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REACTIONS OF THE $AlBr_3$ σ COMPLEX OF TETRAMETHYLCYCLOBUTADIENE WITH CYCLOHEXYLISOCYANIDE HYDROLYTICALLY INDUCED FOUR-TO FIVE-MEMBERED RING EXPANSION

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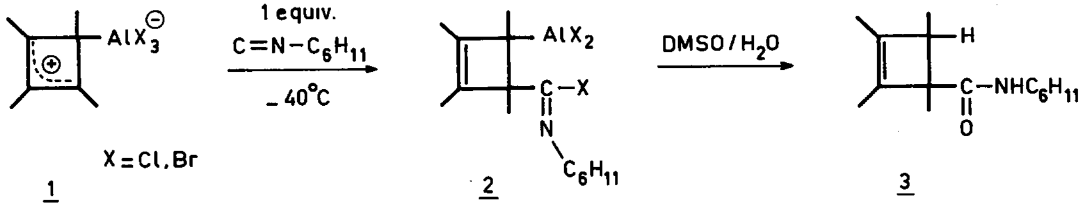
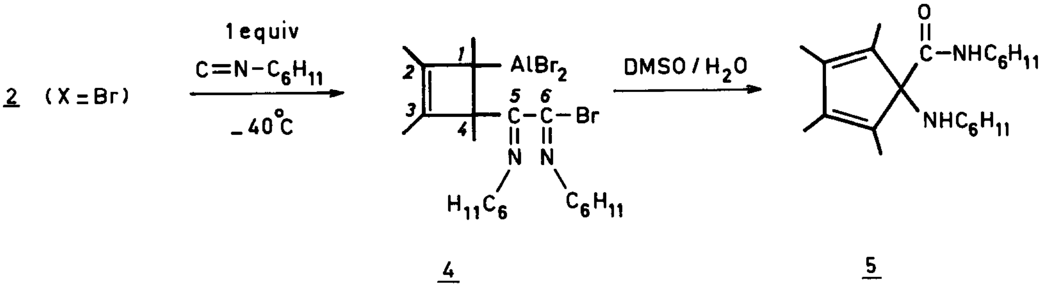
Our current interest in exploring the chemical reactivity of the easily obtainable $AlCl_3$ and $AlBr_3$ σ complexes of cyclobutadienes has led to the discovery of some novel reactions[1)], e.g. with ethylcyanoformate to provide a pyridine synthesis[2)]. In most reactions of these complexes the formation of the products can be rationalised by assuming the addition of a dienophile to "cyclobutadienes"[3)] formed in situ. In contrast, we recently reported that upon reaction at -40°C of complex 1 with one equiv of cyclohexylisocyanide, a nucleophilic attack of the isonitrile carbon atom at the allylic moiety of the complex takes place, as concluded from analysis of NMR spectroscopic data for the obtained species 2[1)]. Hydrolysis of 2 afforded the cyclobutene carboxamide 3. In general, nucleophilic addition of isocyanides to carbonium ions is restricted - because of the acid sensitivity of isocyanides - to those ions which can be prepared under non-acidic conditions, e.g. the tropylium ion[4a)] and immonium ions[4b)].

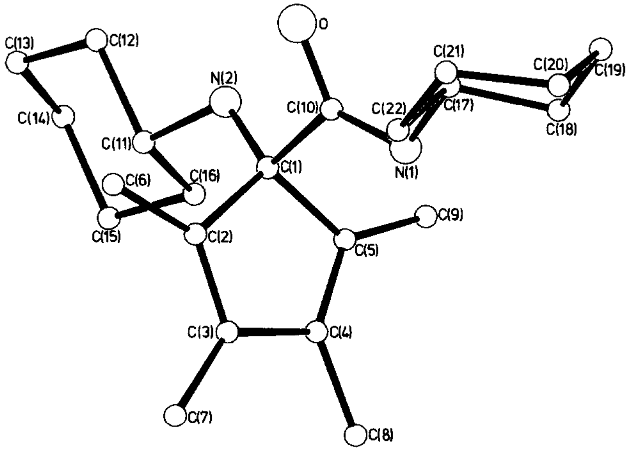
In this communication we report the results of a ring expansion reaction occurring upon hydrolysis of 4, which is formed by treating 2 (X=Br[6)]) with a second equiv of cyclohexylisocyanide[5)]. Structure 4 is assigned to the obtained intermediate species on spectroscopic grounds: ^{1}H-NMR spectrum (-10°C) methyl resonances at δ 1.07, 1.31, 1.55 and 1.58 ppm, broad resonances at δ 0.9-2.1 ppm (cyclohexyl ring protons); ^{13}C NMR spectrum (^{1}H noise decoupled, -10°C) resonances at δ 185.1 (C_6), 149.8, 138.5 and 122.6 (C_2, C_3 and C_5), 66.7 and 63.1 (both d, $J_{^{13}C-^1H}$ = 140 Hz, $=N-\underset{H}{C}<$), 59.1 (C_4), 16.7, 15.8, 12.3 and 11.7 ppm (all q, $J_{^{13}C-^1H}$ = 128 Hz), the remaining resonances of the cyclohexyl ring carbon atoms being obscured by the intense absorption of the solvent (CH_2Br_2) at δ 21.6 ppm. Only three of the four cyclobutene ring carbon atoms are observed, which agrees



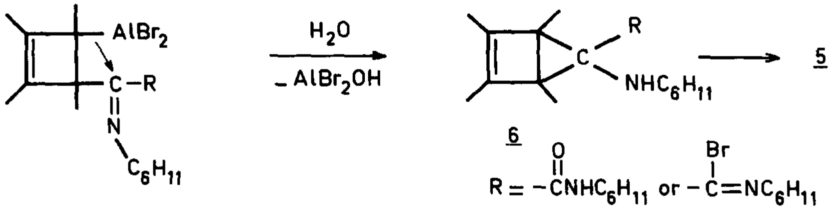


with structure 4 in which the ring carbon atom bonded to aluminum is not expected to be observable in the ^{13}C NMR spectrum$^{7)}$. IR spectrum, several absorptions from 1585-1715 cm^{-1} ($>C{=}N-$, $\overset{Br}{>}C{=}N-$, $>C{=}C<$), an absorption around 2325 cm^{-1} ($-C{\equiv}N^{\oplus}-$) as found in the case of 2$^{1)}$ being absent.

As the structure of the compound obtained on hydrolysis of 4 could not be established unambiguously with the aid of the usual spectroscopic techniques, an X-ray structure determination was undertaken by Gaykema and Spek$^{8)}$; a representation of the spatial structure is given below.



We suggest that in this unusual reaction compound 5 is formed upon a ring closure step involving C_5, under expulsion of the $AlBr_2OH$ group, yielding 6 as an intermediate species, which undergoes ring opening. The conversion of the bromo imine functionality to the carboxamide group does not necessarily occur synchronously with the ring closure / ring opening sequence[9)].



Acknowledgement

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References and Notes

1. P.B.J. Driessen and H. Hogeveen, J. Organomet. Chem., 156, 265 (1978).
2. P.B.J. Driessen, D.S.B. Grace, H. Hogeveen and H. Jorritsma, Tetrahedron Lett., 2263 (1976).
3. It may be that addition of the dienophile is taking place, while the $AlCl_3$ group is not yet entirely removed from the complex.
4. a) I. Ugi, W. Betz and K. Offerman, Chem. Ber., 97, 3008 (1964).
   b) I. Ugi, Angew. Chem., 74, 9 (1962).
5. To a mechanically stirred solution of complex 1 (X=Br, 5 mmol) in CH_2Br_2 (20 mL) was added dropwise at -40°C, a solution of cyclohexylisocyanide (1.09 g, 10 mmol) in CH_2Br_2 (5 ml), affording species 4. This was hydrolysed by adding dropwise a solution of DMSO (2 ml) in CH_2Br_2 (10 ml), followed by pouring the solution into H_2O (100 ml). (Addition of DMSO is not essential, however, it facilitates the work up procedure). The aqueous layer was extracted twice with pentane, the combined organic layers dried (Na_2SO_4) and the solvents removed. Column chromatography (Al_2O_3, eluent pentane/ether) of the organic residue afforded compound 5 (2.1 mmol, 42%). M.p. (pentane), 130.5-132.5°C; elemental analysis, found C 76.73, H 10.55, N 8.05: calc. ($C_{22}H_{36}N_2O$) C 76.69, H 10.53, N 8.13; ^1H NMR ($CDCl_3$); δ 1.74 (s, 6H), 1.84 (s, 6H), 3.7 (br, 1H), 5.6 (br, 1H) and broad absorptions at 0.9-2.6 ppm (≈22H); ^{13}C NMR ($CDCl_3$),

δ 169.4, 137.3, 136.9, 76.9, 51.4 and 46.9 (both d, $J_{^{13}C-^{1}H}$ = 140 Hz), 34.7, 32.1, 25.3, 24.9, 24.6 and 23.9 (all t, $J_{^{13}C-^{1}H}$ = 130 Hz), 10.6 and 9.6 ppm (both q, $J_{^{13}C-^{1}H}$ = 128 Hz); UV (hexane), λ_{max} 273 nm (ε=38100); IR (nujol), i.a. 3320 and 1650 cm^{-1}; Mass spectrum, M^+ 344.

6. Attempts to perform a similar reaction with species 2 (X=Cl) were unsuccessful; besides compound 3 only unidentifiable materials were obtained.
7. A similar feature was encountered in the ^{13}C NMR spectrum of species 2[1).
8. W.P.J. Gaykema and A.L. Spek, Laboratory of General Chemistry, University of Utrecht.
9. On basis of the reaction of two equiv of isocyanide with e.g. 1,1 ditrifluoromethyl-2,2-dicyanoethylene[10) (affording a four-membered ring), the formation of a three membered ring is unexpected. Possibly, the conversion of the bromo imine functionality to the carboxamide group occurs relatively fast, thus preventing the formation of a four-membered ring.
10. W.J. Middleton, J. Org. Chem. 30, 1402 (1965).

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