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REACTIONS OF $AlCl_3$ AND $AlBr_3$ σ-COMPLEXES OF CYCLOBUTADIENES *

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Summary

The useful reactivity of $AlCl_3$ and $AlBr_3$ σ-complexes of cyclobutadienes towards various reagents is demonstrated. In reactions with acetylenic derivatives (affording dewarbenzenes), nitriles (affording pyridines in the case of ethylcyanoformate) and sulfur dioxide, cycloadditions to liberated cyclobutadienes are possibly involved; in reactions with isocyanides a nucleophilic attack at the allylic moiety of the σ-complexes appears to take place. The reactivity differences between the tetramethyl- and the 3,4-dimethyl-1,2-tetramethylene-substituted complexes are pointed out. A novel route to dibromocyclobutene derivatives employing $AlBr_3$ σ-complexes of cyclobutadienes is presented.

Introduction

The present research efforts in this laboratory on $AlCl_3$ and $AlBr_3$ σ-complexes of cyclobutadienes deal mainly with the peralkyl-substituted derivatives I—VI, which are prepared, conveniently and in high yield, by reactions of 1 equiv. of $AlCl_3$ with 2 equiv. of 2-butyne (I), 1 equiv. of a diyne (II and III) or 1 equiv. of a cycloalkadiyne (IV—VI), respectively, at 0°C [1,2]. The X-ray structure determination of complex I [3] has unambiguously shown the species to be a dipolar ion containing a σ carbon—aluminum bond. Recent NMR spectroscopic investigations have demonstrated [1] that the rapid dynamic process which occurs in these complexes consists of intramolecular 1-2 shifts of the $AlCl_3$ group. It was found that the rate of migration of the $AlCl_3$ group in complexes I and III (the latter occurring as two structural isomers) is about 2000 times faster than that in complex II (which occurs as one structural isomer only).

Aluminum trihalide σ-complexes of cyclobutadienes exhibit a remarkable reactivity toward reagents of various types. In this publication we will confine ourselves mainly to the tetramethyl-complex I. The reactions which lead to

* This publication is dedicated to Professor H.C. Brown for his contributions to chemistry.

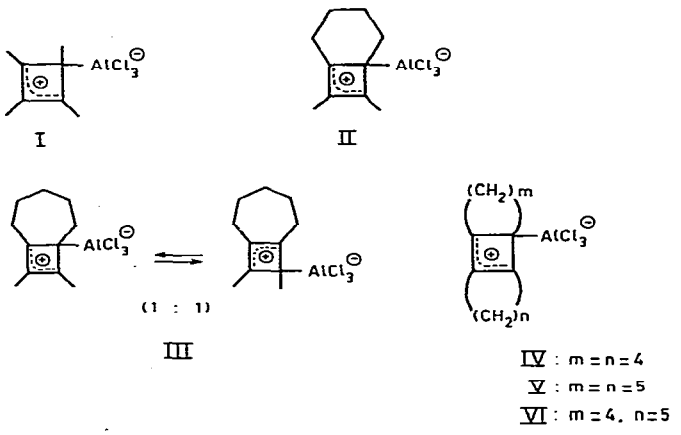


Fig. 1. $AlCl_3$ σ-complexes of cyclobutadienes I—VI.

dewarbenzene, pyridine and dibromocyclobutene derivatives will be described also for the related complex II. An important application of $AlCl_3$ σ-complexes of cyclobutadienes has been found in the cycloaddition of dienophiles to the species, possibly consisting of cyclobutadienes, which are formed in situ by removing the $AlCl_3$ group from the complexes. When acetylenic dienophiles are used, this reaction constitutes an effective synthetic route to various dewarbenzene derivatives [1,2,4]. The $AlCl_3$ group can be removed from the complexes simply by adding a base or, alternatively, by the dienophile itself. The latter condition is encountered also in reactions of complex I with, e.g., sulfur dioxide and nitriles. The reaction of complex I with isonitriles appears to constitute a different type of reaction: the $AlCl_3$ group is not removed from the complex, but instead nucleophilic attack of the isonitrile carbon atom at the allylic part of complex I takes place. Finally, the potential to prepare dibromocyclobutene derivatives via $AlBr_3$ σ-complexes of cyclobutadienes is pointed out. These dibromocyclobutene derivatives are useful precursors for the corresponding $Fe(CO)_3$—cyclobutadiene complexes.

Results and discussion

A. Reactions of complexes I and II with acetylenic dienophiles; synthesis of dewarbenzene derivatives

Attempts to isolate cyclobutadiene derivatives at room temperature have met with very limited success. Only a few cases, in which the easily occurring dimerization reaction is prevented by introduction of large substituents, have been reported [5]. However, methods for preparing stable precursors from which the reactive cyclobutadienes can be generated in situ, have been developed, the $Fe(CO)_3$ complex of the parent cyclobutadiene being a well-known example [6]. Oxidative decomposition of this complex presumably liberates the cyclobutadiene, which has been captured by numerous dienophiles [6]. Although several other $Fe(CO)_3$ complexes of this type have been prepared and used as precursors for the corresponding cyclobutadiene derivatives [6], attempts to use the tetramethyl-substituted $Fe(CO)_3$ complex as such have recently been reported to be

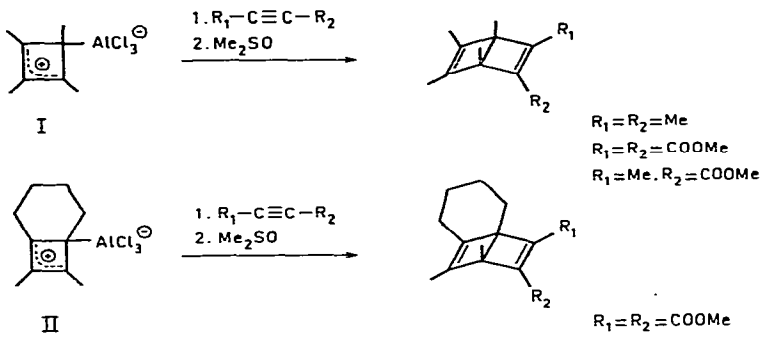


Fig. 2. Formation of dewarbenzene derivatives employing complexes I and II.

unsuccessful [7]. Oxidative decomposition of the latter complex in the presence of dienophiles did not afford the expected addition products, but instead products were obtained which indicated that the organic ligand of the original complex had been oxidized [7]. By using the $AlCl_3$ σ-complex of tetramethylcyclobutadiene I this difficulty does not arise. After removal of the $AlCl_3$ group, the tetramethyl cyclobutadiene which is assumed to be generated can be captured by several dienophiles as depicted for some of them, e.g., 2-butyne [4a], dimethyl acetylenedicarboxylate [2] and methyl tetrolate [4c], in Fig. 2. Attempts to perform the additions of acetylenic dienophiles in similar reactions employing complex II, were only successful in the case of dimethyl acetylenedicarboxylate [4b] (Fig. 2), and not with 2-butyne and methyl tetrolate. Reactions of the latter dienophiles with complex II are summarized in Table 1 together with those of complex I. Upon addition, of Me_2SO to the complexes I and II at —40°C, in the presence of 2-butyne, the main products were the dimers of the cyclobutadienes.

When a higher reaction temperature (15—35°C) was used, the dewarbenzene derivative also was formed, but only in the case of complex I. Using methyl tetrolate, reactions of the complexes I and II do proceed (without adding Me_2SO as base) at ca. 0°C (complex I) and 20°C (complex II), leading to the dewarbenzene derivative and decomposition products, respectively. When the reac-

TABLE 1

REACTION OF COMPLEXES I AND II WITH 2-BUTYNE AND METHYL TETROLATE [a]

	MeC≡CMe		MeOOCC≡CMe	
	Conditions	Main products [b]	Conditions	Main products [b]
I	—40°C, Me_2SO	B	—40°C, Me_2SO	B
I	15—35°C Me_2SO	A + B (ratio 4/3)	0°C	A
II	—40°C, Me_2SO	B	0°C, Me_2SO	B
II	15—35°C, Me_2SO	B + decomposition products	20°C	Decomposition products

[a] Addition of Me_2SO is indicated where necessary. [b] A = hexamethyldewarbenzene in the case of MeC≡CMe and the methyl ester of 1,3,4,5,6-pentamethyldewarbenzene-2-carboxylate in the case of MeOOCC≡CMe [4c]. B = dimer of tetramethylcyclobutadiene in the case of complex I [4a] and of 1,2-dimethyl-3,4-tetramethylenecyclobutadiene in the case of complex II [4b].

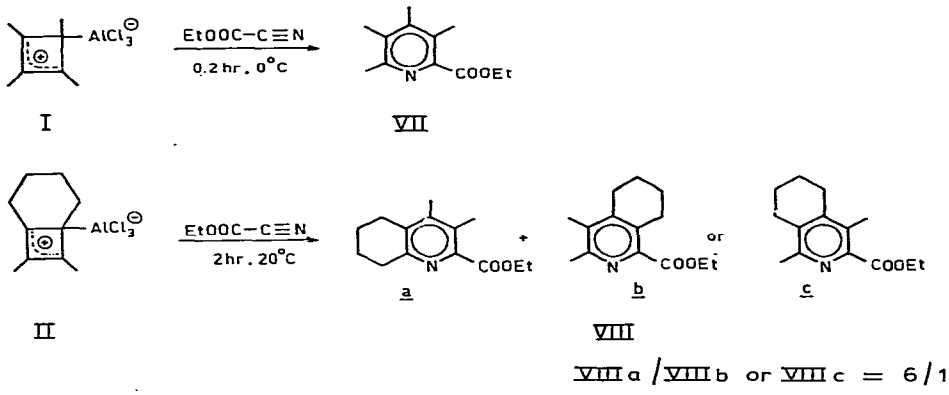


Fig. 3. Formation of pyridine derivatives employing complexes I and II.

tions were carried out at temperatures at which addition of a base is necessary to cause reaction (e.g. —40°C in the case of I, 0°C in the case of II), the dimers of the cyclobutadienes were formed. These observations suggest that removal of the $AlCl_3$ group from the complexes by methyl tetrolate itself constitutes a favorable situation for obtaining a Diels—Alder addition product, provided of course, that decomposition (as found in the case of complex II at 20°C) does not occur. For a further discussion concerning the observed difference in reactivity between the complexes I and II, see section F.

B. Reaction of complexes I and II with nitriles; synthesis of pyridine derivatives

Recently we reported that upon treating solutions of $AlCl_3$ σ-complexes of cyclobutadienes with a solution of ethyl cyanoformate, $AlCl_3$-complexed pyridine derivatives, e.g. VII and VIII, are formed [8]. Two mechanistic possibilities were envisaged for the formation of these pyridine derivatives, as depicted in Fig. 4 for the formation of VII. In mechanism 1, a Diels—Alder addition to the cyclobutadiene, liberated by the ethyl cyanoformate itself, is involved; in mechanism 2 a nucleophilic attack of the nitrogen atom of ethyl cyanoformate at the allylic part of complex I takes place. Based on the following two additional experiments of complex I with other nitriles, we prefer mechanism 1 for formation of VII. Upon treating a solution of complex I with a solution of acetonitrile at 0°C, a pyridine derivative was not formed but instead the dimer of tetramethylcyclobutadiene was isolated [8]. If the reaction of complex I with ethyl cyanoformate were to proceed via mechanism 2, one would expect an analogous reaction of complex I with acetonitrile as with ethyl cyanoformate because the positive charge in the intermediate iminocarbonium ion would be stabilized more effectively in the first case. In contrast to this and in accordance with mechanism 1, acetonitrile is not a sufficiently good dienophile to form a Diels—Alder adduct with the generated cyclobutadiene and as a consequence the latter dimerizes. In the second experiment, a reaction of complex I with acrylonitrile was performed *; instead of a pyridine derivative, which one would

* After acceptance of this manuscript, the same reaction was published by F. van Rantwijk, R.E. van der Stoel and H. van Bekkum, Tetrahedron, 34 (1978) 569.

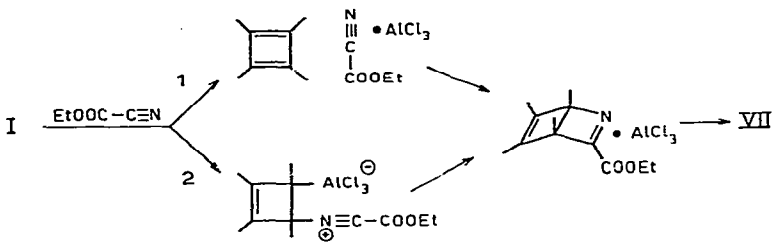


Fig. 4. Mechanistic possibilities for the formation of VII.

expect on basis of mechanism 2, a mixture of bicyclic cyanides IX was obtained. The formation of IX is in good agreement with mechanism 1 in which acrylonitrile both acts via the cyano function to generate the cyclobutadiene and via the activated carbon—carbon double bond in a Diels—Alder addition (Fig. 5).

Upon removing the $AlCl_3$ group from complex I in the presence of ethyl cyanoformate by adding a base at —40°C, at this temperature the reaction between complex I and ethyl cyanoformate does not yet proceed, not the expected pyridine derivative VII, but instead the dimer of tetramethylcyclobutadiene was formed. Apparently to obtain addition products with ethyl cyanoformate it is advantageous that the dienophile itself removes the $AlCl_3$ group from complex I. This reaction of complex I with ethyl cyanoformate proceeds to completion within 0.2 h at 0°C. For completion of the similar reaction of complex II, a reaction time of 2 h at 20°C is needed (Fig. 3). In the latter reaction the pyridine derivative VIIIa was formed as the major isomer. Possibly the $AlCl_3$ group is removed by the cyanide functionality immediately followed by (or even synchronous with) the Diels—Alder cycloaddition in such a manner that there is a preference for formation of a nitrogen—carbon bond involving the ring carbon atom of complex II to which the aluminum atom is attached.

Both the difference in reactivity between the complexes I and II as well as the apparent necessity that the dienophile (ethyl cyanoformate) itself removes the $AlCl_3$ group from complex I in order to obtain the cycloaddition product (pyridine derivative) were also encountered in the reactions of complexes I and II with methyl tetrolate (section A); for a further discussion, see section F.

C. Reaction of complexes I and I-$AlBr_3$ with isonitriles

Upon treating a solution of complex I with a solution of cyclohexyl isocyanide

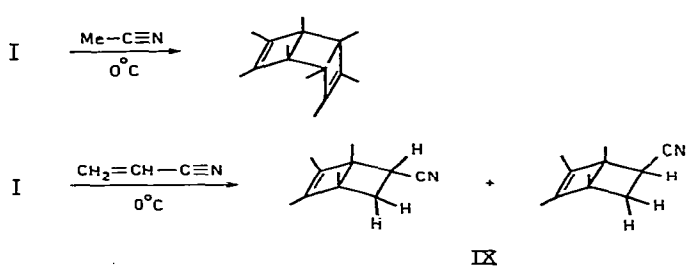


Fig. 5. Reactions of complex I with aceto- and acryl-nitrile.

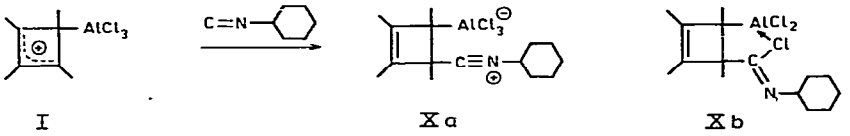


Fig. 6. Reaction of complex I with cyclohexyl isocyanide.

at —40°C, a new species (X) was produced which still possessed a carbon—aluminum bond (Fig. 6). Apparently, in contrast to the reactions with nitriles (section B), the isonitrile functionality did not remove the $AlCl_3$ group from the complex, but instead a nucleophilic attack at the allylic part of complex I took place. In the ^{13}C NMR spectrum of X in CH_2Cl_2 only three of the four resonances of the cyclobutene ring carbon atoms were observable, the missing resonance being ascribed to the carbon atom attached to the aluminum atom *. In order to assure that this missing resonance was not simply obscured by the intense absorption of the CH_2Cl_2 (resonating at δ 54.0 ppm) the ^{13}C NMR spectrum of the related species X-$AlBr_3$ in CH_2Br_2 (resonating at δ 21.6 ppm) was recorded as well. In this case also only three of the four resonances of cyclobutene ring carbon atoms were observable.

Concerning the nature of the carbon—nitrogen bond in X, the interpretations of the IR and ^{13}C NMR spectra were seemingly contradictory. The IR spectrum of X displayed a strong absorption band at 2325 cm^{-1}, characteristic of a $C{\equiv}N^+$ moiety [10] as present in structure Xa. In the ^{13}C NMR spectrum of X a resonance at low field (δ 219.4 ppm) was found, the only atom to which this absorption can be assigned being the carbon atom bonded to the nitrogen atom. A carbon atom of a $C{\equiv}N^+$ moiety is expected however, to absorb in a region about 100 ppm upfield from δ 219.4 ppm [10]; the carbon atom of the ClC=N moiety in Xb, in which the carbon—chlorine bond probably is polarised by the Cl→Al interaction, may account better for the observed low field resonance. It may, of course, be that both isomeric species Xa and Xb are present in solution. If Xa occurs as the minor isomer, its signals might not be observable in the ^{13}C NMR spectrum, either because of the low concentration or of a rapid (on the NMR time scale) interconversion of Xa and Xb. This minor isomer might still be observable in the IR spectrum due to the very intense $C{\equiv}N^+$ absorption and since interconversion of Xa and Xb would be slow on the IR time scale.

After addition of a solution of Me_2SO to a solution of X and subsequent aqueous work up, the amide derivative XI, occurring as only one isomer, was isolated; such a product is indeed expected upon hydrolysis of species X. A similar reaction of complex I with *p*-tolylsulfonylmethyl isocyanide, afforded the amide derivative XII (*cis* and *trans* isomers) (Fig. 7).

D. Reaction of complexes I and I-$AlBr_3$ with sulfur dioxide.

The addition of sulfur dioxide to dienes, yielding cyclic sulfones in a (2 + 4)

* A carbon atom directly attached to an aluminum atom will presumably not be observable under the prevailing conditions; for example, in complex I such a carbon atom signal is also absent in the ^{13}C NMR spectrum [1]. In case such a carbon atom signal is observed, it appears as a broadened peak or as a sextet with a characteristic $J(^{13}C—^{27}Al)$ coupling constant [9].

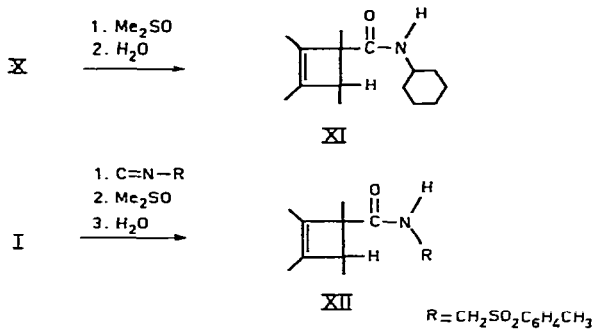
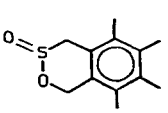


Fig. 7. Formation of XI and XII.

($n + \pi\pi$) type of cycloaddition, constitutes a well-documented reaction [11]. Recently Hogeveen and Heldeweg reported [12] that addition of sulfur dioxide to a bicyclobutane-bridged diene, whose extreme reactivity in Diels—Alder additions had previously been established [13] occurs under much milder conditions than those quoted above. The initially formed product (kinetic control) was not the expected five-membered ring sulfone, rather it was a six-membered ring sulfinate (XIII), which at much higher temperatures rearranged to the isomeric sulfone. On the basis of the idea that very reactive dienes might generally react at low temperatures with sulfur dioxide in a (2 + 4)($\pi + \pi\pi$) fashion under kinetic control rather than in a (2 + 4)($n + \pi\pi$) manner under thermodynamic control, we studied the reaction of sulfur dioxide with complexes I and I-$AlBr_3$, speculating on the in situ formation of reactive cyclobutadienes.

After introduction of a solution of 1—2 equiv. of sulfur dioxide to a solution of complex I at —30°C, the resonances of I in the ^1H NMR spectrum had disappeared and new signals due to XIV had formed. Compound XIV is possibly an $AlCl_3$-complexed sulfinate ester which might have been formed upon addition of sulfur dioxide to the liberated cyclobutadiene. It is not excluded however that XIV arises from a reaction of sulfur dioxide with the allylic part of complex I. Examples in which sulfur dioxide appears to react with carbonium ions have been reported [14a]. Yet another possibility may be that XIV arises from insertion of sulfur dioxide in the carbon aluminium bond of I and subsequent rearrangement to XIV [14b] (Fig. 8). Uncertainty persists, concerning the detailed structure of such a sulfinate-$AlCl_3$ complex. Based on data shown below, we suggest two alternative structures, an $AlCl_3$ complexed cyclic sulfinate structure XIVa and a non-cyclic aluminum sulfinate complex XIVb. NMR spectra (^{13}C and ^1H) of XIV (see Experimental) are in agreement with both structures. The ^{13}C NMR spectrum of XIV displayed the resonances of four cyclobutene ring carbon atoms, which probably excludes structures with a carbon—aluminum bond. The IR spectrum of XIV displayed a broad intense absorption at 980 cm^{-1}. Usually sulfinates absorb at 1100—1120 cm^{-1}, e.g. cyclic sulfinate XIII at 1105



XIII

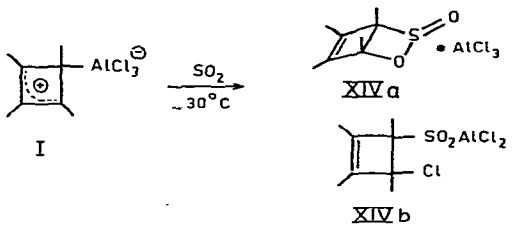


Fig. 8. Reaction of complex I with sulfur dioxide.

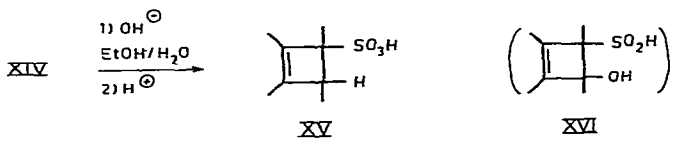


Fig. 9. Formation of XV.

cm^{-1} [12]. A 1/1 complex of XIII with $AlCl_3$ displays, a broad intense absorption at 980 cm^{-1}.

After basic hydrolysis, the sulfonic acid derivative XV (*cis* and *trans* isomers) was isolated. The reason that XV and not XVI was obtained is unclear, since both XIVa and XIVb are expected to yield XVI. Possibly, the presence of $AlCl_3$ alters the behavior of XIV upon hydrolysis (See Fig. 9).

The reaction of sulfur dioxide with the related complex I-$AlBr_3$ was also carried out, the result being similar to that described for I. However, in the ^{13}C NMR spectrum of XIV-$AlBr_3$ (see Experimental) most absorptions were accompanied by minor ones at slightly different positions, suggesting the occurrence of two different isomers. This may be related either to the stereochemical orientation at the $\geq$S=O moiety (*exo* or *endo*) in XIVa-$AlBr_3$, or to *cis—trans* isomerism in XIVb-$AlBr_3$.

E. Reactions of complexes I-$AlBr_3$ and II-$AlBr_3$ with excess sulfur dioxide; synthesis of dibromocyclobutene derivatives

Upon treating a solution of complex I-$AlBr_3$ with a large excess of sulfur dioxide at —30°C and subsequent warming to room temperature, the previously reported *cis*-dibromocyclobutene derivative XVII was formed [15]. It has been known for many years [16] that the $AlBr_3 \cdot SO_2$ complex loses bromine; possibly addition of the latter to cyclobutadiene generated in situ will lead to XVII. The $AlCl_3$ complex I does not show this behavior upon treatment with excess sulfur dioxide. Upon refluxing a solution of I in CH_2Cl_2, treated with an excess sulfur dioxide, in the presence of K_2CO_3, spectroscopic evidence (^1H NMR) was obtained that the dichlorocyclobutene derivative was formed in low yield; it decomposed however under the prevailing reaction conditions. A similar reaction of complex II-$AlBr_3$ with an excess of sulfur dioxide provided the dibromocyclobutene derivative XVIII in reasonable yield (Fig. 10). This reaction constitutes a novel route

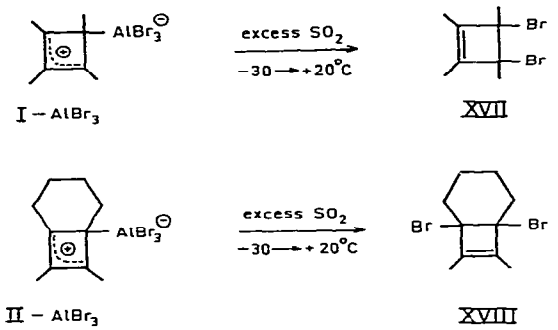


Fig. 10. Formation of dibromocyclobutene derivatives employing complexes I-$AlBr_3$ and II-$AlBr_3$

to the versatile dibromocyclobutene derivatives (from which, e.g., $Fe(CO)_3$ complexes of the corresponding cyclobutadienes can be prepared [6]). The expectation is that this method may be extended to other alkyl-substituted complexes as well. It contrast with the method developed by Criegee [15] for preparing dichlorotetramethylcyclobutene, because the latter method (BF_3-catalyzed addition of Cl_2) is restricted to 2-butyne only *.

F. Concluding remarks

In sections A and B it was described that in the reaction of complex I at ca. 0°C with either methyl tetrolate or ethyl cyanoformate, forming a dewarbenzene and a pyridine derivative, respectively, the $AlCl_3$ group is removed from the complex by the dienophile itself, the latter acting therefore in the first instance as base and subsequently (or synchronously) as dienophile. Furthermore, it was observed that in contrast to these reactions of complex I, those of complex II do not proceed at 0°C, but require higher temperatures and longer reaction times. A second point of interest is, as mentioned in the Introduction, that migration of the $AlCl_3$ group in complex II has been found to occur with a rate which is about 2000 times smaller than that in complex I. This suggests a relationship between the difference in the rate of migration and that of the reactivity in reactions with the dienophiles. If such a relation does exist, one would expect that the reactivity of complex III will resemble that of complex I rather than that of complex II (based on the rate of migration of the $AlCl_3$ group, see Introduction). Preliminary results indicate that this is indeed the case **. The differences between the complexes I and III vs. II can be interpreted in at least two ways. Firstly, the carbon—aluminum bond in the ground state of complex II may be stronger than that in the complexes I and III, causing the migration of the $AlCl_3$ group as well as the removal of the $AlCl_3$ group by the dienophilic base to occur less readily in II than in I and III. Alternatively, it may be that during the migration process, as well as upon removing the $AlCl_3$ group, the six-membered ring in

* We experienced indeed that only negative results are obtained when 2,8-decadiyne is used as starting material [18].

** It was shown by NMR spectroscopy that reactions of complex III with ethyl cyanoformate and methyl tetrolate do proceed at ca. 0°C, the reactions being complete within ca. 0.25 h, affording mixtures of dewarbenzene and pyridine derivatives, respectively.

complex II has to adopt a relatively unfavorable conformation, if compared to the ground state in which it will possess a chair-like conformation [1]. Such an unfavorable situation does not (or not to the same extent) occur during similar reactions of complexes I and III.

Experimental

General remarks

Melting points (uncorrected) were determined on a Reichert apparatus by the Kofler method. Elemental analyses were performed in the analytical section of our department. Mass spectra were obtained on a AEI MS 9 mass spectrometer and IR spectra on a Perkin—Elmer 177 spectrophotometer. 60 and 100 MHz ^{1}H NMR spectra were recorded on a Jeol C-60 HL and a Varian XL-100 spectrometer respectively, both equipped with variable temperature probes. ^{13}C NMR spectra were recorded using a Varian XL-100 spectrometer operating at 25.2 MHz, with the aid of Fourier Transform and were proton-noise decoupled. Proton-coupled ^{13}C NMR spectra were recorded in the gyrogate mode. $CDCl_3$ was used as the solvent (unless stated otherwise) and chemical shifts are given in ppm downfield from Me_4Si and δ 0 ppm. The solvents used were purified by common methods.

Preparation of 0.5 molar solutions of I(I-AlBr$_3$) and related complexes.

1(I-AlBr$_3$). To a stirred suspension (solution) of 5.3 mmol of $AlCl_3$ ($AlBr_3$) in 5 ml CH_2Cl_2 (CH_2Br_2) was added dropwise, under nitrogen at 0°C, a solution of 10 mmol of 2-butyne in 5 ml of CH_2Cl_2 (CH_2Br_2). After warming to room temperature the solutions were used as such. Similar procedures were employed for preparing solutions of complexes II—VI and II-$AlBr_3$; see ref. 1.

Reaction of complexes I and II with 2-butyne [4a], methyl tetrolate [4c], ethyl cyanoformate [8] and acetonitrile [8].

Ca. 1.0 molar solutions of complexes I or II in CH_2Cl_2 and ca. 1.0 molar solutions of the dienophiles (1—2 equiv) in CH_2Cl_2 were used. The reactions were performed under nitrogen at the temperatures indicated in the text. After addition of a solution of Me_2SO (excess) in CH_2Cl_2, the solutions were poured into water, and extracted with pentane. The organic layer was washed with water, dried over Na_2SO_4 and the organic solvent evaporated. ^{1}H NMR spectra of the reaction mixtures were taken before and after aqueous work up to identify the products.

Preparation of IX

To a stirred 0.5 molar solution of I (5 mmol) in CH_2Cl_2 was added dropwise, under a nitrogen atmosphere at 0°C, a 1.0 molar solution of acrylonitrile (6 mmol) (a ^{1}H NMR spectrum indicated that after addition I had disappeared) followed by 5 ml of a solution of Me_2SO (20%) in CH_2Cl_2. The solution was poured into water, extracted with pentane (100 ml) and the latter dried over Na_2SO_4. After evaporation of the solvent the organic residue was purified by column chromatography (Al_2O_3, pentane/ether (10%)), affording 0.52 g (3.25 mmol, 65%) of VII (oil, two isomers). Elemental analysis: found: C, 81.94; H, 9.24; N, 8.64. C_6H_7N calcd.: C, 81.94; H, 9.37; N, 8.68%. ^{1}H NMR (100 MHz) (major isomer): δ 1.01 (s, 3 H), 1.12 (s, 3 H), 1.59 (q, J 1.4 Hz, 3H), 1.73 (q,

J 1.4 Hz, 3H), (minor isomer): 1.08 (s, 3H), 1.20 (s, 3H), 1.53 ppm (s, 6H). The two isomers occur in a ratio of 4/1. The remaining absorptions of both isomers were found as complex multiplets at δ 1.8—2.3 and 2.5—2.9 ppm. ^{13}C NMR (major isomer): δ_c 141.6, 139.2, 121.0, 51.3, 47.9, 32.6 (t, *J* 140 Hz), 26.8 (d, *J* 140 Hz) and 14.7, 14.3, 9.0, 8.4 ppm (four q, *J* 125 Hz); (minor isomer): δ_c 143.7, 140.9, 121.9, 50.9, 48.7, 33.7, 27.1, 15.7, 11.9, 9.2 and 8.7 ppm. IR (neat). i.a. 2223 (—C≡N), 1678 cm^{-1} (—C=C—). High precision mass spectrum: M^+ found at *m/e* 161.117 (calcd. 161.120).

Preparation of X

To a stirred 0.5 molar solution of I (5 mmol) in CH_2Cl_2 was added dropwise, under nitrogen at —40°C, a 1.0 molar solution of cyclohexyl isocyanide (5 mmol) in CH_2Cl_2. ^1H NMR (CH_2Cl_2, —10°C, 60 MHz): δ 1.65 (s, 6H), 1.50 (s, 3H) and 1.25 (s, 3H), the absorptions due to the cyclohexyl ring protons at 1.0—2.5 ppm. ^{13}C NMR (CH_2Cl_2, —10°C): δ_c 219.4, 157.3, 127.2, 58.1 (d, *J* 150 Hz), 39.5, 30.6 (t, *J* 130 Hz), 24.6 (t, *J* 130 Hz), 23.1 (t, *J* 130 Hz) and 16.6, 15.4, 12.4, 4.8 (four q, *J* 125 Hz). IR (CH_2Cl_2): i.a.: 2325 (—C≡N⁺—), 1610 cm^{-1} ( , or alternatively  formed upon some hydrolysis of X).

Preparation of X-$AlBr_3$

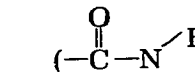
To a stirred 0.5 molar solution of I-$AlBr_3$ (5 mmol) in CH_2Br_2 was added dropwise, under nitrogen at —40°C, a 1.0 molar solution of cyclohexyl isocyanide (5 mmol) in CH_2Br_2. ^1H NMR (CH_2Br_2, —10°C, 60 MHz): δ 1.75 (s, 6H), 1.63 (s, 3H) and 1.33 (s, 3H), the absorption due to the cyclohexyl ring protons at 1.1—2.5 ppm. ^{13}C NMR (CH_2Br_2, —10°C): δ_c 204.0, 155.9, 127.4, 57.4 (d, *J* 155 Hz), 38.8, 29.9 (t, *J* 130 Hz) and 17.1, 15.3, 12.8, 10.3 ppm (four q, *J* 125 Hz). Three resonances of the cyclohexyl ring carbon atoms were obscured by the intense absorption of CH_2Br_2 at 21.6 ppm.

Preparation of XI

To a solution of X (5 mmol) in CH_2Cl_2, prepared as described above, was added 5 ml of a solution of Me_2SO (20%) in CH_2Cl_2. The solution was poured into water and extracted with pentane (100 ml). The organic layer was washed with water, dried over Na_2SO_4 and the solvent evaporated. The residue was crystallised 2 times (from pentane) affording 0.65 g (2.75 mmol, 55%) of XI (one isomer), m.p. 91—92°C. Elemental analysis: found C, 76.44; H, 10.82; N, 5.95. $C_{11}H_{14}AlCl_3N$ calcd.: C, 76.54; H, 10.71; N, 5.95%. ^1H NMR (60 MHz): δ 0.95 (d, *J* 7.3 Hz, 3H), 1.29 (s, 3H), 1.55 (s, 6H) and broad resonances from 0.6—2.5, at 3.6 (1H) and 5.2 ppm (1H). ^{13}C NMR: δ_c, 173.4, 143.8, 136.7, 54.6, 49.3 (d, *J* 140 Hz), 47.7 (d, *J* 140 Hz), 33.5 (t, *J* 130 Hz), 33.2 (t, *J* 130 Hz), 25.5 (t, *J* 130 Hz), 24.8 (t, *J* 130 Hz), and 19.8, 12.7, 11.3, 9.8 ppm (four q, *J* 125 Hz). IR (Nujol): i.a. 3280 (N—H), 1680 (—C=C—), 1640 and 1625 cm^{-1} (). Mass spectrum: M^+ peak at *m/e* 235.

Preparation of XII

To a 0.5 molar solution of I (5 mmol) in CH_2Cl_2 was added dropwise, under

nitrogen at —40°C, a 1.0 molar solution of *p*-tolylsulfonylmethyl isocyanide (5 mmol) in CH_2Cl_2 followed by 5 ml of a solution of Me_2SO (20%) in CH_2Cl_2. The solution was poured into water and extracted with ether; the organic layer was washed with water, dried on Na_2SO_4 and the solvent evaporated. The residue was crystallized three times (ether/pentane), affording 0.55 g (1.75 mmol, 35%) of XII, consisting of two isomers according to ^1H and ^{13}C spectra. Careful crystallization (ether/pentane) afforded an analytically pure sample of XII, consisting of only one isomer, which, according to elemental analysis, contained 1 mol of crystal water, m.p. 89—91°C. Elemental analysis: found: C, 60.27; H, 7.28; N, 4.11; S, 9.46. $C_{17}H_{23}SO_3N \cdot H_2O$ calcd.: C, 60.15; H, 7.42; N, 4.13; S, 9.45%. ^1H NMR (60 MHz) of the isomer used for elemental analysis: δ 0.82 (d, *J* 7.2 Hz, 3H) 1.12 (s, 3H), 1.55 (s, 6H), 2.15 (q, *J* 7.2 Hz, 1H), 2.38 (s, 3H), 4.1—5.35 (AB part of ABX multiplet, 2H), 6.30 (br, 1H), 7.28 and 7.74 ppm (AB system, J_{AB} 7.2 Hz, 4H); second isomer: 0.82 (d, *J* 7.2 Hz, 3H), 1.30 (s, 3H), 1.50 (s, 6H), 2.36 (q, *J* 7.2 Hz, 1H), 2.38 (s, 3H), 4.97 (s, 2H), 6.30 (br, 1H), 7.28 and 7.74 (AB system, J_{AB} 7.2 Hz, 4H). ^{13}C NMR (mixture of isomers): δ_c 173.9, 156.9, 145.0, 144.7, 139.0, 138.7, 136.0, 134.5, 134.0, 129.5, 129.2, 129.0, 128.7, 128.1, 73.6 (t, *J* 150 Hz), 59.9 (t, *J* 150 Hz), 57.9, 54.4, 49.8 (d, *J* 150 Hz), 49.1 (d, *J* 150 Hz), and 21.4, 21.1, 18.9, 13.1, 12.6, 11.1, 10.3, 9.8, 9.6 ppm (all q, *J* 125 Hz). IR (Nujol): i.a. 3330 (N—H), 1670 and 1628 (), 1145 and 1090 cm^{-1} (—SO_2—). Mass spectrum: M^+ peak at *m/e* 321.

Preparation of XIV

To a stirred 0.5 molar solution of I (5 mmol) in CH_2Cl_2 was added, under nitrogen at —30°C, a solution of 1 ml of liquid sulfur dioxide (ca. 10 mmol) in 2 ml CH_2Cl_2. After the addition the solution was warmed to room temperature and spectra recorded. ^1H NMR (CH_2Cl_2, 100 MHz): δ 1.55 (s, 3H), 1.70 (s, 6H), 1.76 ppm (s, 3H); ^{13}C NMR (CH_2Cl_2, —10°C): 150.6, 136.0, 79.4, 72.3 (these four resonances are considerably broadened (linewidth ca. 30 Hz) for yet unknown reasons), 24.4, 9.5, 8.4, 5.9 ppm (four q, *J* 125 Hz). IR (CH_2Cl_2): i.a. 980 cm^{-1}. The same ^1H NMR spectrum was obtained if 0.5 ml (5 mmol, 1 equiv.) of sulfur dioxide was used.

Preparation of XIV-$AlBr_3$

To a stirred 0.5 molar solution of I-$AlBr_3$ (5 mmol) in CH_2Br_2 was added, under nitrogen at —30°C, a solution of 1 ml of liquid sulfur dioxide (ca. 10 mmol) in 2 ml CH_2Br_2, prior to warming the solution to room temperature, the excess sulfur dioxide was removed in vacuo. ^1H NMR (CH_2Br_2, 100 MHz): 1.53 and 1.58 (ratio ca. 1/3, 3H), 1.70 (s, 3H), 1.78 (s, 3H), 1.90 ppm (s, 3H). ^{13}C NMR (CH_2Br_2, —10°C): 152.1, 135.3, 79.4, 65.7 and 27.0, 10.7, 9.9, 7.0 ppm (four q, *J* 125 Hz). Most resonances were accompanied by a smaller one at slightly different position, with a relative intensity of about one-third; IR (CH_2Br_2): i.a. 980 cm^{-1}.

Preparation of XV

A ca. 0.4 molar solution of XIV (5 mmol), obtained as described above, was

added dropwise, to a mechanically stirred solution of 5 g of KOH in 5 ml of water and 20 ml of ethanol. After pouring into 100 ml of water, the aqueous layer was acidified (pH 3—4) and extracted 2 times with CH_2Cl_2. The combined extracts were washed with an aqueous saturated NaCl solution, dried over Na_2SO_4 and the solvent evaporated, affording 0.48 g (2.5 mmol, 50%) of XV. The ^1H NMR spectrum indicated the presence of two isomers in a ratio of 2/3; crystallization (CH_2Cl_2/ether) afforded a mixture of two isomers in 1/1 ratio, m.p. 119—124°C. The following data have been obtained for this mixture. Elemental analysis; found: C, 50.33; H, 7.32; S, 16.73, $C_4H_6SO_3$ calcd.: C, 50.50; H, 7.42; S, 16.85%. ^1H NMR (100 MHz): δ 1.17 and 1.23 (2d, J 7.2 Hz, 6H), 1.57 and 1.61 (s2, 6H), 1.86 and 1.96 (2m, 12H), 2.67 (q, J 7.2 Hz, 2H), 3.70 and 3.85 ppm (2s, 2H). ^{13}C NMR: δ_c 146.2, 145.3, 128.9, 128.2, 89.2, 88.1, 47.9 (d, J 138 Hz), 46.6 (d, J 130 Hz) and 16.6, 14.7 (2X), 14.2, 13.6, 11.2 and 7.0 ppm (five q, J 128 Hz). IR (Nujol): i.a. 3380 (—OH), 1662 (—C=C—), 1260, 1150 and 1080 cm^{-1} (—SO_3H). Mass spectrum: the M^+ peak at m/e 190 was absent, peaks at m/e 173, 157, 141 and 125 were observed, which correspond to the $(M - OH)^+$, $(M - O_2H)^+$, $(M - O_3H)^+$ and $(M - SO_2H)^+$ fragments, respectively

Preparation of XVII

To a mechanically stirred 0.5 molar solution of I-$AlBr_3$ (5 mmol) in CH_2Br_2 was added, under nitrogen at —30°C, a solution of 5 ml of liquid sulfur dioxide in 5 ml CH_2Br_2. After warming to room temperature a solution was obtained, which, according to the ^1H NMR spectrum, contained the dibromocyclobutene derivative XVII. After addition of 5 ml of a solution of Me_2SO (20%) in $CHCl_2$ at 0°C, the solution was poured into water (100 ml) and extracted with pentane (200 ml). The organic layer was washed with water, dried over Na_2SO_4 and the solvent evaporated. The residue was crystallized (pentane) affording 0.56 g (1.9 mmol, 38%) of XVII, m.p. 61.5—62.5°C (lit. [15] 61—62°C). ^1H NMR (60 MHz): δ 1.64 (s, 6H), 2.00 ppm (s, 6H). Mass spectrum: the M^+ peak was absent, peaks at m/e 187 and 189 were observed, corresponding to the $(M - Br)^+$ fragments. IR (Nujol): i.a. 1685 cm^{-1} (—C=C—, lit. [15] 1684 cm^{-1}).

Preparation of XVIII

To a mechanically stirred 0.5 molar solution of II-$AlBr_3$ (5 mmol) in CH_2Br_2 was added, under nitrogen at —30°C, a solution of 5 ml of liquid sulfur dioxide in 5 ml CH_2Br_2. The ^1H NMR spectrum of the solution obtained after warming to room temperature displayed sharp resonances at 1.57 and 2.00 ppm in a ratio of 6/1, respectively, from which it is concluded that a mixture of isomeric dibromocyclobutene derivatives had been formed, existing for 75—86% as the depicted isomer XVIII. After work up as described for XVII and two crystallisations from pentane 0.55 g (1.75 mmol, 35%) of pure XVIII (1 isomer) was isolated. M.p. 88—89°C. Elemental analysis: found: C, 41.21; H, 5.02; Br, 53.61. $C_6H_{10}Br_2$ calcd.: C, 40.84; H, 4.80; Br, 54.36%. ^1H NMR (60 MHz): δ 1.59 (s, 6H), 1.50 (br, 4H), 2.12 ppm (br, 4H). ^{13}C NMR: δ_c 142.0, 75.1, 34.4 (tr, J 130 Hz), 18.0 (tr, J 130 Hz), 9.6 (q, J 128 Hz): IR (Nujol): i.a. 1688 cm^{-1} (—C=C—). Mass spectrum: the M^+ peak was absent, peaks at m/e 213 and 215 were observed, corresponding to the $(M - Br)^+$ fragments.

Preliminary results indicated that from XVIII, the corresponding cyclobuta-

diene $Fe(CO)_3$ complex can be prepared by the following procedure. A solution of 0.22 g (0.7 mmol) of XVIII in benzene at 45°C was treated with $Fe_2(CO)_9$ until gas evolution was not observed anymore. The solid material was removed by filtering through a glass filter and the solvent evaporated. Column chromatography (Al_2O_3, pentane) afforded 0.080 g (0.29 mmol, 41%) of the corresponding cyclobutadiene $Fe(CO)_3$ complex: ^1H NMR: 1.72 (s) and 1.7 (br) together 10 H, 2.15 (br, 4H); IR (Nujol): i.a. 2020 cm^{-1} (s) and 1940 cm^{-1} (vs); high precision mass spectrum: M^+ found at *m/e* 274.025 (calcd. 274.029).

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