trum) and the EPR spectrum was determined at high modulation. Similar curves were obtained for dilute solutions of 1-ethyl-4-carbomethoxypyridinyl (**1**) and the spin concentrations determined by comparing the weights of the area under the curves, assuming that the monopyridinyl radical had 100% of the spin expected for its concentration.

Solvent Transfers. An apparatus carrying at least two break-seals was used. In many cases, the acetonitrile was removed from **3**:MgI_2 and, after 20–40 min pumping, another solvent (e.g., tetrahydrofuran) distilled in from the line. The apparatus was sealed off, the spectrum of the solution determined under a variety of conditions (concentration, temperature), the apparatus reconnected to the line through the first break-seal, and the solvent removed and replaced with acetonitrile. The apparatus was again sealed off, the spectrum redetermined (usually a substantial recovery of the original **3**:MgI_2/CH_3CN spectrum was observed) and, in some cases, a titration with MB^{2+} carried out through the second break-seal. In the case of a transfer from acetonitrile to dioxane and back to acetonitrile, a 97% recovery of the original diradical was ascertained through titration.

Kinetic Studies. A reactant (halocarbon, halocarbon in acetonitrile, alcohol in acetonitrile) was distilled into a calibrated pipet after degassing elsewhere on the line. The apparatus was sealed off from the line, and the reagent introduced through a break-seal into a solution of known concentration of 1,1′-trimethylenebis(4-carbomethoxypyridinyl)magnesium iodide complex (**3**:MgI_2) in acetonitrile. After mixing, the reaction solution was transferred to an optical cell and the spectrum of the solution followed as a function of time. The temperature of the spectrophotometer compartment was controlled at 25 °C. The concentration of the second reactant (i.e., halocarbon or alcohol) was usually checked by gas chromatography after the completion of the reaction. Chromatography on a 20% di-*n*-butyl phthalate/Chromosorb column at 50 °C revealed no acetaldehyde in reactions carried out with ethanol, although control samples containing 10^{-4} M CH_3CHO were analyzed without difficulty.

Tetraethylammonium Ethylenediaminetetraacetate (TEA_4EDTA). Aqueous tetraethylammonium hydroxide (K & K Laboratories) was diluted to 0.1 M and an equivalent amount of ethylenediaminetetraacetic acid (B & A Allied Chemicals) added, yielding a solution of pH 10.5. The solution was diluted with ethanol to yield a 5×10^{-3} M $(TEA^+)_4EDTA^{4-}$ stock solution, always freshly prepared for each experiment. A sample of this solution (1.5 mL, 7.5 μmol) was placed in a tube carrying a break-seal and attached to the vacuum line. Solvent was removed and degassed benzene distilled in yielding a solution. Benzene was removed and the sequence repeated twice more with fresh benzene. The anhydrous salt was dissolved in acetonitrile from the line, the tube sealed off after freezing, and the solution introduced through the break-seal into a solution of **3**:MgI_2 (8.2 mL, 3.6×10^{-4} M, 2.95 μmol) in acetonitrile. The visible absorption of the complex decreased by 90% immediately. The solution was warmed at 58 °C until absorption appearing at 703 nm had reached a limit. The spectrum of the solution was like that of the diradical **3**:, and the yield 78% using λ_{max} 703 nm (ε 3800). Titration with MB^{2+} indicated 85% diradical yield from the original **3**:MgI_2. The product diradical was soluble in benzene, as is authentic diradical **3**: (see synthesis).

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$AlCl_3$ σ Complexes of Cyclobutadienes[1]

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Abstract: The permethyl substituted $AlCl_3$ σ complex of cyclobutadiene **1** (a cyclobutenyl cation) is involved in a dynamic process, which has been investigated by NMR spectroscopic techniques and found to consist predominantly, if not exclusively, of consecutive 1–2 shifts of the $AlCl_3$ group. The extension of complex **1** to those provided with one or two oligomethylene chains (**2**–**6**) is described; attention is paid to the different effect of a tetra- and a pentamethylene chain (**2** and **3**) on the rate of migration of the $AlCl_3$ group between the possible sites of the cyclobutenyl ring. Finally the chemical properties of the cyclobutadienes, generated from the complexes **2** and **3**, are described.

The interest in $AlCl_3$ σ complexes of cyclobutadienes can be viewed as resulting from two successful synthetic procedures, both employing 2-butyne and $AlCl_3$. A first procedure, developed by Schäfer, involved trimerization of 2-butyne, yielding hexamethyl(Dewar benzene), by catalytic action of $AlCl_3$ (5% by weight) for about 6 h at 35 °C.[2] In a second procedure, reported by Rosenberg and Eimutis, 2 equiv of 2-butyne and 1 equiv of $AlCl_3$ were used; after 18 h at room temperature a tetramerization product of 2-butyne, octamethyl-*syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene, was obtained.[3] In both cases an $AlCl_3$-bonded cyclobutadiene complex seemed to be the key intermediate. Later it was found by van Bekkum[4]

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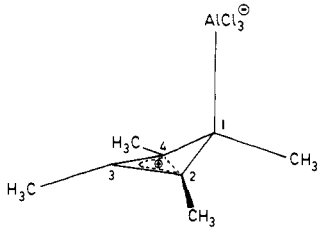


Figure 1. Representation of the spatial structure of complex **1**, according to the x-ray structure.[5a]

that this complex can be prepared as a stable species, using 2 equiv of 2-butyne and 1 equiv of $AlCl_3$. A structure determination by x-ray analysis could be undertaken,[5a] from which the nature of the species as being a σ-bonded $AlCl_3$ cyclobutadiene complex (cyclobutenyl cation) could be established. The short distance between carbon atoms 2 and 4 (1.775 Å) as well as the nonplanarity of species **1** (Figure 1) are features consistent with a considerable contribution of the homocyclopropenium type structure. The extent to which such homoaromatic interaction is occurring in cyclobutenyl cations, prepared in strongly acidic solutions, was examined by Olah and found to be strongly dependent on the nature of the substituents.[6] Examples of cyclobutenyl cations of mainly allylic as well as of mainly homocyclopropenium character were presented, methyl-substituted cyclobutenyl cations being intermediate between these two extremes. MINDO/3 calculations[7a] predicted the parent cyclobutenyl cation to be a puckered, fundamentally allylic species with a barrier to ring inversion of 9.8 kcal mol^{-1}, in excellent agreement with the experimental value of 8.4 kcal mol^{-1}.[6] Ab initio calculations, however, predicted a nearly flat allylic structure to be the most stable one. A satisfactory explanation for this result, contradicting the interpretation of spectroscopic observations, could not be given.[7b]

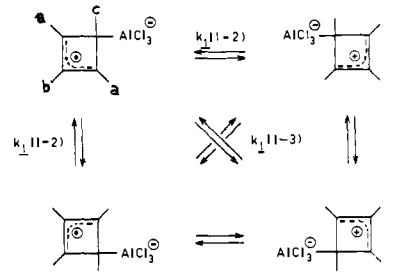
Besides exerting interesting properties, complex **1**, prepared easily and in high yield, is of synthetic interest as a precursor for the corresponding cyclobutadiene. Diels–Alder additions with several dienophiles, such as dimethyl acetylenedicarboxylate,[4] maleic anhydride,[1b] ethyl cyanoformate,[1c] perfluoro-2-butyne,[9] dicyanoacetylene,[9] acetylenecarboxylate derivatives,[8] and even the rather unreactive 2-butyne,[1a] have been performed already.

In this paper the extension of complex **1** to those provided with one or two oligomethylene chains is described. Attention is paid to the migratory aptitude of the $AlCl_3$ group in these complexes between the possible sites of the cyclobutenyl ring.

Finally, the properties of cyclobutadienes provided with a tetra- or a pentamethylene chain, as generated from the corresponding complexes **2** and **3**, will be described.

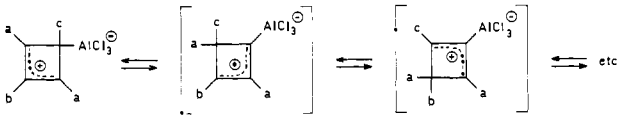
Migration of the $AlCl_3$ Group in 1. The ^1H NMR spectrum (60 MHz) of a 1.0 M solution of **1** in CH_2Cl_2, taken at −10 °C, consists of three sharp signals at 2.40, 2.24, and 1.32 ppm in an intensity ratio of 2:1:1, assigned to the methyl resonances a, b, and c, respectively (Scheme I). Upon warming the solution from −10 to 40 °C reversible line broadening is observed. At 20 °C the two low-field methyl resonances have collapsed into a broad singlet. When a 1.0 M solution of **1** in $CHCl_2CHCl_2$[10] is warmed to ca. 70 °C collapse of all signals to one broad singlet is observed, becoming a sharp singlet after further warming to 96 °C. Besides some decomposition, the original spectrum is restored after cooling. These observations indicate complex **1** to be involved in a dynamic process. The intramolecular nature of this dynamic process has been established as the rate of migration is hardly reduced upon diluting solutions of **1**.[1a] In principle two dynamic processes, completely different in nature, might be responsible for the described reversible

Scheme I. Degenerate Isomerizations in Complex **1** by Means of Migrations of the $AlCl_3$ Group



temperature dependency of the methyl resonances in the ^1H NMR spectrum of **1**: migration of the $AlCl_3$ group (Scheme I) or migrations of the methyl groups (Scheme II). Inspection of temperature-dependent ^{13}C NMR spectra (35, 55, and 75 °C) of **1** (1.5 M solution in $CHCl_2CHCl_2$) revealed that resonances of the methyl groups as well as resonances of the cyclobutenyl ring carbon atoms display reversible temperature dependency of the line shapes. In a mechanism in which 1–2 shifts of the methyl groups are involved (Scheme II), the cyclobutenyl ring carbon atoms will not interchange their positions and hence resonances of these should not display reversible temperature dependency in the ^{13}C NMR spectrum; this possibility can be excluded therefore. In a dynamic process occurring by means of migration of the $AlCl_3$ group (Scheme I), besides the methyl groups also the cyclobutenyl ring carbon atoms do interchange their positions and therefore the observed temperature dependency of the ^{13}C NMR spectrum of **1** is consistent with such a mechanism.

Scheme II. Degenerate Isomerizations in Complex **1** by Means of Migration of Methyl Groups



Concerning the detailed mechanism of the intramolecular migration in **1**, migrations of the $AlCl_3$ group by 1–2 as well as by 1–3 shifts (rate constants $k_1(1-2)$ and $k_1(1-3)$) have in principle to be envisaged. Occurrence of 1–3 shifts of the $AlCl_3$ group in **1** does a priori not seem to be unlikely for two reasons. Firstly, as can be seen from the detailed structure (Figure 1), the spatial arrangement of the $AlCl_3$ group seems to be rather favorable for such a migration. Secondly, due to the contribution of the homocyclopropenium structure, there is a considerable positive charge at carbon atom 3 and as a consequence a 1–3 shift of the $AlCl_3$ group would be feasible.[11]

The following two independent ^1H NMR experiments lead to the conclusion that mainly, if not exclusively, consecutive 1–2 shifts of the $AlCl_3$ group are operative.[12a] The extent to which 1–3 shifts of the $AlCl_3$ group may be operative is determined by the experimental error.

In the first ^1H NMR experiment this conclusion is based on a comparison of the line broadening of the methyl resonances a, b, and c of **1** (0.1 M solution in CD_2Cl_2) in the slow-exchange region. These can be correlated to the migration rate constants according to eq 1 (see Appendix 1).

$$\pi(\Delta_a - \Delta_a^0) = 2k_1(1\text{-}2)$$
$$\pi(\Delta_b - \Delta_b^0) = \pi(\Delta_c - \Delta_c^0) = 2k_1(1\text{-}2) + k_1(1\text{-}3) \quad (1)$$

Δ_a, Δ_b, and Δ_c were measured at 360 MHz. Owing to the relatively great frequency separation of the methyl resonances *a* and *b*, Δ_a and Δ_b could be measured up to temperatures of about 16 and 22 °C, respectively, without being disturbed by the interference of methyl resonances *a* and *b* (Table I). Ac-

Table I. Line Broadening of the Methyl Resonances a, b, and c in **1**[a]

Temp, °C	$\Delta_a - \Delta_a^0$, Hz	$\Delta_b - \Delta_b^0$, Hz	$\Delta_c - \Delta_c^0$, Hz
−3.5	0	0	0
13.0	3.1 ± 0.3	3.5 ± 0.3	3.5 ± 0.3
16.0	6.7 ± 0.3	6.7 ± 0.3	7.1 ± 0.3
22.0	14.1 ± 0.3		14.0 ± 0.3

[a] The line widths of the resonances at −3.5 °C, corrected for homogeneity changes, were taken as Δ_a^0, Δ_b^0, and Δ_c^0.

cording to eq 1, $k_1(1\text{-}3)$ is about zero and therefore migration of the $AlCl_3$ group should occur predominantly, if not exclusively, by means of 1-2 shifts of the $AlCl_3$ group.

For the second ^1H NMR experiment the methyl resonance c of **1** (1.0 M solution in CD_2Cl_2) was completely saturated. The extent to which this saturation label is spread over the two methyl resonances a and b, by means of the migration process, was measured. The phenomenon can be described by modified Bloch equations (see Appendix 3). Once the longitudinal relaxation times (T_{1a} and T_{1b}), which were measured as well (T_{1a} = 2.67 ± 0.04, T_{1b} = 2.91 ± 0.09 s at −12 °C), are known, it is possible to evaluate from these equations the probability of occurrence of 1-2 and 1-3 shifts, respectively, and hence $k_1(1\text{-}2)$ and $k_1(1\text{-}3)$ (Table II). This result confirms the conclusion already reached in the first ^1H NMR experiment: as compared to 1-2 shifts, occurrence of 1-3 shifts of the $AlCl_3$ group is in any case far less important, if occurring at all.

Rate constants for the migration process in **1** (0.3 M solution in $CHCl_2CHCl_2$) were calculated from the line shape of methyl resonance c in the slow-exchange region as well as from the line shape of the coalesced methyl resonances in the rapid-exchange region (see Appendix 2). Experimental activation parameters were obtained from an Eyring plot of the rate constants (Figure 2) ($\Delta H^{\ddagger}$ = 19.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ = +12 eu, $\Delta G^{\ddagger}$ (25 °C) = 15.7 kcal mol^{-1}) and from an Arrhenius plot of the rate constants: E_a = 20.3 kcal mol^{-1},[10] log A = 16.1 s^{-1}.

The positive entropy of activation suggests that upon reaching the transition state, the system obtains a higher degree of freedom. Possibly, the $AlCl_3$ group possesses a restricted rotational freedom in the ground state, owing to an interaction of a chlorine atom of the $AlCl_3$ group with the positively charged allylic part of the cyclobutenyl cation (Figure 1).[5b] Such a rotational restriction might vanish upon reaching the transition state during the migration process, because of the decreased charge separation. Or alternatively, it is conceivable that prior to the migration there is a dissociation of complex **1** into Cl^- and the cyclobutenyl aluminum dichloride species, with the latter showing the actual migration process by means of a pseudopericyclic mechanism.[12b]

So far the behavior of **1** obtained as a solution in $CH_2Cl_2(CHCl_2CHCl_2)$ from stoichiometric amounts of $AlCl_3$ and 2-butyne was described. The influence of either an excess of 2-butyne or an excess of $AlCl_3$ will be described below.

After 2-butyne (about 0.5 equiv based on **1**) was added to a 0.5 M solution of **1**, the ^1H NMR spectrum of **1** remained unchanged and 2-butyne appeared as a sharp singlet, even after line broadening of the methyl resonances of **1** had started.

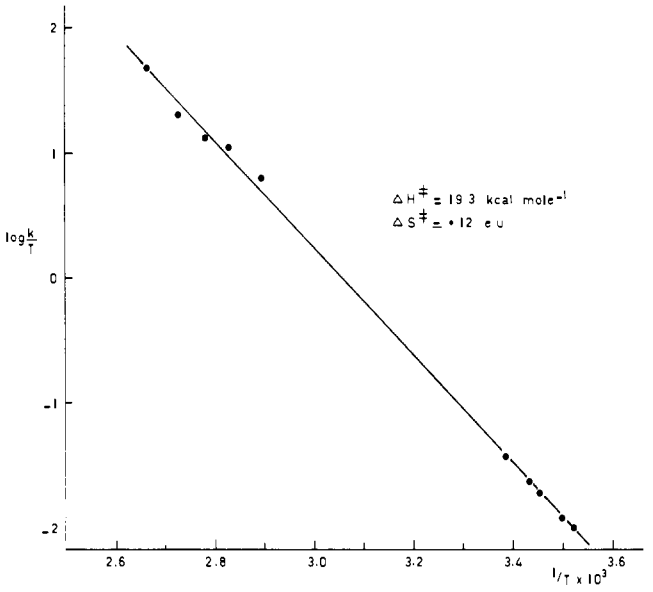


Figure 2. Eyring plot of the rate constants in the slow- as well as in the rapid-exchange region for the migration process of the $AlCl_3$ group in complex **1**.

From this observation involvement of 2-butyne in the migration process can be excluded. Exchange between free 2-butyne and that bonded in the $AlCl_3$ σ complex as cyclobutenyl cation might of course occur slowly on the NMR time scale. However, after 2-pentyne (about 0.5 equiv) was added to a solution of **1**, no indications were found for the existence of such an equilibrium in this very similar case: even after prolonged standing at room temperature (2 h), the spectrum of the solution remained unchanged.

Although $AlCl_3$ is only marginally soluble in CH_2Cl_2, homogeneous solutions are obtained when it is used up to about 100% excess in the formation of the complex.[13] From spectroscopic observations several indications were obtained that actually upon using an excess of $AlCl_3$ a second particle, probably the Al_2Cl_6 σ complex of tetramethylcyclobutadiene (**1a**),[14] is formed. In ^1H NMR spectra of diluted solutions this species displays the same type of signals as those of **1**, in the same relative intensities, at slightly different positions (Figure 3). The signals remain sharp after those of **1** have started to broaden. In ^1H NMR spectra (at 27 °C) of 0.1 M (based on the amount of 2-butyne used) solutions the resonances of species **1a** do increase upon using larger excesses of $AlCl_3$, at the cost of the already broadened resonances of **1**. For 0.5 M solutions, prepared by using varying excesses of $AlCl_3$, three resonances that appear to originate from only one type of σ complex are observed and they become less broadened upon increasing the excess $AlCl_3$. These observations indicate that an equilibrium between **1** and **1a** does exist and moreover that the rate of interconversion at 27 °C is, on the NMR time scale, rapid for 0.5 M solutions and slow for 0.1 M solutions. This concentration dependency suggests an intermolecular exchange of the excess $AlCl_3$ between the species, e.g., **1*** + **1a** ⇄ **1a*** + **1**, although an equilibrium of the type **1a** ⇆ **1** + $AlCl_3$ might play a role as well.

Table II. Values of the Rate Constant k_1 (1-2) and k_1 (1-3) Calculated on the Basis of the Double Resonance Experiments[a]

Temp, °C	$2M_z^a/M_0^a$	M_z^b/M_0^b	k_1 (1-2), s^{-1}	k_1 (1-3), s^{-1}
0.0	1.07 ± 0.03	0.66 ± 0.02	0.43 ± 0.07	−0.05 ± 0.1
−4.0	1.40 ± 0.03	0.88 ± 0.02	0.22 ± 0.04	−0.03 ± 0.06
−8.0	1.63 ± 0.03	0.96 ± 0.02	0.10 ± 0.02	−0.02 ± 0.02

[a] See Experimental Section and Appendix 3.

Table III. ^{13}C NMR Chemical Shifts of **1–6** in CH_2Cl_2[a]

	Cyclobutenyl ring C[c]	$-CH_3$	$-CH_2$
1[b]	162.0 (2X) 164.3	10.4 13.5 (2X) 14.1	
2a	153.9 160.2 162.2	10.4 14.0	22.0–26.4 (4s)
3a + 3b[b]	161.0 163.4 166.6 (2X) 167.2 171.9	9.8 13.3 13.5 14.2	23.9–29.5 (10s)
4	151.9 156.4 171.1		20.8–26.3 (8s)
5a	157.1 160.5 168.1		22.1–29.4 (9s)
6	167.3 169.7 171.0		24.3–30.0 (10s)

[a] Chemical shifts measured relative to internal CH_2Cl_2 (δ 53.16) and converted to internal Me_4Si at δ 0. [b] Taken at −10 °C. [c] Resonances due to $AlCl_3$-bonded carbons are absent.[16]

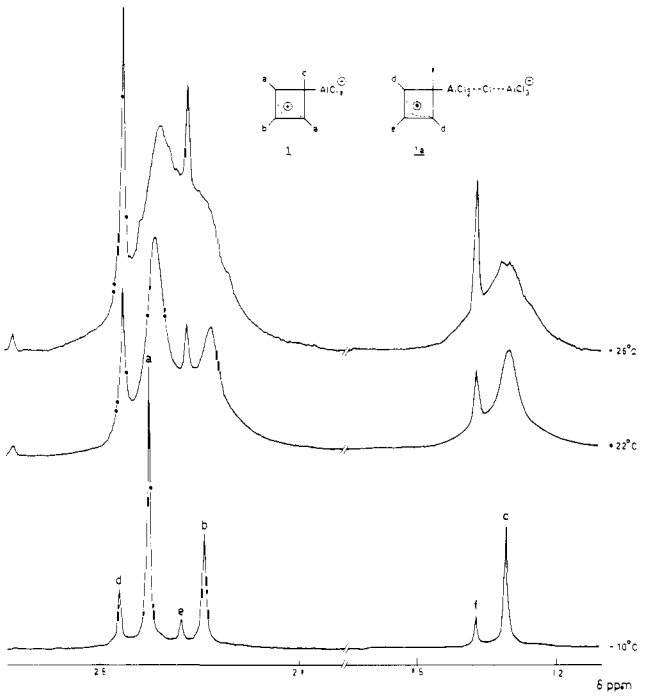
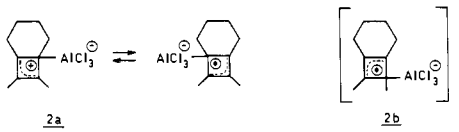


Figure 3. Variable temperature ^1H NMR spectra of a mixture of complexes **1** and **1a** (0.1 M in CD_2Cl_2) at 360 MHz.

In the ^1H NMR spectrum of a 0.1 M solution in $CHCl_2CHCl_2$, prepared by using a 50% excess of $AlCl_3$, the sharp resonances of **1a** remained unchanged up to 75 °C; at higher temperatures they disappeared irreversibly. As compared to the rate of migration of the $AlCl_3$ group in **1** at 75 °C, the rate of migration of the Al_2Cl_6 group in **1a** at 75 °C should be a factor of at least 2500 smaller, if occurring at all.

Complexes Provided with One Oligomethylene Chain. Investigations concerning $AlCl_3$ σ complexes of cyclobutadienes were extended to those provided with a tetra- (**2**) or a penta- (**3**) methylene chain. Solutions of **2** and **3** were prepared easily by adding CH_2Cl_2 solutions of the appropriate diynes to a suspension of 1 equiv of $AlCl_3$ in CH_2Cl_2. For both **2** and **3** two structures are in principle possible, differing in whether the $AlCl_3$ group is attached at a methylene- (a) or a methyl-substituted site (b) (Schemes III and IV).

Scheme III. Migration of the $AlCl_3$ Group in Complex **2**



In the ^1H NMR spectrum of a solution of **2** in CH_2Cl_2 only two sharp signals due to methyl resonances were found at 2.13 and 2.21 ppm. A methyl resonance due to a methyl group attached at the $AlCl_3$-bonded site is absent (compare **1**), indicating only structure **2a** to be present in a solution of **2.** In a solution of **3,** however, both possible structures **3a** and **3b** are present in a ratio of 1:1. This conclusion is based on the ^1H NMR spectrum of **3,** in which three different sharp signals at 2.3, 2.12, and 1.22 ppm, assigned to the methyl resonances a + c, b, and d, respectively, were found.

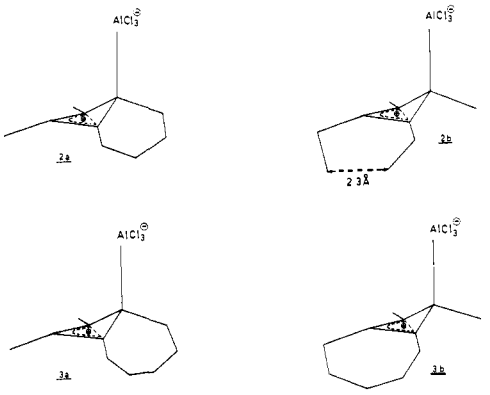
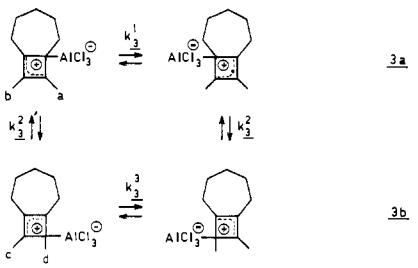


Figure 4. Representation of constructed Dreiding models of possible structures of **2** and **3**, based on the known cyclobutenyl skeleton of **1.**[5a]

Scheme IV. Migration of the $AlCl_3$ Group in Complex **3**



These conclusions were confirmed by ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum of **2** resonances due to only one isomer, whereas in that of **3** resonances due to two different isomers, were found (see Table III).

In order to get some insight into this remarkable difference between **2** and **3,** Dreiding models of possible structures were examined. For this, the cyclobutenyl skeleton of the tetramethyl-substituted complex **1,** known from the x-ray structure determination,[5a] was taken as the most ideal for the complexes **2** and **3** as well. The six- or seven-membered ring could be constructed without severely disturbing the cyclobutenyl skeleton in **2a, 3a,** and **3b,** not in **2b,** however (Figure 4). This explains the observed difference between **2** and **3.**

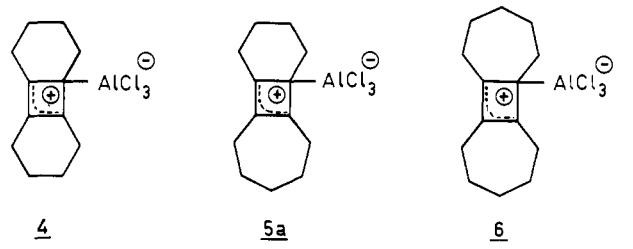
The ^1H NMR spectra of **2** and **3** show, similar to that of **1,** temperature dependency; reversible line broadening is observed in both cases, indicating the $AlCl_3$ group to be involved again in migration processes. We assume, as found for **1,** these migrations of the $AlCl_3$ group to occur by consecutive 1–2 shifts.

In the ^1H NMR spectrum (60 MHz) of a solution of **2** in $CHCl_2CHCl_2$[10] (1.0 M) the two methyl resonances of structure **2a** remained sharp singlets until ca. 80 °C. Further warming caused line broadening, whereas at 92 °C, coalescence of the two methyl resonances was observed. At 120–130 °C the methylene resonances at 2.8 ppm had disappeared and the upfield methylene resonances at 1.7 ppm were broadened considerably. The original spectrum was restored again after cooling, although some decomposition had occurred. The temperature at which the line broadening is beginning contrasts with that found for **1** (ca. 0 °C), e.g., the barrier for the migration of the $AlCl_3$ group in **2a** between the two possible sites is much higher as compared to the same barrier in **1.** Applying the coalescence temperature approximation formula[15] to the methyl resonances a value of $\Delta G_{2a}^{365} = 19.8$ kcal mol^{-1} was calculated whereas a value of $\Delta G_1^{365} = 14.9$ kcal mol^{-1} was obtained in the case of **1.** These values correspond to a rate difference (at 92 °C) of 2100 between the two processes. A higher migration barrier can be due to a more stable ground state and/or, perhaps more likely in this case, a less favorable transition state. The latter might be caused by unfavorable conformations of the six-membered ring during the migration process in **2a.** The transition state for **2a** requires the six-membered ring to adopt an eclipsed boatlike conformation, whereas the ground state dictates a chairlike form.

The temperature dependency of the ^1H NMR spectrum (60 MHz) of a solution of **3** in $CHCl_2CHCl_2$[10] (1.0 M) is completely different from that observed for **2** and shows more similarity with that observed for **1**: beginning of line broadening of all three methyl resonances at 4 °C, coalescence of the methyl resonances a + c and b at 35 °C,[17] and coalescence of all methyl resonances to one broad singlet at ca. 80 °C and finally at 104 °C to one sharp methyl resonance.[18] Further warming did not change the ^1H NMR spectrum anymore, whereas after cooling the original spectrum was restored, disregarding some decomposition. In this case three migration rate constants, k_3^1, k_3^2, and k_3^3, have to be envisaged (Scheme IV) which in principle can be different. Accurate measurement of the line broadening of the single methyl resonances b and d could only be accomplished over a rather small temperature range, owing to overlapping methylene resonances. We have not succeeded therefore in evaluating all three individual rate constants from line-broadening studies. Qualitatively, the great resemblance of the temperature dependency of the methyl resonances in **3** as compared to that of **1** suggests the subsequent migration of the $AlCl_3$ group between all the four possible sites to occur at rates of comparable magnitude (within a factor of 3) as found for **1.** For this necessarily k_3^2 and at least k_3^1 or k_3^3 should be of the same order of magnitude as k_1.[19]

Complexes Provided with Two Oligomethylene Chains. The method described for preparing $AlCl_3$ σ complexes of cyclobutadienes can be extended further to species provided with two oligomethylene chains. Solutions of **4, 5,** and **6** in CH_2Cl_2 were prepared by adding a CH_2Cl_2 solution of the appropriate cyclic diynes to a suspension of 1 equiv of $AlCl_3$ in CH_2Cl_2. Solutions of **4–6** in CH_2Cl_2 display broad absorptions in the ^1H NMR spectra due to methylene resonances and were characterized mainly by their ^{13}C NMR spectra (Table III). For **4** and **6** only one, in the case of **5** two, structures are possible in principle. In the ^{13}C NMR spectrum of **5** resonances due to only one isomer were found. These have been assigned to structure **5a** in view of the results obtained with **2** and **3.**

^{13}C NMR Spectra of 1–6. Chemical shifts of resonances of the positively charged cyclobutenyl ring carbon atoms in ^{13}C NMR spectra of cyclobutenyl cations have been used by Olah[6] for determining qualitatively the extent of the contribution of the homocyclopropenium type structure. In the case of **1** these resonances were found at only slightly different positions



4 5a 6

Figure 5. $AlCl_3$ σ complexes of cyclobutadienes provided with two oligo- (tetra- or penta-) methylene chains.

(Table III), consistent with a considerable contribution of such a type, as already unambiguously shown by the x-ray structure determination.[5a] We have not succeeded in assigning resonances to individual cyclobutenyl ring carbon atoms in the cases **2–6.** However, from the chemical shifts of these it seems to be likely that also in these cases, contributions of the homocyclopropenium type structures mentioned do exist.

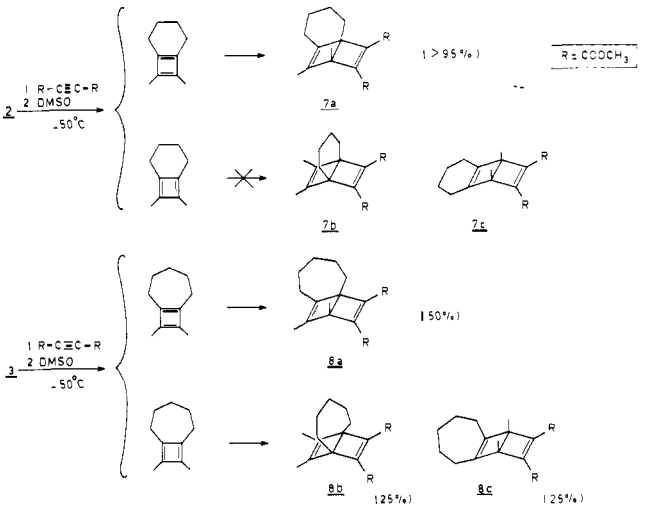
Information about possible differences in carbon–aluminum bonding in **1–6** might have been gathered from the chemical shifts of the relevant carbon resonances; unfortunately, however, these carbon resonances are absent in the ^{13}C NMR spectra of **1–6.**[16]

Complexes 2 and 3 as Cyclobutadiene Precursors. If $AlCl_3$ σ complexes of cyclobutadienes such as **2** and **3** are used as precursors for cyclobutadienes a complicating factor is encountered. The cyclobutadienes are assumed to exist in two valence isomeric forms[20] differing in the location of the double bonds. Upon a Diels–Alder addition these valence isomers will yield different products.

Reactions using **2** and **3** as cyclobutadiene precursors and dimethyl acetylenedicarboxylate (DMAD) as dienophile were performed by adding subsequently a CH_2Cl_2 solution of DMAD and a CH_2Cl_2 solution of Me_2SO to a solution of the complexes in CH_2Cl_2, at −50 °C. As reaction between DMAD and the complexes does not occur at −50 °C, Me_2SO is necessary to cause reaction, supporting the assumption that actually liberated cyclobutadienes are involved in Diels–Alder additions. The addition products were isolated as the diacids and examined by ^{13}C NMR spectroscopy.

In the ^{13}C NMR spectrum of **7** (R = COOH, see Experimental Section) only resonances due to isomer **7a** were found, whereas resonances that might be attributable to either **7b** or **7c** were absent. In the ^{13}C NMR spectrum of **8** (R = COOH, see Experimental Section), however, resonances due to all three possible isomers **8a, 8b,** and **8c** were present. From the intensity

Scheme V. Trapping of Cyclobutadienes Generated from Complexes 2 and 3 by Dimethyl Acetylenedicarboxylate



ratio of comparable resonances of the individual isomers it is concluded that the isomers occur in a ratio of **8a:8b:8c** = 2:1:1.

Differences in Diels–Alder reactivity between two valence isomeric forms[20] might exist owing to steric influence of the oligomethylene chain. However, one would expect the greatest influence for the **8b:8c** product ratio. As this ratio is 1:1 we feel that in these cases great differences in Diels–Alder reactivity between the valence isomers are not very likely. Hence the product ratios should reflect the equilibria, which are assumed to exist between a pair of valence isomeric cyclobutadienes.[20] In that case it has to be assumed that in the case of a six-membered ring, there is great preference for location of a double bond in the six-membered ring.

Experimental Section

Starting Materials. CH_2Cl_2 and $CHCl_2CHCl_2$ were distilled and $AlCl_3$ sublimed before use. 2,8-Decadiyne and 2,9-undecadiyne were prepared from commercially available 1,7-octadiyne and 1,8-nonadiyne, respectively, using a literature procedure.[23] Distillation afforded the diynes in at least 98% purity (GLC).

2-Butyne, 1,7-cyclododecadiyne, 1,7-cyclotridecadiyne, 1,8-cyclotetradecadiyne, and dimethyl acetylenedicarboxylate were commercially available products and used as such.

Spectroscopic Measurements. Proton magnetic resonance spectra at 60, 100, and 360 MHz were recorded using a JEOL C 60-HL, a Varian XL-100, and a Bruker HX-360 (operating in the Fourier transform mode) spectrometer, respectively, all provided with variable temperature probes. Natural abundance carbon-13 magnetic resonance spectra were obtained 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, recorded in the gyrogate mode, were used for the assignment of ^{13}C NMR chemical shifts. IR spectra were measured on a Perkin-Elmer 177 spectrophotometer and mass spectra were obtained on a AEI MS 9 mass spectrometer.

Preparation and ^1H NMR Spectra of the Complexes 1–6. A 1.0 M solution of **1** in CH_2Cl_2 was prepared by adding dropwise, under a dry nitrogen atmosphere, a solution of 0.54 g (10 mmol) of 2-butyne in 2.5 mL of CH_2Cl_2, to a magnetically stirred suspension of 0.75 g (5.5 mmol) of $AlCl_3$ in 2.5 mL of CH_2Cl_2 at 0 °C. The solution was warmed to room temperature and stirred for an additional 30 min. The same procedure was applied for preparing 0.3–1.5 M solutions of **1** in $CH_2Cl_2(CHCl_2CHCl_2)$ and solutions of the complex containing an excess of $AlCl_3$, starting with a 2-butyne solution in $CH_2Cl_2(CHCl_2CHCl_2)$ and a suspension of $AlCl_3$ in the same amount of $CH_2Cl_2(CHCl_2CHCl_2)$. 0.1 M solutions were obtained by diluting 1.0 M solutions of the complex. Concentrating and cooling to −40 °C of a solution of **1** in CH_2Cl_2 afforded **1** as a crystalline compound. The crystals were used for preparing solutions of **1** in CD_2Cl_2.

Solutions of the complexes **2, 3, 4, 5,** and **6** in $CH_2Cl_2(CHCl_2CHCl_2)$ were prepared analogously as described for **1**, by adding dropwise a solution of 5 mmol of 2,8-decadiyne, 2,9-undecadiyne, 1,7-cyclododecadiyne, 1,7-cyclotridecadiyne, or 1,8-cyclotetradecadiyne, respectively, in 2.5 mL of $CH_2Cl_2(CHCl_2CHCl_2)$ to a stirred suspension of 5.5 mmol of $AlCl_3$ in 2.5 mL of $CH_2Cl_2(CHCl_2CHCl_2)$. ^1H NMR spectra (CH_2Cl_2), chemical shifts relative to Me_4Si at δ 0: **1,** 1.32 (s, 3 H), 2.29 (s, 3 H), 2.4 (s, 6 H); **2,** 2.13 (s, 3 H), 2.21 (s, 3 H), 1.7 (br, ≈6 H), 2.8 (br, ≈2 H); **3,** 1.22 (s, 3 H), 2.12 (s, 3 H), 2.3 (s, 6 H), 1.7 (br, ≈14 H), 2.7 (br, ≈6 H); **4,** 1.75 (br, ≈10 H), 2.75 (br, ≈6 H); **5,** 1.75 (br, ≈12 H), 2.75 (br, ≈6 H); **6,** 1.8 (br, ≈14 H), 2.8 (br, ≈6 H).

Double Resonance Technique. The experiments were performed using a 1.0 M solution of **1** in CD_2Cl_2 and ^1H NMR spectra recorded using a 100-MHz instrument. To prevent saturation of the methyl resonances a and b these were observed using a weak rf field. To ensure complete saturation of the methyl resonance c a strong second rf field, irradiating at the position of c, was used. The peak heights of the methyl resonances a and b were used as a measure for M_z^a and M_z^b, respectively, and compared to the corresponding peak heights while irradiating with the second rf field 100 Hz upfield from the position of c (M_0^a and M_0^b). The double resonance experiments were performed at 0, −4, and −8 °C (see Table II). Values in the table are the mean of four scans.

Longitudinal relaxation times (T_{1a} and T_{1b}) were determined at −12 °C using a $|PD\text{-}180°\text{-}t_i\text{-}90°\text{-}AT\text{-}PD\text{-}90°\text{-}AT|_n$ pulse sequence,[22] acquisition time (AT) = 8 s, pulse delay (PD) = 10 s, t_i = 0–6 s, n = 9. The spectral width used was 500 Hz. As can be seen from formula 3 in Appendix 3, the recovery of the z magnetization of the methyl resonances a and b is governed by the longitudinal relaxation times T_{1a} and T_{1b}, respectively, if the second (and third) term is negligible as compared to the first term. At −12 °C this requirement was found to be fulfilled as the contributions of these terms, over the range for which values were used, was less than 4%. From the plots of ln ($M_0^a - M_z^a$) and ln ($M_0^b - M_z^b$) vs. t_i, the T_1's were obtained using the least-squares technique: T_{1a} = 2.67 ± 0.04, T_{1b} = 2.91 ± 0.09 s, the errors being the standard deviations. Probabilities of occurrence of a methyl group moving from site b to site a (λ_{ba}) and from site b to site c (λ_{bc}) and hence k_1 (1–2) and k_1 (1–3) were calculated using formula 4 (see Appendix 3, $dM_z^a/dt = 0$, $dM_z^b/dt = 0$). For all three temperatures at which double resonance experiments were performed the values for T_{1a} and T_{1b}, obtained at −12 °C, were used.

Calculation of Activation Parameters in 1. A 0.3 M solution of **1** in $CHCl_2CHCl_2$ was used and ^1H NMR spectra recorded at 100 MHz. The temperatures were measured accurately before and after recording the spectra, with the aid of a thermocouple. In the slow-exchange region the line width of methyl resonance c (Δ_c) was measured at temperatures from 0 to 23 °C, whereas the line width at 0 °C, corrected for homogeneity changes, was taken as the natural line width (Δ_c^0). In the rapid-exchange region the line width of the coalesced methyl resonances (Δ_j) was measured at temperatures from 72 to 102 °C and the weighted average of the line widths of the separate methyl resonances a, b, and c at 0 °C, corrected for homogeneity changes, was taken as Δ_j^0. ($\nu_a - \nu$), etc., were calculated from the spectrum at 0 °C, taking the weighted average of ν_a, ν_b, and ν_c as ν. Rate constants were calculated using the appropriate formulas (see Appendix 2) and activation parameters obtained from the Eyring plot (see text, Figure 2).

Complex 2 as Cyclobutadiene Precursor. To a mechanically stirred suspension of 1.5 g (11 mmol) of $AlCl_3$ in 10 mL of CH_2Cl_2 at 0 °C was added dropwise, under a nitrogen atmosphere, a solution of 1.34 g (10 mmol) of 2,8-decadiyne in 10 mL of CH_2Cl_2. The solution was warmed to room temperature and stirred for an additional 0.5 h. After cooling to −50 °C, 2.85 g (20 mmol) of dimethyl acetylenedicarboxylate in 5 mL of CH_2Cl_2 was added to the mechanically stirred solution under a nitrogen atmosphere, and subsequently 40 mL of a 5% solution of Me_2SO in CH_2Cl_2. The solution was warmed to room temperature and poured into ice–water (100 mL). The organic layer was separated and the aqueous layer extracted twice with 50 mL of ether. The combined organic layers were washed with water and dried over Na_2SO_4 and the organic solvents were removed. To the crude reaction mixture was added a solution of 6 g of KOH in 30 mL of CH_3OH and 30 mL of H_2O and stirred overnight at room temperature. The basic solution was diluted with 100 mL of H_2O, washed twice with 50 mL of ether, acidified to pH 4, and extracted three times with ether. The combined organic layers were washed with 25 mL of H_2O (slightly acidic) and dried over Na_2SO_4. After removal of the organic solvent 1.85 g (73%) of diacid was obtained: ^1H NMR spectrum (Me_2SO-d_6), chemical shifts relative to Me_4Si at δ 0 1.3 (s), 1.65 (s), 1.25 (br), 1.8 (br); IR (Nujol) 1680 cm^{-1} (–COOH). In the mass spectrum a peak corresponding to the $(M - H_2O)^+$ fragment was observed (the M^+ peak was absent). High precision mass spectrometry: found, 230.097; calcd, 230.094.

Complex 3 as Cyclobutadiene Precursor. Exactly the same procedure as described above for the reaction of complex **2** was employed in this case, starting from 1.48 g (10 mmol) of 2,9-undecadiyne. After hydrolysis 1.67 g (63%) of **8** was obtained. ^1H NMR spectrum (Me_2SO-d_6), chemical shifts relative to Me_4Si at δ 0: 1.3 (s), 1.65 (s), 1.45 (br), 1.85 (br); IR (Nujol) 1690 cm^{-1} (–COOH). In the mass spectrum a peak corresponding to the $(M - H_2O)^+$ fragment was observed (the M^+ peak was absent). High-precision mass spectrometry: found, 244.113; calcd, 244.110.

Crystallizations from hexane/ether mixtures afforded a sample containing mainly **8b** and a sample containing mainly **8c.**

^{13}C NMR Spectra of the Diacids. ^{13}C NMR spectra were recorded using the crude diacids **7** and **8.** With the aid of ^{13}C NMR spectra of the purified samples containing mainly **8b** or **8c,** the remaining resonances found for the diacid mixture could be assigned to isomer **8a.** The product ratio was determined using the intensity ratio of bridgehead carbon resonances, affording **8a:8b:8c** = 2:1:1.

Table IV. ^{13}C NMR Spectra of Diacids in Me_2SO-d_6[a]

	Olefin C	Bridgehead C	C(OOH)	$-CH_2$	$-CH_3$
7a	137.0 143.9 151.5 151.8	54.4 57.7	164.1 164.5	22.7-25.9	10.2 11.0
8a	142.7 152.7	61.4	164.3	26.4-30.9	11.5
8b	148.1 152.8	54.9	164.3	26.4-30.9	10.1
8c	142.3 147.1 151.4[b]	55.3 59.8	164.8[b]	26.4-30.9	10.1 11.5

[a] Chemical shifts measured relaive to internal Me_2SO-d_6 (δ 39.56) and converted to internal Me_4Si at δ 0. [b] The lacking resonance probably coincides with similar resonances of **8a**, **8b**, or **8c**.

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Appendix 1

The following expression can be applied in the slow-exchange approximation.[15]

$$\pi(\Delta_j - \Delta_j{}^0) = \sum_{k \neq j} \tau_{jk}{}^{-1} \left(= \sum_{k \neq j} k_{jk}\right)$$

$(k_{jk} =)\ \tau_{jk}{}^{-1}$ = probability per second of a methyl group at site j moving to site k
Δ_j = observed line width of the methyl resonance j
$\Delta_j{}^0$ = observed line width of the methyl resonance j in the absence of exchange

In the case of complex **1** one obtains

$$\pi(\Delta_a - \Delta_a{}^0) = k_{ab} + k_{ac} = 2k_1(1\text{-}2)$$
$$\pi(\Delta_b - \Delta_b{}^0) = k_{ba} + k_{bc} = 2k_1(1\text{-}2) + k_1(1\text{-}3)$$
$$\pi(\Delta_c - \Delta_c{}^0) = k_{ca} + k_{cb} = 2k_1(1\text{-}2) + k_1(1\text{-}3)$$

Appendix 2

In the slow-exchange region the expression $\pi(\Delta_c - \Delta_c{}^0) = 2k_1(1\text{-}2)$ (Appendix 1, $k_1(1\text{-}3) = 0$) was used. Applying the rapid-exchange approximation to the general Bloch equation[15] the following expression was derived for this particular case.

$$\Delta_j - \Delta_j{}^0 = -2\pi\tau_{ba}V$$
$$V = (\nu_a - \nu)(\nu_b - \nu) + (\nu_b - \nu)(\nu_c - \nu) + (\nu_a - \nu)(\nu_c - \nu)$$

Δ_j = observed line width of the coalesced methyl resonances
$\Delta_j{}^0$ = observed line width of the coalesced methyl resonances in the case τ_{ab} is infinitely small
$(\nu_a - \nu)$ etc. = frequency separation between methyl resonance a etc. in the absence of chemical exchange and the coalesced methyl resonances
$\tau_{ba}{}^{-1}$ = probability per second of a methyl group at site b moving to site a. $(=2k_1(1\text{-}2))$

Appendix 3

Taking into account chemical exchange processes the following general expressions can be applied.[21]

$$\frac{dM_z{}^k}{dt} = \frac{M_0{}^k}{T_{1k}} - \frac{M_z{}^k}{\tau_{1k}} + \sum_{j \neq k} \lambda_{jk} M_z{}^j \quad (1)$$

$$\sum_j \lambda_{kj} M_0{}^k = \sum_j \lambda_{jk} M_0{}^j$$

$$\frac{1}{\tau_{1k}} = \frac{1}{T_{1k}} + \frac{1}{\tau_k}$$

$$\frac{1}{\tau_k} = \sum_{j \neq k} \lambda_{kj}$$

$M_z{}^k$ = z magnetization at site k
$M_0{}^k$ = z magnetization at site k under equilibrium conditions
T_{1k} = longitudinal relaxation time of a methyl group at site k
τ_{1k} = lifetime of a spin state at site k
τ_k = lifetime of a methyl group at site k
λ_{jk} = probability per second of a methyl group at site j to be transferred to site k

In the case of **1** applied to the methyl groups at sites a and b one obtains

$$\frac{dM_z{}^a}{dt} = \frac{M_0{}^a}{T_{1a}} - \frac{M_z{}^a}{\tau_{1a}} + \lambda_{ba} M_z{}^b + \lambda_{ca} M_z{}^c$$
$$\frac{dM_z{}^b}{dt} = \frac{M_0{}^b}{T_{1b}} - \frac{M_z{}^b}{\tau_{1b}} + \lambda_{ab} M_z{}^b + \lambda_{ac} M_z{}^c \quad (2)$$

$$\frac{1}{\tau_{1a}} = \frac{1}{\tau_a} + \frac{1}{T_{1a}}, \quad \frac{1}{\tau_{1b}} = \frac{1}{\tau_b} + \frac{1}{T_{1b}}$$

$$\frac{1}{\tau_a} = \lambda_{ab} + \lambda_{ac}, \quad \frac{1}{\tau_b} = \lambda_{ba} + \lambda_{bc}$$

$$\left.\begin{aligned}(\lambda_{ab} + \lambda_{ac}) M_0{}^a &= \lambda_{ba} M_0{}^b + \lambda_{ca} M_0{}^0 \\ M_0{}^a &= M_0{}^b + M_0{}^c\end{aligned}\right\} \lambda_{ba} = 2\lambda_{ab}$$

From symmetry considerations $\lambda_{ab} = \lambda_{ac}$, $\lambda_{ba} = \lambda_{ca}$. Then for eq 2 can be written

$$\frac{dM_z{}^a}{dt} = \frac{1}{T_{1a}}(M_0{}^a - M_z{}^a) - \lambda_{ba}(M_z{}^a - M_z{}^b - M_z{}^c)$$
$$\frac{dM_z{}^b}{dt} = \frac{1}{T_{1b}}(M_0{}^b - M_z{}^b) - \lambda_{ba}\left(M_z{}^b - \frac{1}{2}M_z{}^a\right) - \lambda_{bc}(M_z{}^b - M_z{}^c) \quad (3)$$

In the case of the double resonance experiment $M_z{}^c = 0$ and one obtains

$$\frac{dM_z{}^a}{dt} = \frac{1}{T_{1a}}(M_0{}^a - M_z{}^a) - \lambda_{ba}(M_z{}^a - M_z{}^b)$$
$$\frac{dM_z{}^b}{dt} = \frac{1}{T_{1b}}(M_0{}^b - M_z{}^b) - \lambda_{ba}\left(M_z{}^b - \frac{1}{2}M_z{}^a\right) - \lambda_{bc}M_z{}^b \quad (4)$$

in which

$$\lambda_{ba} = 2k_1(1\text{-}2)$$
$$\lambda_{bc} = k_1(1\text{-}3)$$

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Radical Brominations of Some Chloroalkanes. Evidence for Anchimeric Assistance by Neighboring Chlorine[1]

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Abstract: In contrast to the rate-retarding effect of a chloro substituent on hydrogen abstraction at a secondary position by bromine atom, a chloro substituent facilitates the reaction at a vicinal teritiary position. This assistance by neighboring chlorine has been demonstrated by both intra- and intermolecular competitive radical brominations. For example, 1-chloro-2,3-dimethylbutane undergoes bromination (32 °C) at the 2 position about seven times faster than at the 3 position, and that rate enhancement is enough to make the overall rate for the substrate about 2.23 times that for 2,3-dimethylbutane. The dependence of the participation of neighboring halogen in the hydrogen abstraction reactions on the identity of the halogen and on the classification (primary, secondary, tertiary) of the reaction site is rationalized in terms of substantial polar contributions to the structure (and energy) of the radical transition states.

Enhancement of ionic substitution reactions by various neighboring groups has been extensively documented,[3] and evidence for similar effects of neighboring bromine on radical reactions has been reported by various investigators.[4] We report here selectivity and other kinetic data which reveal assistance by neighboring chlorine in hydrogen abstraction reactions.

In free-radical processes, a chloro substituent retards hydrogen abstraction at vicinal secondary positions relative to more remote ones; this effect has been taken to be a manifestation of normal electron withdrawal by halogen,[5,6] and an effect other than retardation has required explanation. High vicinal selectivity in brominations of alkyl bromides, stereoselectivity, and 1,2 rearrangements of a bromo substituent during chlorinations of selected alkyl bromides have been rationalized in terms of bromine-bridged radicals.[4] For a while, the vicinal selectivity was attributed, not to the kinetic effect of neighboring bromine, as first suggested,[6] but to a thermodynamic effect brought about by reversal of the hydrogen-abstraction reaction (i.e., $R\cdot + HBr \rightarrow RH + Br\cdot$).[7] Extensive investigations by different research groups[8] have set aside that challenge, however, and have shown that attack at a secondary position vicinal to a neighboring bormine is indeed kinetically favored over attack at more remote secondary positions during radical brominations.

Since a chloro substituent retards hydrogen abstraction at vicinal secondary positions relative to more remote ones, the kinetic assistance by a bromo substituent seems to require significant participation by neighboring bromine in the transition state, which presumably takes place because of the favorable energy associated with a bridged intermediate.

Kinetic assistance by neighboring bromine is now well documented,[6,8] but reports of such assistance by neighboring chlorine are scanty.[9] In addition to an early report of portions

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