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DYNAMIC BEHAVIOUR OF THE ALUMINUM TRICHLORIDE σ-COMPLEX OF A 1,2-TETRAMETHYLENECYCLOBUTADIENE. SYNTHESIS OF 1,2- AND 5,6-TETRAMETHYLENEDEWARBENZENE DERIVATIVES

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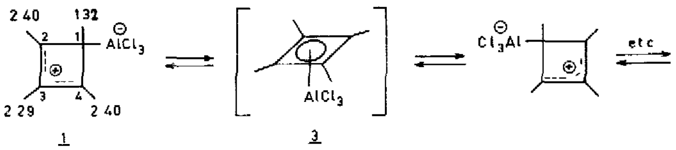
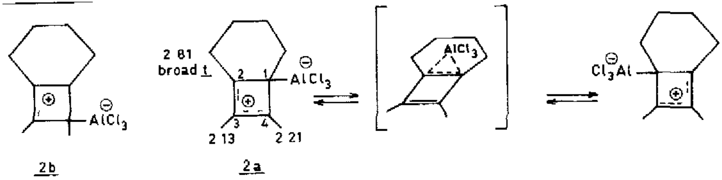
We have a dual interest in aluminum trichloride σ-complexes[1] of cyclobutadienes The tetramethylcyclobutadiene complex 1 exhibits a temperature-dependent pmr spectrum due to an unusual intramolecular migration of the aluminum trichloride group,[2] furthermore, such complexes are useful as synthetic precursors to substituted Dewarbenzenes [2-6] We discuss here the temperature-dependent pmr spectrum of the aluminum trichloride σ-complex (2a) of a 1,2-tetramethylenecyclobutadiene. We also report the use of complexes 1 and 2a in two separate syntheses leading to tetramethylene-bridged Dewarbenzene derivatives[7] from which we hope, eventually, to prepare pyramidal dicarbonium ions containing methylene bridges [8]

Scheme 1



Complex 2a was obtained from 2,8-decadiyne and aluminum trichloride as a dark-red solution in methylene chloride [9] Two structures - 2a and 2b - are, in principle, possible for this complex but only one is observed Comparison of the pmr shifts of methyl groups in 2 with those in the tetramethylcyclobutadiene complex 1[2] supports structure 2a[10] (see diagrams 1 and 2a for data) The pmr spectrum of complex 2a (1M solution in 1,1,2,2-tetrachloroethane)[14] was unchanged until ca 80° when broadening commenced The methyl resonances (δ = 2 13 and 2 21) coalesced at 92° At 120-130° the methylene resonance at 2 81 δ had disappeared and the upfield methylene signals were considerably broadened Cooling restored the original spectrum, although some decomposition had occurred We have reported[2] that aluminum trichloride migration in complex 1 causes coalescence of the methyl resonances at 2 29 and 2 40 δ below +20° This contrasts with the much higher coalescence temperature (92°) observed here for complex 2a and indicates that the rate of the degenerate isomerization of

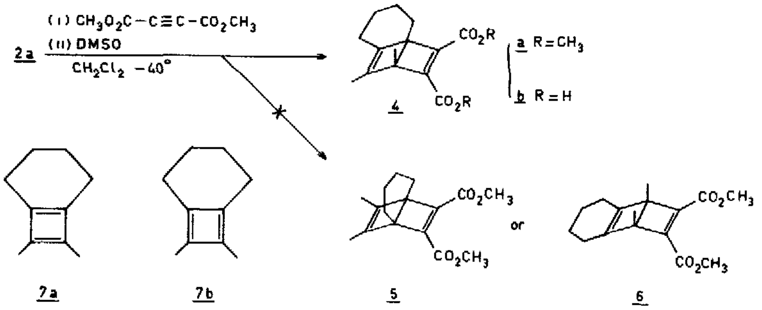
Scheme 2



complex 2a is much lower than that of complex 1[15] Degenerate isomerization of complex 1 occurs via the symmetrical transition state (or intermediate) 3 depicted in scheme 1, rather than by consecutive 1,2-shifts of aluminum trichloride.[2] In view of the preference shown by aluminum trichloride for methylene- rather than for methyl-substituted sites in complex 2, we suggest that the isomerisation route in scheme 2 is more probable for the latter complex and that the higher migration barrier may be the consequence of a more stable ground state

The syntheses of some Dewarbenzene derivatives based on complexes 1 and 2a are described below.

A methylene chloride solution of complex 2a, cooled to -40° and treated consecutively with dimethyl acetylenedicarboxylate (DMAD) and DMSO, yielded diester 4a. Neither of the isomeric diesters 5 or 6 was detected in the pmr of the crude product mixture.[18] The tetramethylene-substituted Dewarbenzene 4 was isolated, after hydrolysis, as the dicarboxylic acid 4b in 40% yield based on the starting decadiyne.[19]



No reaction was observed in the absence of DMSO when a similar solution of complex 2a and DMAD in methylene chloride was maintained at -40° in the pmr probe for the same reaction time (ca. 0.5 hr) We conclude that, at this temperature, DMSO is necessary to cause reaction between these species We therefore tentatively suggest that reaction occurs via the tetramethylenecyclobutadiene 7[20] which reacts with DMAD to give the Diels-Alder adduct 4a. The absence of 5 or 6 suggests that the double bonds of 7 are localised as in 7a. A rapid equilibrium between 7a and 7b cannot be excluded,[21] but it seems unlikely that 7a should be a better Diels-Alder diene than 7b in this case [22]

The above synthesis can be extended to construct, simultaneously, polymethylene bridges over both the 1,2 and 3,4 positions of Dewarbenzene derivatives;[23] however, an alternative method is required to bridge the 5,6 positions. Accordingly, we have synthesized the Dewarxylylene 8 by the route detailed in scheme 3.[24] Reaction of tetracyanoethylene (TCNE) with the Dewarxylylene 8 gave the expected Dewarbenzene adduct 9 in which the 5,6-bridge has been formed.[25]

These topics are currently under further investigation.

Acknowledgement.

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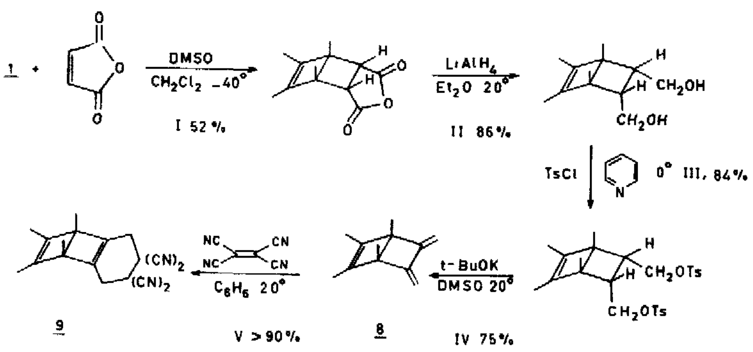
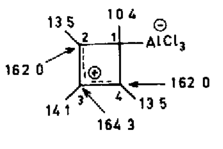
Scheme 3

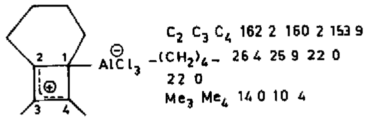


Notes and References.

1. C. Krüger, P.J. Roberts, Y.-H. Tsay, and J.B Koster, J Organometal Chem, 78, 69 (1974) and references cited
2. H. Hogeveen, H Jorritsma, P A Wade, F van Rantwijk, J.B Koster, J.J Prooi, A Sinnema, and H van Bekkum, Tetrahedron Letters, 3915 (1974)
3. W Schäfer and H Hellmann, Angew Chem, 79, 566 (1967)
4. J.B Koster, G.J Timmermans, and H van Bekkum, Synthesis, 139 (1971).
5. J H. Dopper, B. Greijdanus, and H Wynberg, J. Amer. Chem. Soc., 97, 216 (1975).
6. P.B.J. Driessen, D S B. Grace, H. Hogeveen, and H. Jorritsma unpublished results
7. See for a different route I J Landheer, W.H. de Wolf, and F Bickelhaupt, Tetrahedron Letters, 2813 (1974)
8. H. Hogeveen and P W Kwant, Accounts Chem Res, (1975), in press.
9. 2,8-Decadiyne (1 61 g, 12 mmol) in methylene chloride (6 ml) was added dropwise under a dry nitrogen atmosphere to a stirred mixture of aluminum trichloride (1.60 g, 12 mmol) and methylene chloride (20 ml) at -50°. The mixture was allowed to warm to $+5^{\circ}$ over 20 minutes, then was maintained at this temperature for a further 20 minutes
10. We have recorded the cmr spectra of 1[11] (at -20°) and of 2a (at -5°) in methylene chloride, shifts are recorded in ppm from TMS The chemical shifts of carbons in 2a have not yet been definitely assigned



1



2a

The C_1 resonances are absent[12] The chemical shifts of C_3 suggest some 2,4-interaction[13] as predicted from the molecular structure of 1[1]

11 The cmr spectrum of 1 was obtained by H Jorritsma of this laboratory

12 T D Westmoreland, Jr , N.S Bhacca, J D Wander, and M C Day, J Amer Chem Soc , 95, 2019 (1973)

13 G A Olah, P R Clifford, Y Halpern, and R G Johanson, J Amer. Chem Soc , 93, 4219 (1971), G A Olah, J S Staral, R J. Spear and G Liang, ibid , 97, 5489 (1975)

14 The spectrum of 2a is essentially unaltered by the replacement of methylene chloride with 1,1,2,2-tetrachloroethane as solvent

15 The extrapolated[2] value, ΔG_{365} = 17 5 kcal mol^{-1}, has been calculated for 1 ΔG_{365} = 19.3 kcal mol^{-1} was obtained in the case of complex 2a from the methyl coalescence temperature approximation formula $\Delta G = RT_c \ln\{\frac{\sigma k T_c \sqrt{2}}{\pi \Delta \nu h}\}$[16] The latter figure may contain a small error as this formula is only strictly applicable when the frequency separation of the coalescing signals is large compared with the line widths[16,17]

16 J A Pople, W.G Schneider, and H J Bernstein, "High-resolution Nuclear Magnetic Resonance", Chapter 10, Mc Graw-Hill, New York, 1959

17 A Allerhand, H S Gutowsky, J Jonas, and R A Meinzer, J Amer Chem Soc., 88, 3185 (1966)

18 We observe[6] an identical selectivity in the reaction of complex 2a with ethyl cyanoformate leading to substituted pyridines In the present case, 4a (5 + 6) ⩾ 92 8

19 Complex 2a (12 mmole) in methylene chloride (26 ml) at -40°, under an atmosphere of dry nitrogen, was treated with DMAD (1 71 g, 12 mmol) in methylene chloride (5 ml) followed by DMSO (1 87 g 24 mmol) in methylene chloride (1 3 volume ratio) Work-up and hydrolysis were as detailed in reference 4 except that the diacid was isolated by ether extraction of the acidified aqueous layer, rather than by filtration

20 Treatment of a methylene chloride solution of complex 2a with DMSO at -40° in the absence of DMAD gives a mixture of dimers ($C_{20}H_{28}$) of the cyclobutadiene 7

21 P. Reeves, T. Devon, and R Pettit, J Amer. Chem Soc , 91, 5890 (1969)

22. Synthesis and oxidative decomposition - in the presence of DMAD - of the iron tricarbonyl complex of 7 may clarify the nature of the intermediate in this reaction

23 P B J Driessen, and H Hogeveen, unpublished results

24 Following step IV, the reaction mixture was evaporated (20°, 0 1 mm) The product - condensed at -78° - was dissolved in ether, washed with water and dried Solvent evaporation left tetramethylDewarxylylene 8 as a pale-yellow oil pmr (CCl_4) δ 5.14 (s, 2H), 4 73 (s, 2H), 1 53 (s, 6H), 1 14 (s, 6H), mass spectrum M^+ = m/e 160

For steps II and III see R. Criegee, H Kristinsson, D Seebach, and F Zanker, Chem Ber , 98, 2331 (1965) Step IV was reported by F R Farr, and N L Bauld, J Amer. Chem Soc , 92, 6695 (1970) for the parent Dewarxylylene.

25. A mixture of Dewarxylylene 8 (0 16 g, 1 mmol) and TCNE (0 13 g, 1 mmol) in benzene (7 ml) was stirred under a nitrogen atmosphere for 46 hours at 20° Solvent evaporation and recrystallisation gave adduct 9 in 50% yield mp 140-142°, pmr ($CDCl_3$) δ 3.08 (broad s, 4H), 1 58 (s, 6H), 1 19 (s, 6H), mass spectrum M^+ = m/e 288, correct elemental analysis.