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REVERSIBLE AND IRREVERSIBLE PROCESSES IN ALKYNE - $AlBr_3$ CHEMISTRY

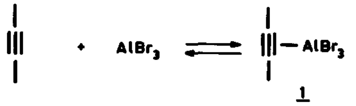
H. Hogeveen and D.M. Kok

Department of Organic Chemistry, University of Groningen,
Nijenborgh 16, 9747 AG Groningen, The Netherlands

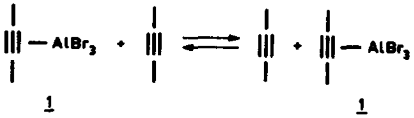
Summary: NMR line-broadening has shown the existence of a rapid exchange between 2-butyne and 2-butyne-$AlBr_3$ π complex. The $AlBr_3$-induced heterocyclodimerization of 2-butyne with propyne is preferred to the corresponding homo-cyclodimerisations.

Little is known about the interaction of alkynes with aluminum trihalides.[1] Many years ago it was reported that at low temperature aluminum trichloride and acetylene form a complex of unknown structure with composition (Al_2Cl_6) $(C_2H_2)_{12}$.[2] More recently, it has been shown by IR measurements at -100°C that di-alkyl substituted alkynes interact with aluminum tribromide; in the case of the mono-alkyl substituted alkynes only polymerization could be detected.[3]

Our interest in the physical and synthetic aspects of aluminum trihalide σ-complexes of cyclobutadienes,[4] which are prepared from alkynes and aluminum trihalides, led us to investigate the behaviour of 2-butyne with aluminum tribromide by ^{1}H- and ^{13}C-NMR spectroscopy at low temperature.[5] The ^{1}H-NMR spectrum of a solution of 2-butyne (0,20 molar) and aluminum tribromide (0.11 molar) in $CH_2Cl_2/CH_2Br_2/CDCl_3$ taken at -100°C,[6] shows two signals of about the same intensity at δ 1.80 ppm (2-butyne) and at δ 2.35 ppm, the latter being ascribed to a 2-butyne-$AlBr_3$ Π complex (1). When the solution is warmed up, reversible line-broadening of the signals is observed,[7] and at about -76°C the two signals have coalesced into one broad singlet at δ 2.04 ppm.[8] These observations indicate the occurrence of an exchange process between 2-butyne and complex 1. In principle, at least two different dynamic processes might be responsible for the observed line broadening.



(I)



(II)

A mono-bimolecular equilibrium of type I has been observed with aluminum tribromide and cyclohexene,[9a] and with $Ag^{\oplus}$ and various di-alkyl substituted alkynes.[9b] Process II is degenerate and involves a bimolecular-bimolecular exchange between 2-butyne and complex 1. To determine the nature of the exchange process, the line width ($\Delta\upsilon\frac{1}{2}$) of the peak due to complex 1 was determined as function of the concentration of 2-butyne[10] (Fig. 1)

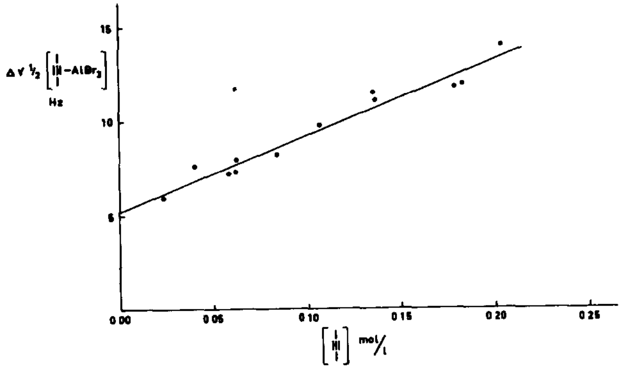


Figure 1. Plot of the line width of complex 1 (corrected for the natural line width) vs. the concentration of 2-butyne. (temp. -100°C).

These results clearly indicate that $\Delta\upsilon\frac{1}{2}$ (complex 1) increases proportional with the concentration of 2-butyne and that process II contributes to the measured line-broadening.[11]

Additional evidence for the presence of complex 1 in solution arises from the ^{13}C-NMR spectrum taken at -100°C (Fig. 2), which clearly shows the presence of 2-butyne and complex 1.

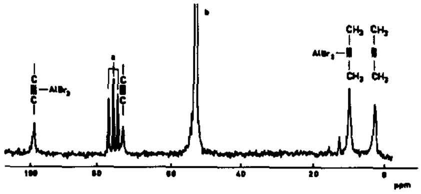
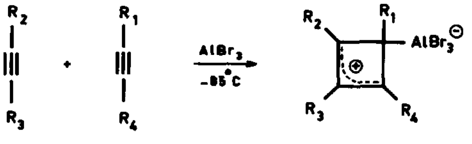


Figure 2. ^{13}C-NMR spectrum at 25.16 MHz of 2-butyne with aluminum tribromide (molar ration 2:1) in $CH_2Cl_2/CDCl_3$ $(2.5{:}1.5\,^{v}/_{v})$ at -100°C[12] (a: $CDCl_3$, b: CH_2Cl_2)

Quite remarkable is the downfield shift of about 25 ppm of the alkyne sp-carbon atoms on complexation with $AlBr_3$.[13] This may be accounted for by the electron withdrawing property of the aluminum tribromide which causes a decrease in pi-character on the alkyne carbon atoms, thereby tending to change the hybridization from sp to sp^2, so causing a downfield shift.

In addition to the spectroscopic measurements of the reversible π complex formation mentioned above, experiments leading to the synthesis of new $AlBr_3$ cyclobutadiene σ-complexes based on 2-butyne and propyne have been performed.[14] When a solution of propyne (20 mmol) or of a 1:1 mixture of 2-butyne and propyne in 25 ml CH_2Cl_2 is added dropwise to a suspension of aluminum tribromide (10 mmol) in 25 ml CH_2Cl_2 at -85°C, complexes 2b and 2c[15] are formed (yields 70 and 76%), respectively. The beneficial effect of low temperature on the yield is exemplified by the fact that if the cyclodimerization of propyne is performed at -40°C, the yield drops to 35%.



2a $R_1=R_2=R_3=R_4=CH_3$
2b $R_1=R_3=H, R_2=R_4=CH_3$
2c $R_1=H, R_2=R_3=R_4=CH_3$
2d $R_1=R_4=H, R_2=R_3=CH_3$

The absence (at least less than 5%) of the homo-cyclodimerization complexes 2a and 2b in the reaction of the 1:1 mixture of 2-butyne and propyne with $AlBr_3$ shows a remarkable preference for the hetero-cyclodimerization. Furthermore, the regioselective formation of complex 2b from propyne (isomeric complexes such as 2d, being formed in less than 5%) is in agreement with a stepwise cationic mechanism although a ${}_{\pi}2_{s}+{}_{\pi}2_{a}$ concerted cycloaddition cannot be excluded.[16]

The synthetic aspects of the $AlBr_3$ cyclobutadiene σ complexes 2a, b and c are under current investigation and the results obtained will be published soon.

Notes and references.

1. H.H. Perkampus, Wechselwirkung von π-Elektronsystemen met Metallhalogeniden, chapter 4, Springer-Verlag, 1973.
2. E. Band, *Ann.Chem. Phys.*, **1**, 36 (1904).
3. H.H. Perkampus and W. Weiss, *Z. Naturforsch.*, **29b**, 61, (1974).
4. P.B.J. Driessen and H. Hogeveen, *J. Amer. Chem. Soc.*, **100**, 1193 (1978); *J. Organomet. Chem.* **156**, 265 (1978) and references cited therein.
5. The choice of aluminum tribromide instead of aluminum trichloride was determined by the greater solubility of aluminum tribromide in the mixture $CH_2Cl_2/CH_2Br_2/CDCl_3$.
6. The samples were prepared as follows: a standard solution of $AlBr_3$ (1.31 mol/l) in CH_2Br_2 was added to $CDCl_3/CH_2Cl_2$ kept at -110°C to -120°C, followed by a standard solution of 2-butyne in CH_2Cl_2 (1.00 mol/l) (final ratio CH_2Cl_2 : $(CH_2Br_2 + CDCl_3)$ = 4 (1) $^{v}/v$). The solid mixture was slowly warmed up to -100°C, while stirring with a rod to homogenise the solution.
7. Along with the observed line broadening the signals of the $AlBr_3$-σ complex of tetramethylcyclobutadiene appear slowly on warming up the sample.
8. The difference between experimental (2.04 ppm) and calculated (2.08 ppm) values of the

chemical shift of the coalesced signal is ascribed to the occurrence of process I and the formation of (small) quantities of the Al_2Br_6 σ complex of tetramethylcyclobutadiene.

9a. H.H. Perkampus, G. Prescher, Z. Physik. Chem. N.F., **77**, 333 (1972).

b. G.S. Lewandos, D.K. Gregston and F.R. Nelson, J. Organomet. Chem., **118**, 363 (1976).

10. J.A. Pople, W.G. Schneider and H.J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, chapter 10.

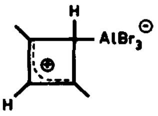
11. At [2-butyne]=0 the line width ($\Delta\upsilon\frac{1}{2}$(complex 1)) still differs from zero (Fig. 1). This may indicate that there is a contribution from processes I to the overall exchange of 2-butyne and complex 1 . On basis of both processes I and II a linear relationship between $\Delta\upsilon\frac{1}{2}$ (2-butyne) and [complex 1] is not expected and indeed not observed.

12. The sample was prepared by adding 270 mg of 2-butyne (5 mmol) in 1 ml CH_2Cl_2 to 667 mg of aluminum tribromide (2.5 mmol) in 1.5 ml CH_2Cl_2 and 1.5 ml $CDCl_3$ kept at -110°C, followed by stirring with a rod and allowing the sample to warm up to -100°C.

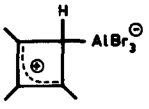
13. Several alkyne-transition metal complexes (e.g. from Ag(I), Pt(0), Pt(II) and Co(0)) are known. However, both upfield and downfield shifts are observed for the signals of the alkyne carbon atoms, depending on the relative importance of donation and back donation by the transition metal. G.S. Lewandos, Tetrahedron Letters, 2279 (1978) and references cited therein.

14. The reaction of propyne with HCl or HBr at -70°C and room temperature has been reported to afford cyclobutanes in low yields. K. Griesbaum, A. Singh and M. El-Abed, Tetrahedron Letters, 1159 (1978). K. Griesbaum, W. Naegele and G.G. Wanless, J. Amer. Chem. Soc., **87** 3151 (1965).

15. We have recorded the ^{13}C(25.2 MHz) and ^{1}H(60 MHz) NMR spectra of complexes 2b and 2c at -70°C in $CH_2Cl_2/CDCl_3$ (2.5:1.5$^{v}/_{v}$) and CH_2Cl_2 respectively; chemical shifts have been measured relative to $CDCl_3$ (^{13}C NMR) and to CH_2Cl_2 (^{1}H NMR) and converted to δ_{TMS} values using δ_{CDCl_3} = 76.9 and $\delta_{CH_2Cl_2}$ = 5.29 ppm respectively.



2b



2c

2b: ^{13}C spectrum, C_1 62.1 (d,J≈135Hz), $C_{2,4}$ 184.0 (s), C_3 152.4 (d,J≈210Hz), $C_{2,4}$ (CH_3) 20.0 (q,J=130Hz), ^{1}H spectrum, H_1 2.94 (d, =4.1Hz), CH_3(2,4) 2.74 (s), H_3 7.70 (d,J=4.1Hz).

2c: ^{13}C spectrum, C_1 61.9 (d,J≈130Hz), $C_{2,4}$ 162.8 (s), C_3 165.4 (s), $C_{2,4}$ (CH_3) 15.8 (q,J=130Hz), C_3(CH_3) 10.3 (q,J=130Hz). ^{1}H spectrum H_1 2.42; CH_3(2,4) 2.42 (s), CH_3(3) 2.21 (s).

16. R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", p. 165, Academic Press, New York, N.Y. 1970.

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