Functionalization of saturated hydrocarbons by aprotic superacids

5.* Regioselective carbonylation of propane in an organic solvent initiated by aprotic organic superacids $CX_4 \cdot nAlBr_3$ (X = Br, Cl; n = 1 or 2)

I. S. Akhrem,* A. V. Orlinkov, L. V. Afanas'eva, and M. E. Vol'pin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085

Aprotic organic superacids $CX_4 \cdot nAlBr_3$ (X = Br, Cl; n = 1 or 2) are effective initiators of carbonylation of propane with CO in an organic solvent at -10 to -20 °C.

Key words: propane, carbonylation, carbon monoxide; aprotic superacids; polyhalomethanes, aluminum bromide.

Carbonylation of C_1 , $^2 C_3$, 3a,b and C_5-C_9 , 4 alkanes with CO in protic superacids has been described previously. It has been found 3c,d that the nonselective carbonylation of propane in an HF-SbF₅ mixture becomes selective in the presence of some halogen-containing compounds (CCl₄, CHCl₃, Br₂, and NaBr) and gives the PrⁱCO⁺ cation as the only (or the main) product. In some cases (for example, when CCl₄ is used), the degree of conversion of propane also markedly increases. The carbonylation of propane with CO in the presence of Br₂ (-10 °C, 1 h)^{3d} followed by treatment of the reaction mixture with ethanol gives PrⁱCOOEt, its maximum yield based on propane being 67 % and that based on SbF₅ being only 11 %.

Conversely, carbonylation of propane catalyzed by the $Pd(OAc)_2$ — CuX_2 system in the presence of $K_2S_2O_8$ in CF₃COOH (80 °C, 20 h) is nonselective.⁵

Obviously, the reactions in organic solvents containing aprotic superacids have advantages over the reactions carried out in protic superacids. However, carbonylation of alkanes carried out under mild conditions in an organic solvent and promoted by electrophiles has not yet been described.

In the present work we report on the first example of effective regioselective carbonylation of propane with CO in CH_2Br_2 in the presence of aprotic organic superacids $CBr_4 \cdot nAlBr_3$ (n = 1, 2), $CCl_4 \cdot 2AlBr_3$, and $CHBr_3 \cdot 2AlBr_3$. Previously these systems have been successfully used to initiate cracking, isomerization, and oligomerization of alkanes;⁶ ionic bromination of alkanes and cycloalkanes with bromine;⁷ carbonylation of cyclopentane,⁸ cyclohexane, and methylcyclopentane⁹ with CO; and formylation of adamantane.¹⁰

In the presence of aprotic superacids listed above, propane reacts with CO at -20 °C to give, after the treatment of the reaction mixture with isopropyl alcohol, $Pr^{i}COOPr^{i}$ (1) in a 92–130 % yield based on the superacid as the only product (Scheme 1, Table 1).



 $E = CBr_4 \cdot 2AIBr_3, CBr_4 \cdot AIBr_3, CCI_4 \cdot 2AIBr_3$

The activities of the $CBr_4 \cdot 2AlBr_3$ and $CBr_4 \cdot AlBr_3$ systems are rather similar, that of CHBr, 2AlBr, is markedly lower, and AlBr, in CH₂Br, is absolutely inert; the equimolar complex $CCl_4 \cdot AlBr_3$ is also inert, and this distinguishes it fundamentally from the corresponding complex of the composition 1:2. Other systems that exhibit high activity in promoting cracking and isomerization of alkanes at ~20 °C, such as $Br_2 \cdot 2AlBr_3^{-11}$ or SOCl₂ · 2AlBr₃,¹² are also inert under the conditions studied. Thus, the difference in the activities of superacidic systems with respect to the carbonylation of propane proves to be much more pronounced than that in the case of the cracking of the $C_5 - C_{12}$ alkanes. This is probably due to the fact that propane is less reactive than its higher homologs and, consequently, abstraction of a hydride ion from it requires the presence of a stronger superacid.

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 5, pp. 1214-1216, May, 1996.

1066-5285/96/4505-1154 \$15.00 © 1996 Plenum Publishing Corporation

^{*} For Part 4, see Ref. 1.

Superacid	CO : C ₃ H ₈ (%, v/v)	Yield 1 (mol. %) ^a
AlBr ₃	1.2 : 1.0	0
CBr ₄ ·AlBr ₃	1.2:1.0	114
$CBr_{4} \cdot 2AlBr_{1}$	1.1:1.0	130
$CBr_4 \cdot 2AlBr_3$	1.7 : 1.0	119
$CBr_4 \cdot 2AlBr_3$	1.4 ; 1.0	130 ^b
$CBr_4 \cdot 2AlBr_3$	1.2:1.0	123¢
$CCl_4 \cdot 2AlBr_3$	1.2:1.0	92
CHBr ₃ · 2AIBr ₃	1.2:1.0	23

Table 1. Carbonylation of propane with CO in the presence of aprotic organic superacids in CH_2Br_2 (-20 °C, 2.5 h)

^a Based on the superacid.

^b Duration of the reaction was 4 h.

^c The reaction occurs at -10 °C.

The fact that the yield of compound 1 in the reaction initiated by $CBr_4 \cdot 2AlBr_3$ reaches 1.3 moles per mole of the superacid is probably explained by the fact that the $CHBr_3 \cdot 2AlBr_3$ complex formed from $CBr_4 \cdot 2AlBr_3$ also initiates the carbonylation of propane (see Table 1).

From the data of Table 1, one can also see that the yields of the carbonylation product are slightly dependent on the reaction conditions. In fact, an increase in the content of CO in the gas mixture, with the CO : C_3H_8 ratio changing from 1.1 to 1.7, only slightly decreases the yield of ester 1 (see Table 1). Conversely, an opposite and more pronounced dependence of the yield of Pr^iCO^+ on the CO : C_3H_8 ratio has been observed previously in the carbonylation of propane in the presence of Br_2 in an HF-SbF₅ medium; this served as evidence in support of the suggestion that this reaction involves the BrCO⁺ cation.³⁴ A scheme involving participation of the carbonylation of propane has also been proposed for this reaction^{3c} (Scheme 2).

Scheme 2



Doubts on the correctness of this mechanism were raised by the data of ¹³C NMR spectroscopy for the CCl_3^+ cation, which indicated that this carbocation possesses only medium electrophilicity. Therefore, it has been suggested¹³ that the reaction (see Scheme 2 (*b*)) involves superelectrophiles 2, 3, or 4 (Scheme 3).



In one of the recent papers,^{3e} structure of cation 5 has also been attributed to the reactive species.



On the basis of the results of quantum-chemical calculations of the complexes $CBr_4 \cdot nAlBr_3$ (n = 1, 2,4) and cations CX_3^+ , CHX_2^+ , CH_2X^+ (X = Cl, Br, or I but not F), we assume that the key role in the acceptance of the hydride ion withdrawn from the alkane molecule by the $CX_4 \cdot nAlBr_3$ systems is played by the $CX_3^+Y^-$ complexes (Y = AlBr₄ or Al₂Br₇). Strictly speaking, the latter are not carbenium cationic complexes, since the positive charge of the cationic part of the complex is localized exclusively at the halogen atoms. More electrophilic though thermodynamically extremely unfavorable dicationic complexes $[X^+=C=X^+]Y_2^-$, which are also responsible for minima on the potential energy surface,¹⁴ can hardly be regarded as real intermediates of the reaction of propane with CO, the more so as no difference is observed between the activities of the systems in which cationic and dicationic complexes can be generated (CBr₄ · AlBr₃ and $CBr_4 \cdot 2AlBr_3$). Based on the foregoing we believe that the superelectrophilic properties of these systems are due to the halogenium cationic complexes containing a monocoordinated positively charged halogen atom. Apparently, the key step of the carbonylation of propane in the presence of aprotic superacids is the generation of the isopropyl cation from the alkane; this

Scheme 4



cation then adds CO according to the Koch-Haaf¹⁵ reaction to give the $Pr^{i}CO^{+}$ cation, which is stable under the reaction conditions (Scheme 4).

An alternative mechanism that includes the attack by the superelectrophile on CO seems less probable.

Experimental

GC analysis was carried out on a Model'-3700 chromatograph equipped with a flame ionization detector (FID) on a quartz capillary column (25 m \times 0.23 mm, SE-54 as the stationary phase, temperature programming from 25 °C to 200 °C, rate of heating 8 deg per min).

The reaction products were identified by GC/MS using a VG 7070E (EI, 70 eV) spectrometer equipped with a similar capillary column.

Carbonylation of propane (typical procedure). Anhydrous $AlBr_3$ (0.5 g, 1.87 mmol) and CBr_4 (0.31 g, 0.93 mmol) were placed in a two-necked round-bottom flask (100 mL), and the mixture was completely dissolved with stirring in 1 mL of CH_3Br_2 .

The system was evacuated at -30 °C and filled with a mixture of propane (3.1 L) and CO (3.4 L) (1.0 : 1.1, mol/mol) prepared beforehand in a rubber gas bag. Then the temperature was rapidly increased to -20 °C, and the solution was stirred for 2.5 h under a pressure of the gas mixture that occurred in the gas bag. After the reaction was completed, 3 mL of PrⁱOH was added, the mixture was stirred for an additional 0.5 h at -20 °C and hydrolyzed in the cold, and the aqueous layer was extracted with ether. The combined extracts were washed with a 5 % solution of NaHCO₃ and analyzed by GC using hexyl butyrate as the internal standard. The yield of compound 1 was 0.157 g (1.21 mmol, 130 % based on CBr₄). The target isopropyl isobutyrate was identified by GC/MS. The MS of PrⁱCOOPrⁱ (EI, 70 eV), m/z (I_{rel} (%)): 130 [M]⁺ (1), 115 [M-Me]⁺ (4), 89 [M-C₃H₅]⁺ (17), 71 [M-C₃H₅O]⁺ (36), 59 [M-C₃H₇CO]⁺ (6), 43 [M-C₁H₇COO] (100).

This work was carried out with financial support of the Russian Foundation for Basic Research (Project No.

93-03-04556) and the International Science Foundation (Grant MRA 000).

References

- I. S. Akhrem, A. V. Orlinkov, L. V. Afanas'eva, and M. E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1208 [*Russ. Chem. Bull.*, 1996, **45**, 1148 (Engl. Transl.)].
- 2. H. Hogeveen, J. Lucas, and C. F. Roobeek, J. Chem. Soc., Chem. Commun., 1969, 920.
- (a) S. Delavarenne, M. Simon, M. Fauconet, and J. Sommer, J. Chem. Soc., Chem. Commun., 1989, 1049; (b) S. Delavarenne, M. Simon, M. Fauconet, and J. Sommer, J. Am. Chem. Soc., 1989, 111, 383; (c) J.-C. Culman, M. Simon, and J. Sommer, J. Chem. Soc., Chem. Commun., 1990, 1098; (d) J. Bukala, J.-C. Culman, and J. Sommer, J. Chem. Soc., Chem. Commun., 1992, 481; (e) J. Sommer and J. Bukala, Acc. Chem. Res., 1993, 26, 370.
- 4. N. Yoneda, Y. Takahashi, T. Fukuhara, and A. Suzuki, Bull. Chem. Soc. Jpn., 1986, 59, 2819.
- 5. K. Nakata, T. Miyata, Y. Taniguchi, K. Takaki, and Y. Fujiwara, J. Organomet. Chem., 1995, 71.
- I. S. Akhrem, A. V. Orlinkov, and M. E. Vol'pin, J. Chem. Soc., Chem. Commun., 1993, 671.
- 7. I. Akhrem, A. Orlinkov, L. Afanas'eva, and M. Vol'pin, Tetrahedron Lett., 1996, in press.
- S. Akhrem, S. Z. Bernadyuk, and M. E. Vol'pin, Mendeleev Commun., 1993, 188.
- 9. S. Z. Bernadyuk, I. S. Akhrem, and M. E. Vol'pin, Mendeleev Commun., 1994, 185.
- I. S. Akhrem, I. M. Churilova, S. Z. Bernadyuk, and M. E. Vol'pin, *Tetrahedron Lett.*, 1996, in press.
- I. S. Akhrem, L. V. Afanas'eva, A. V. Orlinkov, and M. E. Vol'pin, *Mendeleev Commun.*, 1994, 131.
- I. Akhrem, S. Gudima, and M. Vol'pin, Chemistry-A European J., 1996, in press.
- 13. G. A. Olah, Angew. Chem., Int. Ed. Engl., 1993, 32, 767.
- A. L. Chistyakov, I. V. Stankevich, I. S. Akhrem, N. P. Gambaryan, and M. E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 554 [*Russ. Chem. Bull.*, 1996, **45**, 514 (Engl. Transl.)].
- 15. H. Koch and W. Haaf, Org. Synth., 1964, 44, 11.

Received November 2, 1995