the reaction is carried out in the presence of benzene, the major product (40%) is the 1-aryl derivative of adamantane **56**, although **55** (20%) is still observed.

The above examples graphically illustrate the value of uti-

Scheme XVI



lizing this reaction for the synthesis of 1,2-disubstituted adamantanes which are difficult to make by existing methods.

Conclusions

The results in this work demonstrate a facile 1,5-hydride shift to a vinyl cation intermediate produced by the acylation of alkynes with cyclohexanecarbonyl cations. It has been shown that this process is an intramolecular process involving the C–H bond of the β carbon in the acylating agent. The nature of the final products are sensitive to the structure of the cation resulting from the 1,5-hydride shift. One of the pathways available for this cation corresponds to the formation of products derived from the migration of the acyl fragment. The possibility of using the 1,5-hydride shift in a synthetic application was demonstrated by the introduction of substituents at a saturated position of the adamantane system to produce a variety of 1,2-adamantane derivatives.

Experimental Section

Analytical. Analytical GLCs were obtained on LChM-8MD-5, and Tracor MT-160 instruments, and preparative work was done on LChM-8MD-5, and LChP instruments (LCh series made in the USSR). The typical analytical column length was 2–3 m with an i.d. of 2.5 mm (or 25–30 μm for the glass capillary columns). For the preparative separations, the columns lengths were 4–6 m with an i.d. of 7–9 mm. The phases employed included SE-30, OV-101, XE-60, OV-17, and poly(ethylene glycol) 20000, on a Chromosorb support, 3–5% by weight for analytical work (or simply a coating on etched glass for the capillary columns) and 5–10% by weight for the preparative separations.

The ^{1}H NMR spectra were obtained on Varian DA-60, Varian EM-360, Varian XL-100A, Bruker WP-60, Bruker WP-200, and BS-497 (100 MHz) instruments (S series made in Czechoslovakia). ^{19}F NMR spectra were obtained on RS-56M (56.4 MHz) and the ^{13}C NMR spectra on Bruker WP-60 (15.08 MHz) or Varian XL-100A (25.2 MHz). The assignment of signals in ^{13}C spectra was done primarily on the basis of literature data.[29] For the fluorinated derivatives, the assignments were aided by the presence of the carbon–fluorine spin–spin coupling constants as well as the spectra obtained with the addition of a Eu(fod)$_3$ or under "off-resonance" conditions.

In every case the chemical shift is presented in δ (ppm) from the internal standard Me_4Si. Spin–spin coupling constants are presented in cps. The NMR spectral data are presented in Tables II–V.

The IR spectra were obtained as CCl_4 solutions on UR-10 or UR-20 spectrometers (made in East Germany). The UV spectra were recorded (as hexane solutions) on a Specord UV-VIS instrument. The MS were obtained on MH-5 (Russian) and Varian CH-5 spectrometers along with the Varian MAT-112 GC-MS system.

The analytical TLC work was done by using 13 × 18 cm^2 glass plates with a nonbonded adsorbent (usually silica gel, 100–160 μm). The preparative separations were accomplished on 24 × 24 cm^2 or 22 × 33 cm^2 plates with a thin layer of about 2 mm. The elutions were carried out with the plates at a slight incline.

In those cases where a microanalysis is not reported for a compound, the reason can be attributed to either an unstable reaction product, or an extremely small sample of the product, or difficulty in removing small quantities (<5% GLC) of insignificant impurities.

Reagents. The silver salts were purchased from Cationics, Inc., Columbia, S.C. All the reactions were carried out in absolute solvents under dry argon.

Synthesis of Starting Carboxylic Acids. 1-Methylcyclohexanecarboxylic acid,[30] *trans*-2-methylcyclohexanecarboxylic acid,[31] *trans*-4-*tert*-butylcyclohexanecarboxylic acid,[32] *cis*- and *trans*-4-*tert*-butyl-1-methylcyclohexanecarboxylic acids,[33] and 2-adamantane carboxylic acid[34,35] were obtained by the reported literature procedures. *cis*-2-Methylcyclohexanecarboxylic acid and *cis*-4-*tert*-butylcyclohexanecarboxylic acid were obtained by hydrogenation over RuO_2 of a water solution of the ammonium salt of the corresponding aromatic acid.

2,2,6,6-Tetradeuterio-1-methylcyclohexanecarboxylic acid was synthesized from 2,2,6,6-tetradeuteriocyclohexanone[36] (d_4 content 97–98% as determined by ^{1}H NMR and MS) by conversion via a Grignard reaction to 2,2,6,6-tetradeuterio-1-methylcyclohexanol (80%). The d_4 acid was obtained in a 70% yield from the d_4 alcohol by carbonylation[33] in the presence of $SbCl_5$ in liquid SO_2 at −70 °C. The ^{1}H NMR spectrum of the corresponding methyl ester of the d_4 acid, obtained in the presence of Eu(fod)$_3$, confirmed the absence of the β hydrogens on the ring. A MS analysis of the methyl ester indicated the product to be a 97–98% d_4 product.

Synthesis of the Acid Halides. All of the acid chlorides were obtained in good yields by the procedure reported for the preparation of *trans*-2-methylcyclohexanecarbonyl chloride (**36**).[37] The acid fluorides were obtained from the corresponding acid chlorides by the method of Olah.[38] Special experiments were carried out to show that no structural isomerizations occurred, either upon conversion of an acid chloride to an acid fluoride, or upon conversion to the corresponding acyl salt.

Ethylidenecyclopentane. In a round-bottomed flask with a dry argon atmosphere was placed 3.22 g (0.134 mol) of NaH (50% suspension in mineral oil). The contents were rinsed several times with hexane. Me_2SO, 50 mL, was then added and the flask was warmed to 70–80 °C for 45–60 min. The solution was cooled to 25 °C and ethyltriphenylphosphonium iodide was added quickly and stirring was continued for 10 min. Cyclopentanone, 4.2 g (0.05 mol), in 30 mL of Me_2SO was added and the reaction mixture was warmed to 50–60 °C for 5 h. The reaction mixture was cooled, poured into ice water, extracted with pentane, dried (Na_2SO_4), filtered through SiO_2, concentrated, and distilled. Ethylidenecyclopentane, 1.6 g (30%), was collected at 113–114 °C (lit.[39] 112 °C) and was homogeneous by GLC.

Interaction of 1-Methylcyclohexanecarbonyl Tetrafluoroborate (14 + 14-d_4) with Propyne. To a solution of the acid fluoride of 1-methylcyclohexanecarboxylic acid, 0.52 g (3.61 mmol), in 20 mL of absolute CH_2Cl_2 at −60 °C was added, with the aid of a syringe, 90 mL (3.75 mmol) of gaseous BF_3. The reaction mixture was kept at −60 °C for 15 min, and 60 mL (2.5 mmol) of gaseous propyne was

added. The mixture was stirred at this temperature for an additional 10 min and then decomposed with an aqueous $NaHCO_3$–ether mixture and allowed to warm to 25 °C. The mixture was extracted with ether, and the extracts were dried (Na_2SO_4). The solvent was removed on a rotovap and the residue distilled under vacuum (2 mm with a bath temperature of 130 °C) in a short-path distillation apparatus. A mixture of **17, 18,** and **19** (0.39 g) was obtained. A preparative GLC separation of this mixture yielded **17,** 0.15 g (36%), **18,** 0.07 g (17%), and **19,** 0.02 g (5%). The ratio, as determined by calibration with a standard, was 40:20:6–7 for **17:18:19.**

17: IR (CCl_4), 1698 (C=O), 1670, 1635 (C=C), 3040, 3010 (=CH) cm^{-1}; UV_{max} (hexane) 222 nm (ϵ 7100); MS, *m/e* 164 (M^+), 69 ($COCH{=}CHCH_3^+$). Anal. Calcd for $C_{11}H_{16}O$: C, 80.04; H, 9.76. Found: C, 79.43; H, 9.82.

18: IR (CCl_4) 1700 (C=O), 1630, 1670 (C=C), 3040 (=CH) cm^{-1}; UV_{max} (hexane) 225 nm (ϵ 10 400); MS, *m/e* = 164 (M^+), 69 ($COCH{=}CHCH_3^+$) Anal. Calcd for $C_{11}H_{16}O$: C, 80.04; H, 9.76: Found: C, 79.62; H, 9.79.

19: IR (CCl_4) 1700 (C=O), 1635 (C=C) cm^{-1}; MS, *m/e* = 184 (M^+); 164 ($M-HF^+$); 87 ($COCH{=}CFCH_3$). Anal. Calcd for $C_{11}H_{17}OF$: C, 71.74; H, 9.25; F, 10.32. Found; C, 7201; H, 9.60; F, 10.40.

In the labeled experiment with **14-d_4** the isotope ratio d_3:d_4 in **17** was 80:20 and in **18** it was 31:69 as determined by MS. The fragment ($COCH{=}CDCH_3^+$) shows up clearly in both spectra. ^1H NMR of **19-d_4**: δ 6.17, d, J = 20 Hz (H—C=C—F); δ 2.34, d, J = 20 Hz (=C(—F)CH_3); δ 1.05, s (ring methyl).

Independent Synthesis of Ketone 17. To a solution of $AgBF_4$, 1.62 g (8.33 mmol), in 20 mL of absolute $CH_2Cl_2/C_2H_4Cl_2$(1:1) at −60 °C, was added crotonyl chloride, 0.87 g (8.33 mmol), in 3 mL of CH_2Cl_2. The solution was stirred at −60 °C for an additional 5 min and then 1-methylcyclohexene, 0.48 g (5 mmol), was added. The reaction mixture was kept at this temperature for an additional 10 min and then worked up in the usual manner. The recovered residue was distilled under vacuum in a short-path distillation apparatus (ca. 2 mmHg with a bath temperature of 130 °C). A single product, 0.6 g (73%), was obtained that was identical in all respects with ketone **17.**

Independent Synthesis of Ketone 18. Ketone **18** was synthesized in a manner analogous to **17** from $AgBF_4$, 1.95 g (10 mmol), crotonic acid, 0.84 g (8.0 mmol), and ethylidenecyclopentane, 0.58 g (6.8 mmol). A short-path distillation yielded 0.81 g (83%) of ketone **18,** identical in all respects with one of the ketones obtained in the propyne acylation reaction.

Interaction of *cis*-4-*tert*-Butyl-1-methylcyclohexanecarbonyl Tetrafluoroborate (22) with Propyne. This reaction and workup was carried out as with **14.** The yields in the crude residue as determined by calibration with standards were 28% and 25% for **23** and **24,** respectively.

23: IR (CCl_4) 1696 (C=O), 1632 (C=C), 3045 (=CH) cm^{-1}; MS, *m/e* = 220 (M^+), 69 ($COCH{=}CHCH_3^+$), 57 ($^+C(CH_3)_3$).

24: IR (CCl_4) 1693 (C=O), 1635 (C=C), 3042 (=CH) cm^{-1}; MS, *m/e* = 220 (M^+), 69 ($COCH{=}CHCH_3^+$), 57 ($^+C(CH_3)_3$).

Interaction of *trans*-4-*tert*-Butyl-1-methylcyclohexanecarbonyl Hexafluoroantimonate (26) with Propyne. To a solution of $AgSbF_6$, 1.38 g (4 mmol), in 20 mL $CH_2Cl_2/C_2H_4Cl_2$ (1:1) at −60 °C was added 0.80 g (3.8 mmol) of the acid chloride in 5 mL of CH_2Cl_2. The reaction mixture was kept at this temperature 5 min and then 120 mL (5 mmol) of propyne was added (via syringe). The reaction mixture was stirred an additional 15 min and then worked up in the usual fashion. The crude product, 0.9 g, was partially crystalline and consisted of ketones **24, 27–29.** Separation by preparative TLC (silica gel L, ether/hexane, 1:3) gave 0.12 g (14%) of **28,** 0.2 g (24%) of **24a,b** and **27,** and 0.1 g (12%) of **29.** Ketones **24** and **27** (approximately 1:1) were separated by GLC. The mixture of isomeric ketones **24a,b** was identical with the ketones obtained from the cis isomer **22.**

27: IR (CCl_4) 1698 (C=O), 1635 (C=C), 3075 (=CH) cm^{-1}; MS, *m/e* = 220 (M^+), 69 ($COCH{=}CHCH_3^+$), 57 ($^+C(CH_3)_3$).

28: IR (CCl_4) 1706 (C=O), 1629 (C=C), 3080 (=CM) cm^{-1}; MS, *m/e* = 220 (M) Anal. Calcd for $C_{15}H_{24}O$: C, 81.81; H, 10.91. Found: C, 81.92; H, 10.85.

29: MS, *m/e* =256, 258 (3:1) (M^+), 103, 105 (3:1) ($COCH{=}CClCH_3^+$), 57 ($^+C(CH_3)_3$).

Interaction of Propyne with *trans*-4-*tert*-Butylcyclohexanecarbonyl Tetrafluoroborate (6). To a solution of the acid fluoride, 0.56 g (3 mmol), in 20 mL of CH_2Cl_2 at −60 °C was added 72 mL (3 mmol) of gaseous BF_3 (via syringe). The reaction mixture was kept at this temperature for 20 min (the $RCO^+BF_4^-$ precipitated) and then propyne, 60 mL (2.5 mmol), was added. The mixture was stirred an additional 5 min (the mixture became homogeneous) and worked up in the usual fashion to yield 0.6 g of **7–9.** A preparative GLC separation gave 0.17 g (30%) of **7,** 0.06 g (8%) of **8.** The yields of **7, 8,** and **9,** as determined by standardization, were 35–40%, 15%, and 15%.

7: IR (CCl_4) 1720, 1695 (C=O), 1630, 1670 (C=C), 1060 (C—F) cm^{-1}; UV_{max} (hexane) 223 nm (ϵ 11 400); MS, *m/e* = 226 (M^+), 206 ($M-HF^+$), 69 ($COCH{-}CHCH_3^+$). Anal. Calcd for $C_{14}H_{23}OF$: F, 8.40. Found: F, 8.55.

8: IR (CCl_4) 1704 (C=O), 1672, 1632 (C=C) cm^{-1}; UV_{max} (hexane) 228 nm (ϵ 8850); MS, *m/e* = 226 (M^+), 87 ($CO{-}CH{=}CFCH_3^+$).

9: Characterized by GC/MS. *m/e* =240, 242 (3:1) (M^+), 103, 105 (3:1) ($COCH{=}CClCH_3^+$).

Interaction of Propyne with *cis*-4-*tert*-Butylcyclohexanecarbonyl Tetrafluoroborate (10). This reaction was carried out with the trans isomer **12** to yield 1.5 g of a solid mixture containing ketones **11–13.** The ketones **11** and **12** are the β-fluoro and β-chloro derivatives (GC/MS).

Product 13, 0.25 g (25%), mp 103–105 °C, was separated by preparative TLC (silica gel L, ether/hexane, 1:9).

11: GC/MS, *m/e* -226 (M^+), 87 ($COCH{=}CFCH_3^+$).

12: GC/MS, *m/e* -240, 242 (3:1) (M^+), 103, 105 (3:1) ($CO{-}CH{=}CClCH_3^+$).

13: IR (CCl_4) 1705 (C=O), 1605 (C=C), 3029 (=CH) cm^{-1}; UV_{max} (hexane) 209 nm (ϵ 2720); MS, *m/e* = 304 (M^+), 167 ($(CH_3)_3CC_6H_{10}{-}^+O$), 137 ($(CH_3)_3C{-}C_6H_{11}^+$).

Interaction of Propyne with *cis*-2-Methylcyclohexanecarbonyl Tetrafluoroborate (32). This reaction was carried out as with **19.** A short-path vacuum distillation yielded **17, 33, 34,** and **34a.** This mixture was separated by preparative GLC to give **17** (35%), **33** (8%), and **34** and **34a** (9%). The yields of **17, 33,** and **34** and **34a** as determined by calibration with standards were 40%, 10%, and 10%, respectively. The spectral characteristics of **17** were identical with the previously obtained sample.

33: IR (CCl_4) 1700 (C=O), 1670, 1630 (C=C) cm^{-1}; UV_{max} (hexane) 230 nm (ϵ 11 800); MS, *m/e* = 184 (M^+), 87 ($COCH{-}CFCH_3^+$).

34 and 34a: IR (CCl_4) 1695 (C=O), 1610 (C=C) cm^{-1}; UV_{max} (hexane) 243 nm (ϵ 17 400); MS, *m/e* = 200, 202 (3:1) (M^+), 103, 105 (3:1) ($COCH{=}CClCH_3^+$).

Interaction of Propyne with *trans*-2-Methylcyclohexanecarbonyl Tetrafluoroborate (36). In a procedure identical with the one described above for the cis isomer were obtained **17** (18%), **37** (11%), **38** (11%), and **39** and **39a** (8%). The actual yields as determined by calibration for **17, 37, 38,** and **39** and **39a** were 25%, 15%, 15%, and 10%, respectively. Again **17** was identified by comparison to samples of **17** obtained earlier.

37: IR (CCl_4) 1699 (C=O), 1634, 1673 (C=C), 3043 (=CH) cm^{-1}; UV_{max} (hexane) 222 nm (ϵ 12 400); MS, *m/e* = 184 (M^+), 164 ($M-HF^+$), 69 ($COCH{=}CHCH_3^+$).

38: IR (CCl_4) 1700 (C=O), 1630, 1670 (C=C) cm^{-1}; UV_{max} (hexane) 229 nm (ϵ 8500); MS, *m/e* = 184 (M^+), 87 ($CO{-}CH{=}CFCH_3^+$).

39 and 39a: IR (CCl_4), 1696 (C=O), 1622 (C=C) cm^{-1}; UV_{max} (hexane) 243 nm (ϵ 7150); MS, *m/e* = 200, 202 (3:1) (M^+), 103, 105 (3:1) ($COCH{=}CClCH_3^+$).

The Interaction of Terminal Alkynes with 1-Adamantanecarbonyl Tetrafluoroborate (43a). These reactions were carried out in the usual fashion except the alkynes were added to the preformed salt at −40 °C. The ketones **44–48** were separated by preparative TLC and their ^1H NMR spectral data are listed in Table V. The structures are also consistent with their ^{13}C NMR spectra and, along with other spectral and physical characteristics, will be published shortly.

Chloroketone 49. The chloroketone was isolated as in case of **44–48** except the hexafluoroantimonate salt **43b** was employed.

The Interaction of 1-Adamantanecarbonyl Hexafluoroantimonate (43b) with Propyne in the Presence of Aromatic Nucleophiles. The ketones **50–53** were obtained in an analogous fashion except an excess of the aromatic solvent was added before the introduction of the propyne. The data for ketones **50** and **51** are given in Table V.

52: ^1H NMR ($COCH_A{=}CCH_3C_6H_5$) δ 7.28 (5 H, C_6H_5), 6.59 (d, H_A, J = 1.2 Hz), δ 2.43 (3 H, CH_3, J = 1.2 Hz); IR (CCl_4) 1678 (C=O), 1605 (C=C) cm^{-1}; MS, *m/e* = 280 (M^+), 145 (CO-

$CH{=}CCH_3C_6H_5^+$), 135 (Ad^+).

53: IR (CCl_4) 1678 (C=O), 1605 (C=C) cm^{-1}; MS, *m/e* = 294 (M^+), 135 (Ad^+), 159 ($COCH{=}CCH_3C_6H_4CH_3^+$).

The Interaction of 2-Adamantanecarbonyl Hexafluoroantimonate (54) with Butyne. The reaction was carried out as with the 1-adamantane derivatives. The pyran **55** was isolated in a 60% yield by preparative TLC, mp 57-59 °C.

55: ^1H NMR, δ 5.3 (dq, 1 H, J = 6 and J = 1.2 Hz), 2.55 (1 H, broad s). Furthermore the ^{13}C NMR spectrum is clearly consistent with the symmetry in this molecule: IR (CCl_4), 1707 (=C—O—C=), 1659 (C=C) cm^{-1}; MS, *m/e* = 270 (M^+), 215 ($M - C_4H_7^+$), 255 ($M - CH_3^+$). Anal. Calcd for $C_{19}H_{26}O$: C, 84.44; M, 9.63. Found: C, 84.25; H, 9.85.

Diketone 57. To a solution of the pyran **55,** 0.22 g in 20 mL of dioxane, was added 10 mL of 30% $HClO_4$. The solution was stirred for 3 min and then 50 mL of H_2O was added. A chloroform extraction was performed and the extracts were washed with a $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated under vacuum. A preparative TLC separation (silica gel-hexane) produced 0.17 g (73%), mp 107-109 °C of **57.**

57: ^1H NMR ($COCH_3{=}CHCH_3$) δ 6.72 (q, 1 H, J = 7 Hz), 1.77 (d, 3 H, CH_3, J = 7 Hz), 1.65 (s, 3 H, CH_3), 3.3 (broad s, CHCO); ($CH(CH_3)COCH_3$) δ 2.6 (q, 1 H, J = 7 Hz), 0.76 (3 H, CH_3, J = 7 Hz), 2.07 (s 3 H, CH_3); IR (CCl_4) 1711, 1665 (C=O), 1640 (C=C), 3061 (=CH) cm^{-1}; MS, *m/e* = 288 (M^+), 245 ($M - COCH_3^+$), 83 ($COCCH_3{=}CHCH_3^+$). Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.17; H, 9.72. Found: C, 79.31; H, 10.03.

Acylation of 2-Butyne with 2-Adamantanecarbonyl Hexafluoroantimonate (54) in the Presence of Benzene. This reaction was effected in the same fashion as for the reactions of **43b** except the enitre reaction was run at −60 °C. A preparative TLC separation produced ketone **56** (40%, mp 152-155 °C) and the pyran **55** (15%).

56. ^1H NMR ($COCCH_3{=}CHCH_3$) δ 6.43 (q, 1 H, J = Hz), 1.71 (d, CH_3, J = Hz), 1.53, s, (CH_3), 3.68 (broad s, 1 H, -CHCO); IR ($CDCl_3$), 1668 (C=O), 1641 (C=C), 840, 860 (C_6H_5); MS, *m/e* = 294 (M^+), 211 ($M - COCCH_3^+$ and $CHCH_3^+$). The ^{13}C NMR spectrum was consistent with this assignment.

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