3. M. Vidal, M. Vincens, and P. Arnaud, Bull. Soc. Chim. France, 657 (1972).
4. N. Petiniot, A. J. Anciaux, A. F. Noels, A. J. Hubert, and P. Teyssié, Tetrahedron Lett., 1239 (1978).
5. H. Reimlinger, Chem. Ber., 92, 970 (1959).
6. I. Heilbron, E. R. H. Jones, and F. Sondheimer, J. Chem. Soc., 604 (1949).
7. O. M. Nefedov, I. E. Dolgii, and E. A. Shapiro, Izv. Akad. Nauk SSSR, Ser. Khim., 1209 (1978).
8. I. E. Dolgii, G. P. Okonnishnikova, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 197 (1970); 822 (1979).
9. I. A. D'yakonov, M. I. Komendantov, and T. S. Smirnova, Zh. Org. Khim., 2, 559 (1966); 3, 1903 (1967); 5, 1742 (1969); M. I. Komendantov, I. N. Domnin, and E. V. Bulucheva, Tetrahedron, 20, 2495 (1975).
10. I. A. D'yakonov and M. I. Komendantov, Zh. Obshch. Khim., 31, 3881 (1961); 33, 923 (1963).
11. R. Breslow, R. Winter, and M. Battiste, J. Org. Chem., 24, 414 (1959).
12. T. W. Richards, Proc. Am. Acad., 26, 240 (1891).
13. E. D. Campbell, Am. Chem. J., 17, 681 (1895).
14. R. Paulissen, H. Reimlinger, E. Hayes, A. J. Hubert, and P. Teyssié, Tetrahedron Lett., 2233 (1973).
15. W. R. Mozer, J. Am. Chem. Soc., 91, 1135 (1969).
16. T. E. Dolgii, E. A. Shapiro, A. Ya. Shteinshneider, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 2514 (1977).
17. F. M. Rapoport and A. A. Il'inskaya, Laboratory Methods for Obtaining Pure Gases [in Russian], Goskhimizdat, Moscow (1963), p. 373.
18. G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, J. Chem. Soc., 3197 (1954).

DIRECTION OF CARBONIUM ION REARRANGEMENTS DURING ACYLATION OF PROPYNE BY STEREOISOMERS OF 4-tert-BUTYL-1-METHYLCYCLOHEXANOYLCARBONYL CATION

M. I. Kanishchev, A. A. Shchegolev, V. A. Smit, R. Caple, and N. F. Sepetov

UDC 541.124:542.951.1:547.314.3

On the example of the acylation of propyne by 1-methylcyclohexanoyl tetrafluoborate and its 2,2,6,6-d_4-analog it was shown by us [1] that the cyclohexyl cation, formed as the result of a 1,5-hydride shift, is stabilized either via contraction of the ring or via a 1,2-shift of the acyl. Here it was also postulated that together with the main direction of the process, namely a 1,2-acyl shift, is also observed a slight 1,2-shift of methyl and hydride ion, which is possibly related to the conformational lability of the employed acylium salt. In connection with this we studied the reaction of propyne with acylium salts (I) and (II), in which the orientation of the substituents in the cyclohexane ring is fixed.

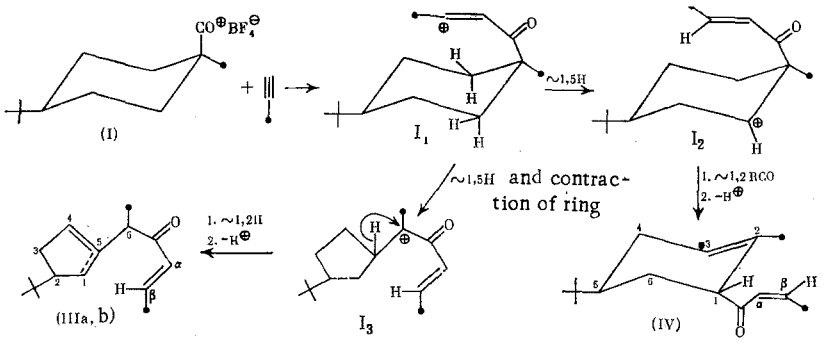
The reaction of propyne with the cis-4-tert-butyl-1-methylcyclohexanoyl cation (I) leads to a mixture of cyclopentene ketones (IIIa, b) and cyclohexenyl ketone (IV). A specific trait of acylium cation (I) is a fixed axial conformation of the acyl group, and on account of this the 1,5-hydride shift in the intermediate I_1 (Scheme 1) can proceed only with involvement of the equatorial (e) bonds (C–H) at C_2 and C_6: In such case the formation of ketone (III) is easily depicted as being a synchronous removal of the e-hydride ion (1,5-hydride shift) and contraction of the ring in harmony with the usual stereoelectronic concepts. From the rigorously proved structure* of ketone (IV) it follows that its formation should include the step of a 1,2-acyl shift. The mechanism of this process is not sufficiently clear, but apparently it includes the step of the

* The structure proof for the obtained compounds is discussed below.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. University of Minnesota, Duluth, USA. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2102-2107, September, 1980. Original article submitted October 11, 1979.

0568-5230/80/2909-1499$07.50

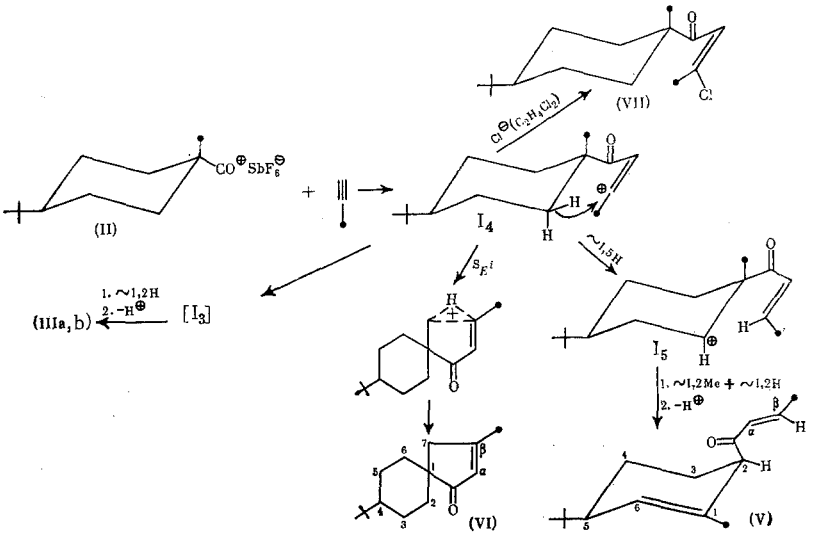
Scheme 1



intermediate formation of the cyclohexyl cation I_2, since the synchronous mechanism of a 1,5-hydride shift and acyl migration in I_1 is impossible since it requires an overlapping of the e and *a* orbitals.

The reaction of propyne with the trans-isomer (II) is more complicated (Scheme 2) and leads to a difficultly separable mixture of products, from which the pure compounds could be isolated by a combination of the preparative GLC and TLC methods. The overall yield of ketones (IIIa, b) and (V)-(VII) in a 1:1:1:1 ratio was 60%.

Scheme 2



The formation of ketones (IIIa, b), identical with those obtained in the reaction of propyne with (I), testifies to the fact that in the intermediate I_4, with an e-orientation of the acyl moiety, the 1,5-hydride shift, as in the case of I_1, is accomplished with involvement of the C–H e-bond at C_2 and C_6. A detailed analysis of the ^1H and ^{13}C NMR spectra of cyclohexyl ketone (V) clearly shows that the formation proceeds via a 1,2-shift of the CH_3 group and hydride ion, as was postulated by us when studying the reaction of propyne with 1-methylcyclohexanoyl tetrafluoborate [1].

A comparison of the results of reacting propyne with (I) and (II) reveals that in both cases the 1,2-shift is accomplished with the exclusive involvement of the *a*-substituent from the geminal node, and it can be assumed that also in the 1,2-shift of the CH_3 group the transformation $I_4 \rightarrow$ (V) proceeds via the step of the discrete carbonium ion I_5. An examination of the space models disclosed that in the intermediates I_2 and I_5 the vacant p-AO and the sp^2 center is found practically in the same plane as the migrating group, which is apparently responsible for the exclusive 1,2-shift of the *a*-substituent. The observed strict stereospecificity of the 1,2-shift of either methyl or acyl from the geminal node is one of the few examples that confirm the validity of the previously advanced theory concerning the "orbital control" of the direction of the rearrangements in carbonium ions [2, 3].

The formation of spiroketone (VI) is a fact of special interest. The simultaneous presence of ketones (III), (V), and (VI) shows that in intermediate I_4 it is possible to have not only a 1,5-hydride shift, involving

TABLE 1*

Compound	$COCH_A=CH_BMe_X$			Other signals
	H_A	H_B	Me_X	
(IV)†	6,07 d $J_{A,B}=15,5$	6,83 d.q $J_{A,X}=1,2$	1,87 d.d $J_{B,X}=7$	5,65 m(H_3, $J_{H_3H_{3a}}=5,5$, $J_{H_1H_3}=J_{H_3H_4}=1,8$), 3,25 m($H_1$, $J_{H_1H_{6a}}=10$, $J_{H_1H_{4e}}=4$, $J_{H_1H_{6e}}=$ $=J_{H_1Me}=1,5-1,8$), 2,1 m(H_{3a}, $J_{gem}=16$), 1,57 m(Me at C_2), 1,93—1,95 m(H_{4e}), 0,86 s (CMe_3)
(V)†	6,12 d $J_{A,B}=15,5$,	6,66 d.q $J_{A,X}=1,2$	1,89 d.d $J_{B,X}=7$	5,57 br.s (H_6), 2,95 br.d (H_2, $J_{H_2H_{3a}}=7$), 1,91 m(H_{3e}, $J_{gem}=13,5$), 1,79 m (H_{4a}), 1,76 m(H_{5a}), 1,7 m(H_{3a}, $J_{H_{3a}H_{4e}}=2,5$, $J_{H_{3a}H_{4a}}=J_{H_{3a}-H_{3e}}=13,5$), 1,52 m(Me at C_1, $J_{H_5Me}=2,5$, $J_{H_6Me}=1,5$), 1,45 m (H_{4e}, $J_{gem}=14$, $J_{H_{4e}-H_{5a}}=J_{H_{4e}-H_{3e}}=3,5-4,0$), 0,77 s ($CMe_3$)
(IIIa,b)‡	6,07 d $J_{A,B}=15,5$	6,77 d.q $J_{A,X}=1,2$	1,85 d.d $J_{B,X}=7$	1,25 d (Me at C_6, $J=7$), 3,18 & 3,22q (H_6, $J=7$), 2,1 (signals of allylic protons) 5,41 m (H_1 & H_4), 0,82 s (CMe_3)
(VI)‡	5,8 m	2,13 d $J_{A,X}=1,2$	$J_{A,X}=1,2$	2,5 br.s. (2H at C_7, 0,88 s (CMe_3)

*The chemical shifts are given on the σ scale in ppm for $CDCl_3$ solutions; internal standards = TMS and J is expressed in Hz.
† The spectra were recorded at at operating frequency of 360 MHz.
‡ The spectra were recorded at an operating frequency of 100 MHz.

TABLE 2*

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C=O	C_α	C_β	Other signals
(IV)	54,4	130,96	126,1	26,96	43,47	28,28	202,6	129,38	142,98	21,25 (Me at C_2), 18,21 (Me at C_6) 32,24 and 27,26 (CMe_3)
	+3,52 †	+3,4	+1,88	+1,2	+1,4	+4,5	+8,87	+3,52	+5,4	+0,97 and +0,91 +0,61 and +0,36
(V)	131,9	50,57	26,71	23,74	46,14	127,55	200,6	130,23	142,4	20,13 (Me at C_1) 18,15 (Me at C_6) 33,02 and 27,32 (CMe_3)
(VI)	50,0	34,6	24,6	48,0	24,6	34,6	192,5	128,8	176,2	46,2 (C_7), 27,8 & 32,9 (CMe_3) 19,3 (Me)

*The chemical shifts are given on the δ scale (ppm) relative to TMS at the internal standard; the solvents were $CDCl_3$ for (IV) and (V), and $(CD_3)_2CO$ for (VI).
† Values of pseudocontact shift in presence of $Eu(fod)_3$. $Eu(fod)_3$:(IV) ratio = 0,5:0,16 (g).

the β-C atom of the cyclohexane ring, but also substitution at the CH_3 group, similar to that observed previously [4] in the reactions of alkynes with pivaloyl tetrafluoborate.

A careful analysis by the GLC method of the mixture, obtained in the reaction of propyne with (II) disclosed that it also contains β-chlorovinyl ketone (VII), which is formed via the usual reaction of adding acyl cation and "external" nucleophile (Cl^- from the solvent), while the product, corresponding to 1,2-acyl migration, is absent.

The structure of ketones (IV) and (V) was proved mainly on the basis of the ^1H and ^{13}C NMR spectral data. From the PMR spectra at a frequency of 60 and 100 MHz it follows that both ketones contain the same sets of structural fragments: MeC=CH and CHCOCH=CHMe-trans, which was shown by the double $\{^1H-^1H\}$ resonance (DR) method, and consequently (IV) and (V) are isomers as regards the location of the substituents in the cyclohexane ring. The structure of ketones (IV) and (V) was established from the PMR spectra at a frequency of 360 MHz.

The DR data for (IV) made it possible to detect two unconnected CH_2 links, in which connection the protons of one of the links have an SSCC with the CHCO group, while the protons of the other link are allylic. An analysis of the SSCC values (Table 1) leads to the unequivocal conclusion that the COR group in (IV) has an e-orientation, since substantially smaller SSCC values should be observed for the proton at C_1 with an α-arrangement of this substituent.

Based on the DR data, (V) has two connected CH_2 links, in which connection the protons of one of the links have an SSCC with the α-carbonyl proton, while the protons of the other link have an SSCC with the allylic CH group (see Table 1). From the SSCC values it follows that in ketone (V) the COR group occupies an α-position.

The ^{13}C NMR spectra for ketones (IV) and (V) (Table 2) correspond to the postulated structures. In the spectrum of (V) the signal of the carbon, attached to the C atom of the $C(CH_3)_3$ group, is found further downfield than the analogous signal in (IV) (Δ = 2.6 ppm), which corresponds to the allylic position of this center in (V). When the ^{13}C NMR spectrum of (IV) is recorded in the presence of $Eu(fod)_3$ of the ring C atoms the olefinic C_2 atom and the methylene C_6 link undergo the greatest paramagnetic shift. The C_4 and C_6 atoms, judging by the closeness of their chemical shifts, are located symmetrically relative to the branching at C_5, while the C_4 center is affected the least by the shift reagent.

Cyclopentyl ketone (III) represents a mixture of two isomers. Its structure follows from the PMR spectral data (see Table 1), which indicate the presence of the signals of the protons of the CH(Me)COCH=CHMe-trans and CMe_3 fragments and of the olefinic ring proton.

The structure of spiroketone (VI) follows from the PMR spectrum (see Table 2), which resembles the spectra of cyclopentenone derivatives (see [4]). An examination of the space models shows that the (VI) molecule has a plane of symmetry, which passes through the cyclopentenone ring. In harmony with this, the ^{13}C NMR spectrum of (VI) has only two signals of the CH_2 group of the cyclohexane fragment of double intensity at 34.6 (C_2 and C_6) and 24.6 (C_3 and C_5) ppm.

EXPERIMENTAL

The GLC method was used to check the purity of the starting compounds and to analyze the reaction mixture. For this we used an LKhM-8MD-5 instrument equipped with a 30-m glass capillary column packed with SE-30. The preparative separation was run on an LKhP-6I instrument using 4-6 m × 4-6 mm columns, a flame-ionization detector, and usually the liquid phases SE-30, XE-60, OV-101, and OV-17.

The IR spectra were recorded on a UR-20 instrument in CCl_4 solution, the PMR spectra were recorded on Tesla BS-497 (100 MHz) and Bruker WH-360 (360 MHz) instruments, and the ^{13}C NMR spectra were recorded on Bruker WP-60 (15.08 MHz) and Varian XLFT-100 (25.2 MHz) instruments. The chemical shifts are given on the δ scale (ppm) relative to either TMS or HMDS as the internal standard.

The starting acids and their acid chlorides were obtained as described in [5-7].

Reaction of 1-Methyl-4-tert-butyl-cis-cyclohexanoyl Tetrafluoborate (I) with Propyne. To a solution of 0.81 g (4.2 mmoles) of $AgBF_4$ in 20 ml of abs. $CH_2Cl_2-C_2H_4Cl_2$ (1:1) at −60°C was added 0.85 g (4 mmoles) of the acid chloride in 5 ml of abs. CH_2Cl_2. The reaction mass was kept at this temperature for 15 min, and then 85 ml (3.5 mmoles) of propyne was added using a syringe, after which the mixture was stirred for another 10 min and decomposed with an ether−H_2O−$NaHCO_3$ mixture. After extraction with ether and distilling off the solvent we obtained 1.1 g of a residue that contained mainly ketones (III) and (IV).

Ketones (III) and (IV) could not be separated by preparative TLC (SiO_2, 1:2 ether–hexane mixture). We obtained 0.4 g (52%) of a mixture of (III) and (IV) in a 1:1 ratio. Using preparative GLC we isolated 0.13 g (17%) of (IV) and 0.14 g (18%) of (IIIa, b). The yields, determined by the calibration method using a standard, are respectively 28 and 25%.

Compound (IIIa, b): IR spectrum (ν, cm^{-1}): 1697 (C=O), 1635 (C=C), 3047 (=CH); mass spectrum, m/z: 220 $(M)^+$, 69 $(COCH=CHCH_3)^+$, 57 $(C(CH_3)_3^+)$.

Compound (IV): IR spectrum (ν, cm^{-1}): 1696 (C=O), 1632 (C=C), 3045 (=CH); mass spectrum, m/z: 220 $(M)^+$, 69 $(COCH=CHCH_3)^+$, 57 $(C(CH_3)_3^+)$.

Reaction of 1-Methyl-4-tert-butyl-trans-cyclohexanoyl Hexafluoantimonate (II) with Propyne. To a solution of 1.38 g (4 mmoles) of $AgSbF_6$ in 20 ml of abs. CH_2Cl_2–$C_2H_4Cl_2$ (1:1) at −60° was added 0.8 g (3.75 mmoles) of the acid chloride in 5 ml of abs. CH_2Cl_2. The reaction mass was kept at this temperature for 5 min, and then 120 ml (5 mmoles) of gaseous propyne was added using a syringe, after which the mixture was stirred for another 15 min and decomposed in the usual manner. After extraction with ether, drying over Na_2SO_4, and removal of the solvent we obtained 0.9 g of a semicrystalline mass, which contained ketones (III) and (V)-(VII).

Separation by preparative TLC (SiO_2, 1:3 ether–hexane) led to the isolation of 0.12 g (14%) of (VI), 0.2 g (24%) of (IIIa, b) and (V), and 0.1 g (12%) of (VII). Ketones (IIIa, b) and (V) were separated by preparative GLC to give 0.07 g of (IIIa, b) and 0.06 g of (V).

Compound (V): IR spectrum (ν, cm^{-1}): 1696 (C=O), 1633 (C=C), 3044 (=CH); mass spectrum m/z: 220 (M^+), 69 $(COCH=CHCH_3^+)$, 57 $(C(CH_3)_3^+)$.

Compound (VI): IR spectrum (ν, cm^{-1}): 1705 (C=O), 1629 (C=C); mass spectrum m/z: 220 $(M)^+$. Found: C 81.92; H 10.82%. $C_{15}H_{24}O$. Calculated: C 81.81, H 10.91%.

Compound (VII): PMR spectrum (δ, ppm): 6.54 m (1H, γ = 1.2 Hz), 2.49 d (3H, J = 1.2 Hz), 0.87 s (9H, $C(CH_3)_3$), 1.07 s (3H); mass spectrum, m/z: 256, 258 (3:1) (M^+), 103, 105 (3:1) $(COCH=CClCH_3^+)$, 57 $(C(CH_3)_3^+)$.

The authors express their gratitude to L. A. Sibel'dina (Institute of Chemical Physics of the Academy of Sciences of the USSR) for assistance in taking the high-resolution PMR spectra.

CONCLUSIONS

A stereospecific migration of the axial substituent (either methyl or acyl group) from the geminal node was discovered when propyne is acylated with the cis- and trans-4-tert-butyl-1-methylcyclohexanoylcarbonyl cations.

LITERATURE CITED

1. M. I. Kanishchev, A. A. Shchegolev, V. A. Smit, and R. Caple, Izv. Akad. Nauk SSSR, Ser. Khim., 714 (1977).
2. D. M. Brouwer and H. Hogeveen, Rec. Trav. Chim., 89, 211 (1970); R. Haseltine and T. S. Sorensen, Can. J. Chem., 53, 1067 (1975).
3. Yu. G. Bundel', K. G. Pankratov, M. B. Gordin, and O. A. Reutov, Dokl. Akad. Nauk SSSR, 199, 1314 (1971); R. M. Delaney, S. Middleton, and M. J. Rosser, Austral. J. Chem., 23, 1013 (1971).
4. A. A. Schegolev (Shchegolev), W. A. Smit, G. V. Roitburd, and V. F. Kucherov, Tetrahedron Lett., 3373 (1947).
5. P. J. Beeby and S. Sternhell, Austral. J. Chem., 23, 809 (1971).
6. M. Yoshimura, M. Nojima, and N. Tokura, Bull. Chem. Soc. Jpn., 46, 2164 (1973).
7. H. O. House and P. A. Richey, J. Org. Chem., 32, 2151 (1967).