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CHEMISTRY OF THE ALUMINUM TRICHLORIDE σ-COMPLEX OF TETRAMETHYLCYCLOBUTADIENE

H. Hogeveen, H. Jorritsma, and P.A. Wade
Department of Organic Chemistry, The University,
Zernikelaan, Groningen, The Netherlands
and
F. van Rantwijk, J.B. Koster, J.J. Prooi, A. Sinnema, and H. van Bekkum,
Laboratory of Organic Chemistry, Delft University of Technology,
Julianalaan 136, Delft - 2208, The Netherlands

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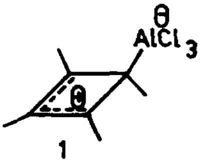
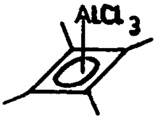
A number of synthetic procedures employing 2-butyne and aluminum trichloride have recently been developed.[1-3] Some of us have previously reported the reaction of 2-butyne with aluminum trichloride in which the title compound 1 is produced. The structure of 1 has recently been confirmed by X-ray analysis.[4,5]

$\boxed{-\equiv CH_3}$



1



2

The nmr spectrum of 1[6], taken at -10° in methylene chloride solution, consists of three sharp peaks. These occur at 1.32, 2.29, and 2.40 ppm in a ratio of 1:1:2. If the sample is warmed, reversible line-broadening is observed. By 20° the two low-field peaks have collapsed into a broad singlet. And, when a methylene bromide or benzene solution[7] of 1 is warmed to 80°, coalescence to one peak is observed. These phenomena indicate that 1 is involved in a dynamic process; the aluminum trichloride group is migrating around the four-membered ring.

The intramolecular nature of this process has been established. Alternative pathways (eg., exchange of aluminum trichloride groups between two molecules of 1) have been excluded, since no reduction in the rate of migration was observed when solutions of 1 were diluted.[8] Nor is 2-butyne involved in the migration process, for in low concentration it still gives a sharp nmr signal, even after the peaks of 1 have begun to broaden. Addition of excess aluminum trichloride does not enhance migration; instead, one equivalent reduces the rate of migration by a factor of at least 50.[9]

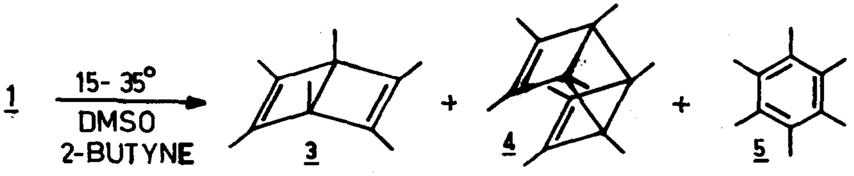
Double irradiation nmr experiments[10] indicate that migration is not simply due to consecutive 1,2-shifts of the aluminum trichloride group. When 1 was strongly irradiated at 1.32 ppm, the intensities of the 2.40 and 2.29 ppm signals were equally reduced. This equal transfer of saturation shows that, irrespective of its original position, the aluminum trichloride group can migrate equally well to any of the other positions on the four-membered ring.

Experimental activation parameters were calculated from the line-width of the high-field nmr peak at -10 to 45° using the slow-exchange approximation procedure[11]: $\Delta H^{\ddagger}$, 10.7 $kcal.mol^{-1}$; $\Delta S^{\ddagger}$, -17 eu. These parameters were also calculated from the line-shape of the two low-field peaks[10,12] at 0.5 to 18°: $\Delta H^{\ddagger}$, 9.7 $kcal.mol^{-1}$; $\Delta S^{\ddagger}$, -23 eu. The uncertainty in these values is estimated to be 20%.

We suggest that the π-complex 2 is an intermediate in the migration process. Complete disruption of the carbon-metal bonding to give "free" tetramethylcyclobutadiene is also possible, but intuitively less likely. Furthermore, the negative entropy of activation better accords with 2 as the intermediate.

A number of Diels-Alder reactions employing 1 have been performed.[1] For example, treatment of 1 with dimethyl acetylenedicarboxylate, either with or without DMSO, led to the expected dewarbenzene derivative. Presumably, both the diester and DMSO can remove aluminum trichloride from 1 generating "free" tetramethylcyclobutadiene.[1] It is this intermediate, then, that actually undergoes cycloaddition with the dienophile.

Addition of DMSO to a methylene chloride solution of 1 and two equivalents of 2-butyne at 15-35° led chiefly to three products[13] (eq 1): the expected hexamethyldewarbenzene (3) (40%), tetramethylcyclobutadiene dimer 4 (30%), hexamethylbenzene (5) (15%), and 15% of unidentified materials. When the experiment was repeated in the absence of 2-butyne,[14] 4 (62%) and 5 (11%) were still obtained, but only a trace of 3 (2%) was present. The products 3 and 4 presumably derive from competing Diels-Alder reactions of the intermediate tetramethylcyclobutadiene with itself,[15] or, alternatively, with 2-butyne.



eq 1

At -40° addition of DMSO to a solution containing 1 and two equivalents of 2-butyne gave only one major product (eq 2): 4[16] (79%) and 5 (3%). There was no 3 present. Thus, the intermediate is now reacting selectively with itself and not at all with 2-butyne.

$$\underline{1} \xrightarrow[\text{DMSO} \atop \text{2-BUTYNE}]{-40^{\circ}} \underline{4} + \underset{\text{TRACE}}{\underline{5}} \qquad \text{eq 2}$$

The well-known reactivity of cyclobutadienes, particularly the parent compound,[17] might seem to exclude the possibility of any selectivity in their reactions. However, recent work[19] indicates that certain highly substituted cyclobutadienes, most notably the tri-t-butyl derivative[19a], are at least stable enough to be isolated. We submit that the reactivity of tetramethylcyclobutadiene is intermediate between that of the parent compound and the tri-t-butyl derivative.

Results with various dienophiles[20] indicate some limitations to the synthesis of substituted dewarbenzene derivatives from 1. The dienophile must be at least moderately reactive (eg., possess a conjugated ester group) for a useful synthesis. Otherwise non-selective conditions (i.e., moderate temperature) must be employed, and, at best, low yields accepted.

We are continuing our investigations of 1 and related species derived from other alkynes.

Notes and references.

1. J.B. Koster, G.J. Timmermans, and H. van Bekkum, Synthesis, 1971, 139.
2. W. Schäfer and H. Hellmann, Angew. Chem., 79, 566 (1967).
3. H.M. Rosenberg and E.C. Eimutis, Can. J. Chem., 45, 2263 (1967).
4. C. Krüger, P.J. Roberts, Y.H. Tsay, and J.B. Koster, J. Organometal, Chem. (Amsterdam), in press.
5. A number of other structures[2,3] have previously been assigned to the initial reaction product of 2-butyne and aluminum trichloride, cf., G.M. Whitesides and W.H. Ehman, J. Amer. Chem. Soc., 91, 3800 (1969) and a personal communication from W. Schäfer to L.F. Fieser as appearing in M. Fieser and L.F. Fieser, "Reagents for Organic Synthesis", vol 2, Wiley-Interscience, London, 1969, p. 23.
6. Prepared by reaction of 2.1 equivalents of 2-butyne and 1.0 equivalent of aluminum trichloride in methylene chloride at -30 to 3° under nitrogen. The resulting solution of 90% pure 1 can be used directly, or, alternatively, concentrated at -30° to give dark red crystals. Recrystallization of these crystals from methylene chloride at low temperature under nitrogen gives 1 with a purity of about 95%.
7. The spectrum of 1 in benzene at 2° consists of two peaks at 2.33 and 1.72 ppm.
8. For 2.0, 1.0, and 0.5 M solutions of 1 in methylene chloride at 15°, the relative rates were 1.0, 1.4, and 1.8, respectively. We don't place much emphasis on these relatively small changes. Perhaps intermolecular association at high concentration occurs stabilizing 1 somewhat.

9. Aluminum chloride is only marginally soluble in methylene chloride itself. The fact that it readily dissolves in solutions of 1 indicates molecular association with 1; perhaps this occurs through a chloride bridge. Such association should remove electron density from the metal atom of 1 thus strengthening the metal-carbon bond. This would be expected to result in a lower rate of migration.
10. J.A. Pople, W.G. Schneider, and H.J. Bernstein, "High-resolution Nuclear Magnetic Resonance", Chapter 10, McGraw-Hill, New York, 1959.
11. L.H. Piette and W.A. Anderson, J. Chem. Phys., 30, 899 (1959).
12. Spectra were simulated by elaborating the Bloch equation (The non-specific nature of the exchange process was taken into account) and compared with the recorded spectra.
13. After aqueous sodium bicarbonate work-up and concentration of the organic layers, the products were investigated by nmr.
14. Solutions of 1 are stable at room temperature for several days if no excess 2-butyne is present. The tetramethylcyclobutadiene dimer 4 is only formed after 1 is treated with a Lewis base - either DMSO or water.
15. It is not likely that 4 arises from reaction of 1 with tetramethylcyclobutadiene. When a solution of 1 is treated with only 0.5 equivalent of DMSO (presumably generating 0.5 equivalent of tetramethylcyclobutadiene), the deep red color of 1 persists; nmr indicates that the remaining 0.5 equivalent of 1 is unaffected and only 0.2 equivalent of 4 is produced. Preliminary experiments indicate that 1 does indeed react with dienes such as cyclopentadiene and piperylene. However, the products are polymeric.
16. A 75% yield of 4 was isolated from this reaction. This would appear to be the method of choice in synthesizing 4.
17. For example, warming cyclobutadiene in an argon matrix to 35°K results in dimerization.[18]
18. O.L. Chapman, C.L. McIntosch, and J. Pacansky, J. Amer. Chem. Soc., 95, 614 (1973).
19. a. S. Masamune, Nobuo Nakamura, M. Suda, and H. Ona, J. Amer. Chem. Soc., 95, 8481 (1973);
    b. H. Kimling and A. Krebs, Angew. Chem. Int. Ed. Engl., 11, 932 (1972);
    c. G. Maier, ibid., 13, 425 (1974).
20. With methyl phenylpropiolate a mixture of 4 and the dewarbenzene derivative is obtained at low temperature.[21] We have not been able to obtain a substituted dewarbenzene derivative from the reaction, either at low or moderate temperature, of cyclododecyne with 1; instead 4 is formed.
21. We thank Dr. J. Dopper of the Groningen laboratory for this result.