

data in ref 8b, we note that $[\text{ArCO}_2\text{H}]^+ / [\text{ArCO}_2\text{H}_2]^+$ drops from 0.16 in hexyl benzoate to 0.008 in the hexyl ester of TMA; in the respective *n*-hexadecyl esters, the values are 0.083 (benzoate) and 0.004 (TMA). Neglecting *n* and *o* introduces an error of less than 1% to the amount of hydrogen abstraction by the anhydride group inferred from the *m/e* 194/(192 + 193) ion ratio.

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stants for hydrogen abstraction from the triplet states of benzophenones substituted in the para position with long hydrocarbon chains. The experiments, at room temperature in CCl_4 , were simulated with the totally planar conformation of aromatic rings and carboxyl groups. The results indicate that the distance separating the remote functional group from the point of attachment of the chain is not important in determining the validity of the calculations.

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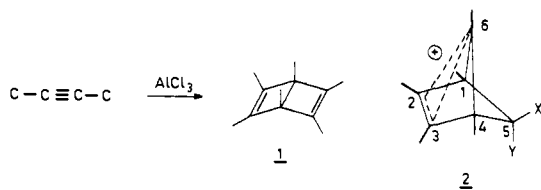
Electrophilic Additions to Hexamethyl(Dewar benzene) and Subsequent Cationic Rearrangements¹

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Abstract: Reactions of hexamethyl(Dewar benzene) (**1**) with HCl , Cl_2 , and Br_2 are reported, as well as the reaction of hexamethyl(Dewar benzene) epoxide (**15**) with HCl . It is shown that **1** is protonated exclusively (or nearly so) on the endo side. The resulting carbonium ion is not observed; it immediately undergoes intramolecular rearrangement. At low temperature bicyclo[2.1.1]hexenyl cations **2a** and **2b** are formed. At higher temperatures these convert to the bicyclo[3.1.0]hexenyl cation **7b**, which in turn gives cyclopentadienyl cation **9**. Finally, **9** is isomerized to the relatively stable hexamethylbenzenium ion **11**. At all stages in this sequence the ions can be trapped providing covalent products. The reactions of **1** with Cl_2 and Br_2 and the reaction of **15** with HCl all give bicyclo[2.1.1]hexenyl cations analogous to **2b**. These can be observed spectrally and in some cases can be trapped. They rearrange to give cyclopentadienyl cations analogous to **9**. These cations then give rise to various reaction products.

In 1966 it was discovered that 2-butyne could be trimerized, thus providing a simple synthetic route to hexamethyl(Dewar benzene) (**1**).² Numerous studies employing **1** have



been reported. In particular a number of electrophilic additions to **1** have been examined; they afford synthetic routes to a large number of strained cyclic compounds and also involve interesting mechanistic problems.^{3,4}

One would predict electrophilic attack upon **1** to occur preferentially on its endo side due to the greater concentration of electron density on the endo face of the molecule.⁵ However, exo attack might well be preferred from steric considerations. In fact hexamethyl(Dewar benzene) reacts with a few electrophilic reagents at the exo side,⁴ so that it must be concluded that the electronic factor does not always determine the direction of attack. Unambiguous examples of endo attack were not presented until just recently^{1a,6} because previous work on this subject dealt with the intermediacy of 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations (**2**). Various endo- and exo-5-methyl isomers of **2** have been shown to undergo rapid interconversion, thus destroying any information about the orientation of the initial attack.⁷

The reaction of **1** with chlorosulfonyl isocyanate provides

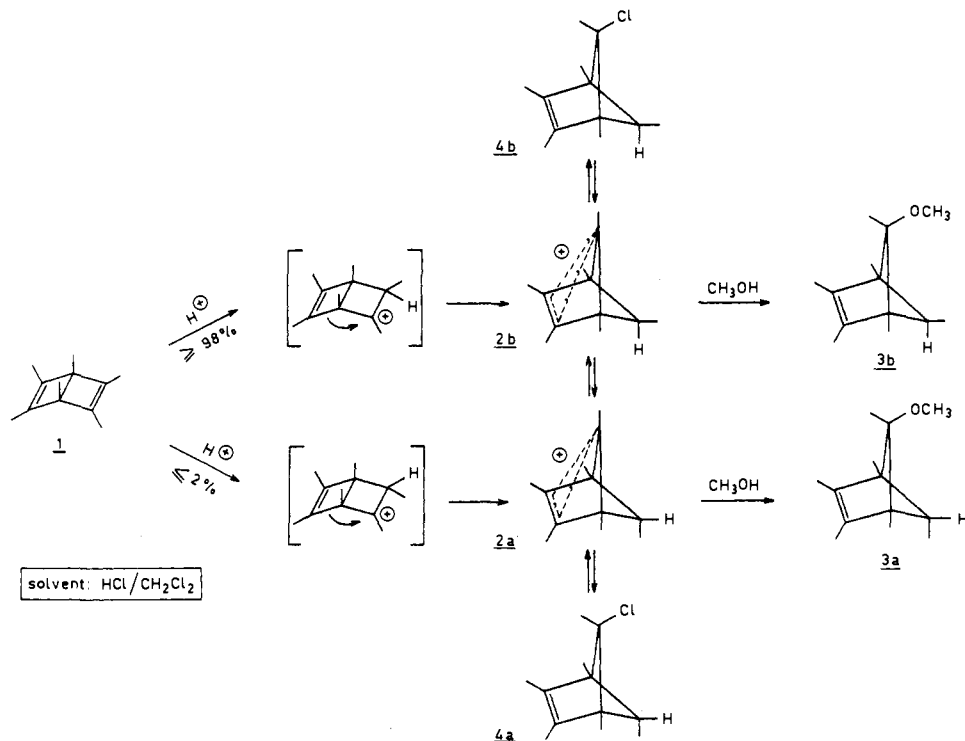
an example of the problems involved in assigning the stereochemistry of the initial attack of an electrophile. From the exo-exo methyl stereochemistry of the bicyclo[3.1.0]hexenyl product, it was concluded that the initial attack occurred from the endo side.⁵ Performing the reaction at -70° , however, yielded a bicyclo[2.1.1]hexenyl product.⁸ This suggests that the reaction at higher temperature to give [3.1.0] structures proceeds *via* [2.1.1] intermediates (a phenomenon that will be discussed in more detail below). Therefore conclusions about the direction of the initial attack cannot be safely made on the basis of the stereochemistry of [3.1.0] products. Such a conclusion would be valid only if it were established that the exo-endo relationship of the [3.1.0] product was unchanged from that of the first-formed [2.1.1] ion.

Discussion

Endo Attack on 1 by Acids. The exo 5-H and endo 5-H ions **2a** and **2b** were previously prepared by reaction of **1** with strong acid (HF-BF_3 , $\text{FHSO}_3\text{-SbF}_5$).⁷ It is also possible to do this using the more weakly acidic system⁹ $\text{HCl-CH}_2\text{Cl}_2$ (1:2 v/v) (Scheme I). At temperatures between -50 and -100° , the pmr spectrum of these ions is the same in either the more strongly acidic solutions or in $\text{HCl-CH}_2\text{Cl}_2$, a 3:1 equilibrium mixture, respectively, of ions **2a** and **2b**. Quenching of such a mixture in $\text{HCl-CH}_2\text{Cl}_2$ with sodium methoxide in methanol gives the ethers **3a** and **3b** in a 3:1 ratio. These too are identical with the products obtained on quenching a more strongly acidic solution.^{7d}

The amount of HCl was decreased in a subsequent experiment at -80° to twice that of **1**. Not only the ions **2a** and

Scheme I



2b (3:1 ratio) appeared under these conditions but also chloride **4a**. On prolonged reaction at -80° , and also quickly at -60° , chloride **4a** was formed at the expense of **2a** and **2b**. The assignment of structure **4a** depends on the pmr spectrum and a quenching experiment in which a solution of **4a** afforded the known ether **3a** when added to sodium methoxide and methanol at -85° .^{7d} On addition of more HCl to a solution of **4a** at -80° the ions **2a** and **2b** (3:1 ratio) were again formed. This indicates the important role that the concentration of HCl plays in determining which products are obtained from low temperature reactions of HCl-CH₂Cl₂ with hexamethyl(Dewar benzene). Unfortunately not enough is known about this behavior.

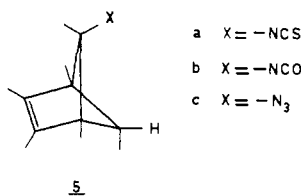
Reaction of equimolar amounts of HCl and **1** at -85° provided, under the conditions described in the experimental section, a mixture of **4a** and **4b**. Compound **4b** rapidly disappeared to give **4a**. The structure of **4b** was assigned on the basis of the pmr spectrum and a quenching experiment in which a mixture of **4a** and **4b** afforded a mixture of the ethers **3a** and **3b**.^{7d} In experiments where only 0.5 equiv of HCl was treated with **1** in methylene chloride at -95° , the pmr spectra of the reaction mixture taken at -90° indicated that, besides starting material, the chlorides **4a** and **4b** were present in a 3:10 ratio. The solutions were stable for 1 hr under these conditions. Conversion of **4b** into **4a** was observed on warming to -60° . Quenching of these solutions with sodium methoxide in methanol at low temperatures afforded starting material and the ethers **3a** and **3b**. The ether ratios varied between 10:1 and 10:7.

Why do the ratios of chlorides and ethers differ so much? To answer this question one has to take into account that the interconversion of the ions **2a** and **2b** is rapid even at low temperatures (e.g., $k = 1.4 \text{ sec}^{-1}$ at -46°).^{7b,c} From the equilibrium ratio of 3:1, it appears that **2a** is thermodynamically more stable than **2b**. This difference in stability is greatly enhanced in the case of chlorides **4a** and **4b**, perhaps due to steric crowding of the chlorine and the methyl group in **4b**. On this basis the conversion of the chloride **4b** into **4a** can readily be explained; **4b** ionizes (more rapidly when the HCl concentration is higher) to ion **2b**, which exists in equilibrium with **2a**. Subsequent recombination with chloride

anion will give **4a** as well as **4b**, a partial conversion of **4b** to **4a** being the result. The situation when a **4b**-rich mixture is quenched is analogous. Again ionization of the chloride takes place, but, before reaction of the ions with methoxide anion occurs, the interconversion of the ions changes the **2b:2a** ratio in favor of **2a**. This effect is enhanced by the reaction rate of **2b** with methoxide ion, which should certainly be lower than the reaction rate of **2a**. Partial steric blocking of the incoming anion by the methyl group in **2b** must occur.

The observation that, in reactions of hexamethyl(Dewar benzene) with stoichiometric amounts or less of HCl at temperatures of -80° (or lower), the thermodynamically least stable chloride **4b** is predominantly formed has two implications. First, the endo 5-H ion **2b** must be formed predominantly in the rearrangement of protonated hexamethyl(Dewar benzene). Second, the reaction of the chloride anion with **2b** under these conditions is faster than the interconversion to **2a**. This means that conclusions about the initial proton attack can be safely drawn from the stereochemistry of the [2.1.1] product. In an optimized reaction a solution of **1** in vinyl chloride was treated at -115° with 0.5 equiv of HCl. Now the pmr spectrum of the reaction mixture taken at -105° indicated that the endo 5-H chloride **4b** only is formed. The exo 5-H chloride **4a** could not be detected by pmr and is therefore present in less than 2%. When one assumes that no interconversion occurs before rearrangement to the [2.1.1]hexenyl cation **2b**, then protonation of hexamethyl(Dewar benzene) must occur to the extent of at least 98% from the endo side.

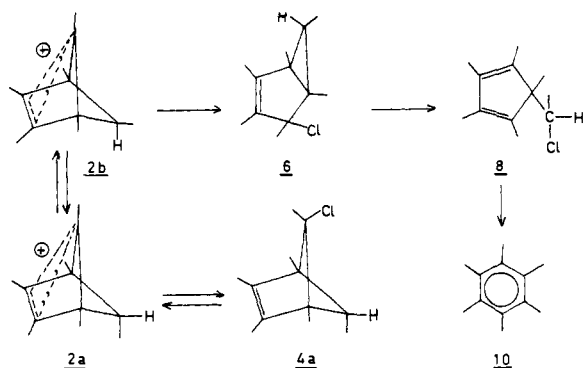
Attempts were now made to trap ions **2a** and **2b** with various nucleophiles. Reactions of **1** with a large excess of HCl were performed at -80° in the presence of sodium thiocyanate, sodium cyanate, and sodium azide, respectively. After neutralization and work-up, the different exo 6-substituted 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenes (**5a-c**) were isolated. Repeating the experiment with sodium azide at -150° in vinyl chloride and at a much lower HCl concentration did not yield the endo 5-H isomer of **5c**. Besides much starting material only **5c** was found. It appears in this experiment that heterogeneous reaction with sodium



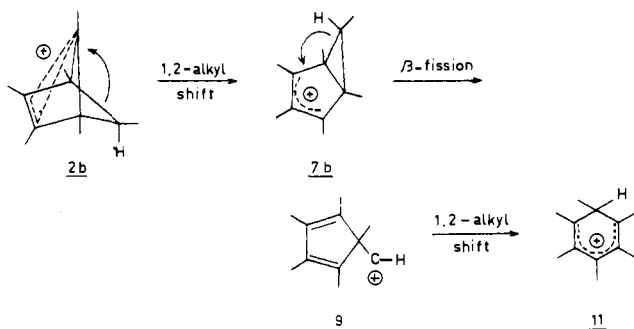
azide is slow. The lifetime of the intermediate [2.1.1] ions **2a** and **2b** is then so long that isomerization, giving rise to only exo 5-H compounds, is complete. This conclusion is in accordance with the one drawn from reaction of **1** with 2 equiv of HCl. In that case complete isomerization to the exo 5-H chloride **4a** is also favored by increased lifetime of the ions **2a** and **2b**, there due to the presence of HCl.

Cationic Rearrangements of Ions 2a and 2b. Intramolecular rearrangements following protonation of hexamethyl-(Dewar benzene) have been intensively studied and a number of products have been reported.^{10,11} On the basis of these products a number of mechanisms have also been proposed.^{5,7,11} These rearrangements occur at room temperature or lower, so that they apparently involve low activation barriers. Also, an easy pathway must be available to the product with the lowest energy—hexamethylbenzene. The reactions of **1** with HCl reveal many details concerning these cationic rearrangements. In the above experiments information about the initial attack was obtained because the high reaction rate with chloride anion compared favorably with the rearrangement rate of **2b** to **2a**. Thus **2b** is trapped as a chloride. This trapping phenomenon also provides information about the subsequent rearrangements. Again chlorides are observed, which are indicative of the presence of rearranged precursor cations.

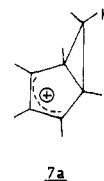
The experiment in which **1** was treated with 2 equiv of HCl at -80° (*vide supra*) was continued with warming of the reaction mixture. The ions **2a** and **2b** were converted to the chloride **4a** on warming to -60° . At this temperature



pmr also indicated the presence of 4-chloro-1,2,3,4,5,6-hexamethylbicyclo[3.1.0]hex-2-ene (**6**), the structural assignment of which will be discussed below. The presence of this compound indicates the intermediacy of the corresponding ion **7b**. Since the isomerization of the ions **7a** and **7b** can be

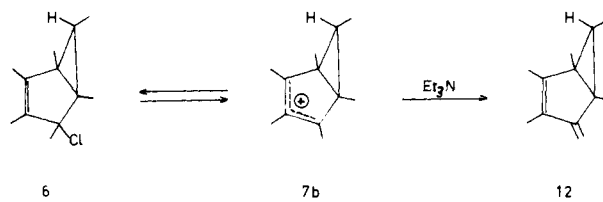


excluded at this temperature,¹² it must be concluded that **7b** is formed from the endo 5-H isomer **2b**. Mechanistically this means that **4a** ionizes under the experimental conditions and that the ion **2a** formed in this way interconverts to **2b**. Thus one has to assume that the reaction of **2b** to **7b** is much faster than the reaction of **2a** to **7a**.

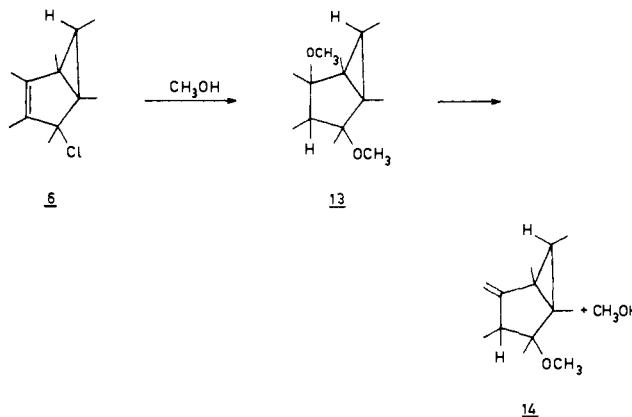


The next rearrangement is seen on warming to 0° . The chloride **8**^{10c,11} is now observed. Presumably **6** ionizes to **7b**, which undergoes a β -fission to give ion **9**. Carbonium ion **9** is then trapped by chloride anion. On treating **8** at room temperature with more HCl, hexamethylbenzene (**10**) is formed. This can be readily rationalized as resulting from ionization of **8** to **9** followed by a 1,2-alkyl shift to give **11**, which then deprotonates yielding **10**.

This pmr experiment forms a key in understanding the sequence of intramolecular rearrangements following the protonation of hexamethyl(Dewar benzene), because the various products are formed consecutively rather than simultaneously. It is likely that this sequence of rearrangements is general for many cationic rearrangements following electrophilic additions to **1**. The assignment of structure **6** depends on its pmr spectrum and on a number of reactions. It was possible to eliminate HCl by use of triethylamine to give the homofulvene **12**.¹³ Another reaction of **6** is ionization in FHSO₃ solution to the ion **7b**, which was observed by pmr and distinguished from **7a** by the much lower rate of its rearrangement to **11**. Pouring a solution of **6** into



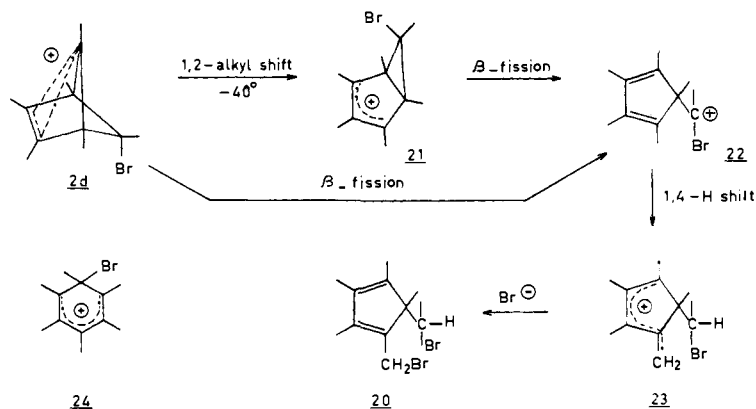
sodium methoxide and methanol afforded compound **13**, a symmetrical species with the methoxy groups arranged *cis*. The structure of **13** has been tentatively assigned on the basis of its pmr spectrum and the observation that **13** decomposes into 1 equiv of methanol and 1 equiv of **14**. Com-



pound **14** was obtained previously by quenching a strongly acidic solution of **2a** and **2b** with sodium methoxide in methanol. The pmr, ir, and mass spectral data of **14** prepared in these two ways are identical.^{7c}

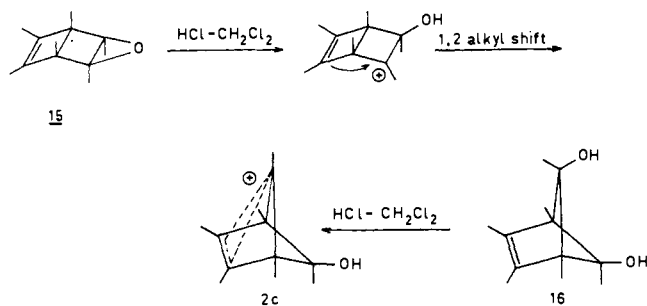
It was previously observed that the ions **7a** and **7b** give

Scheme II



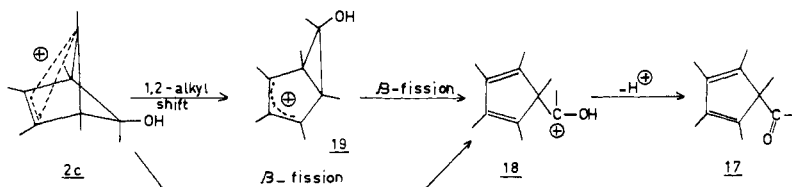
hexamethylbenzenium ion **11** in a thermal reaction.^{12,14} These reactions are symmetry forbidden and should, therefore, not be concerted. Yet no intermediates were observed. To test whether it is consistent that **9** does occur as an intermediate but is not observed, it was generated in a separate experiment from **8** and SbF_5 . The pmr spectrum taken at -60° within 8 min after preparation indicated only **11** to be present. Accordingly the half-life of **9** is much shorter than the half-life of either **7a** or **7b** at this temperature,¹² which makes it clear why **9** was not observed as an intermediate during the isomerization of **7a** and **7b** to **11**. It is then quite likely that, in contrast to the symmetry allowed, concerted photochemical ring closure of **11** to **7a**,¹⁴ the reverse thermal reaction is a stepwise process proceeding *via* **9**.

Reactions Proceeding via Exo 5-OH Ion 2c. In order to obtain experimental evidence about similar rearrangements, hexamethyl(Dewar benzene) epoxide **15**¹⁵ was treated with HCl in methylene chloride at -70° . By using a $\text{HCl}-\text{CH}_2\text{Cl}_2$ mixture (1:2 v/v), a solution of the ion **2c**¹⁶ was obtained. The assignment of structure **2c** depends on its pmr spectrum and the observation that the same pmr spectrum is obtained when diol **16**^{6,15} is used as a precursor. Another indication derives from quenching reactions of **2c**.¹⁷



Mechanistically the formation of **2c** from **15** can be seen as an analog of the reaction of protonated hexamethyl(Dewar benzene); the protonation of the epoxide is followed by a 1,2-alkyl shift which converts the bicyclo[2.2.0]hexenyl ion into a bicyclo[2.1.1]hexenyl structure.

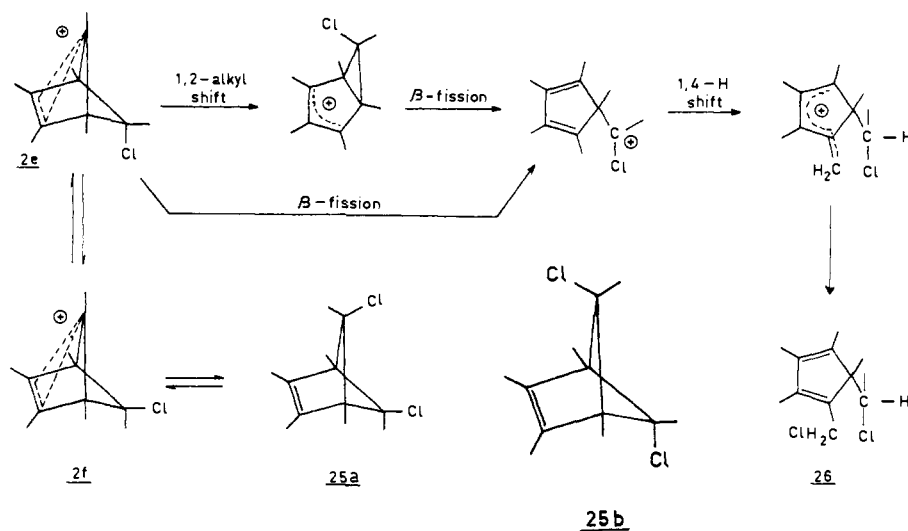
The exo 5-OH ion **2c** has been proposed as an intermediate in some reactions in which the substituted cyclopentadiene ketone **17** was formed.^{6,15} Compound **17** can be viewed as the deprotonated ion **18**, which is closely related to ion **9**. An intermediate (**19**) corresponding to **7b** was not



postulated and it seemed of interest to repeat the pmr experiment described above, in which the rearrangement of **2a** and **2b** was followed as a function of temperature, now using the ion **2c**. A solution of **2c** in methylene chloride was warmed and reaction was followed by pmr. At temperatures higher than -40° new peaks appeared, partly due to **17**.¹⁵ Although the remaining peaks in the pmr spectrum were not identified, it was shown in a separate experiment, in which an authentic sample of **17**¹⁵ was treated with HCl in methylene chloride under the same conditions, that they are likely due to products derived from protonated **17**. Thus, although **17** is indeed formed from **2c**, the intermediate **19** could not be observed. Ion **18** may be formed either directly by β -fission from **2c** or *via* the intermediate **19**.

Reactions Proceeding via Endo 5-Bromo Ion 2d. A solution of endo 5-Br ion **2d** was prepared by reaction of a slight excess of bromine and **1** in methylene chloride at low temperature. The structure **2d** is assigned on the basis of the pmr spectrum¹⁶ and quenching reactions.^{1b,17} It can be concluded therefore, that **2d** is more stable than its exo 5-Br isomer. Two mechanistic pathways have to be considered for the formation of **2d**. Exo attack on **1** followed by rearrangement to the *exo*-5-bromohexamethylbicyclo[2.1.1]hexenyl ion, which rapidly interconverts to its endo 5-Br isomer **2d**, or an endo attack followed by a 1,2-alkyl shift to give **2d**. Although the former cannot rigorously be excluded, the latter is preferred on the basis of electronic factors (*vide supra*). Moreover one does not need to postulate an additional intermediate.

At -40° pmr indicated the disappearance of **2d**. Compound **20** was formed, no intermediates being observed (Scheme II). It could be isolated as a crude product by evaporating the solvent, but appeared to be unstable at room temperature, giving a number of compounds with high molecular weight (mass spectrum). Structure **20** was assigned on the basis of the spectral data. The pathway here is likely to be similar to that of the rearrangements of ions **2a** and **2b**. Just as in the case of ion **2c** it is not clear whether bicyclo[3.1.0]hexenyl cation **21** is an intermediate, since ion **22** might be formed either directly from **2d** or *via* this intermediate. Ion **22** has a structure which is related to the ions **9** and **18**, but the reactions of the three ions are all different. Ion **18** loses a proton to give ketone **17**, while ion **9** reacts with chloride ion or rearranges to **11**. Ion **22** is proposed to undergo a 1,4-hydride shift to give **23** which subsequently reacts with the gegenion, Br^- , to give **20**.



Why should the ions **9** and **22** give such different reactions? The major difference between **9** and **22** is in the nature of the carbonium ion center, which is H-substituted in **9** but Br-substituted in **22**. The large bromine atom might well be responsible in the latter case for the presence of a dominant conformation of **22**, in which a 1,4-hydride shift to give **23** is preferred rather than a 1,2-alkyl shift to give **24**. And, too, the ion **22** might be stabilized by electron donation from bromine. Compound **24** has been recently prepared in a thermal reaction of **2d** in the presence of AlBr_3 .¹⁸ Its pmr spectrum was absent from the rearrangement products of **2d**.

The hydride shift of **22** is *intramolecular* rather than *intermolecular*. Strong evidence supporting the intramolecular nature of the reaction of **2d** to **20** arises from kinetic studies. The reaction rate was measured at two different starting concentrations of **2d**, 0.2 and 2 *M*. The rate constant for formation of **20** at -40° was $2 \times 10^{-3} \text{ sec}^{-1}$ in both cases; straight first-order plots were obtained over at least two half-lives for **2d**. Moreover, the product derived from a 10^{-4} M solution of **2d** at -20° was identical with the product from 1 *M* solutions, so that no other products (e.g., those derived from **24**) were obtained under conditions favoring intramolecular reaction.¹⁹

Reactions Proceeding via Endo 5-Chloro Ion 2c. The chlorination of hexamethyl(Dewar benzene) (**1**) in methylene chloride has now been studied in detail.^{1c,20} With a twofold excess of chlorine, reaction is complete in less than 5 min at -65° . Only one product, the previously reported cation **2e**,²¹ is shown by pmr. The pathway followed here is apparently analogous to that of the bromination of **1**.

On slow warming to -45° , **2e** is partially converted to a second species, the dichloride **25a**, and, if **2e** is prepared using less than 1 equiv of chlorine, it is completely converted to **25a** when warmed (Scheme III). Structure **25a** was assigned on the basis of the pmr spectral data; it is an analog of chloride **4b** obtained from **2a** and **2b**. While the pmr spectra do not exclude the possibility of **25b** rather than **25a**, it is considered far less likely because it would be formed by attack of chloride ion on the electron-rich side of **2e**. Instead, **2e** is thought to isomerize to its exo 5-Cl isomer **2f**. Attack by chloride ion on the electron-poor side of **2f** then gives **25a**.

When excess chlorine is present, pmr peaks assigned to **25a** disappear after 10 min at -40° . However, when less than 1 equiv of chlorine has been employed, **25a** is stable in solution for a short while even at 0° . If this latter solution is warmed to 20° , a second dichloride (**26**) is formed. The

pathway here is likely to be analogous to that by which dibromide **20** is formed. Once again it is not clear whether a [3.1.0] cation occurs as an intermediate.

It is now apparent from previous studies and from the results included here, that hexamethyl(Dewar benzene) is a useful starting material for the preparation of numerous compounds difficult at best to obtain in any other way. Reaction with electrophiles does not normally lead to bicyclo[2.2.0]hexenyl compounds but, instead, to the rearranged [2.1.1] isomers, and, as has been shown, these undergo further rearrangements with great ease.

Experimental Section

General Procedure. Proton magnetic resonance spectra were recorded at 60 MHz using Varian A-60D or Jeol C60HL spectrometers equipped with variable temperature probes. Chemical shifts are calculated relative to internal TMS at δ 0.00. Mass spectra were obtained with an AEI 902 mass spectrometer and ir spectra were obtained on a Perkin-Elmer 257 spectrophotometer; only representative peaks are given. Uv spectra were measured with a Beckman DB-G spectrophotometer. Methylene chloride was distilled from calcium chloride and stored over molecular sieves. The other chemicals are commercially available products unless otherwise stated. Particular attention must be paid to the maintenance of proper temperatures and concentrations in the following experiments.

Reaction of Compound 1 with $\text{HCl}-\text{CH}_2\text{Cl}_2$ (1:2 v/v). A solution of 48 mg (0.3 mmol) of **1** in 0.3 ml of methylene chloride was cooled in an nmr tube to -80° (solid **1** separated). Dry HCl gas was dissolved until the total volume of the solution was 0.5 ml. Meanwhile the precipitate dissolved and the solution turned yellow. The pmr spectrum of the solution at -70° showed peaks at δ 3.08 (q, $J = 7$ Hz, 1 H), 2.05 (s, 6 H), 1.61 (s, 6 H), 1.36 (s, 3 H), and 0.68 (d, $J = 7$ Hz, 3 H) (**2a**) and 2.35 (q, $J = 7$ Hz, 1 H), 2.07 (s, 6 H), 1.47 (s, 6 H), 1.42 (d, $J = 7$ Hz, 3 H), and 1.39 (s, 3 H) (**2b**), the **2a:2b** ratio being 3:1.

Reaction of Compound 1 with 2 Equiv of HCl. A solution of 48 mg (0.3 mmol) of **1** in 0.4 ml of methylene chloride in an nmr tube was cooled to -85° (solid **1** precipitated). Dry HCl gas (0.6 mmol) was introduced from a syringe and the reaction mixture was stirred; the precipitate dissolved and the solution turned yellow. The pmr spectrum at -85° , taken 5 min after preparation, showed the peaks of **2a** and **2b** (3:1) and peaks at δ 2.62 (q, $J = 7$ Hz, 1 H), 1.43 (s, 6 H), 1.04 (d, $J = 7$ Hz, 3 H), and 1.03 (broad s, 9 H) (**4a**). The intensity of the latter peaks increased at the expense of those of **2a** and **2b** on prolonged reaction. The rate of this reaction increased sharply on warming to -60° . At this temperature new peaks were observed at δ 2.18 (q, $J = 6.5$ Hz, 1 H), 1.10 (d, $J = 6.5$ Hz, 3 H), 1.54, 1.45, 1.11, 1.04, and 1.01 (s, each 3 H) (**6**). The reaction mixture was warmed to -40° and after 20 min at this temperature, pmr indicated 90% of **6** to be present. On warming to

room temperature HCl evaporated readily, the solution turned purple and the pmr signals of **6** were replaced by those of **8**^{10c} (80%) and **10** (5%). Treatment of this solution with a stream of dry HCl gas at room temperature gave rise to the formation of more **10** at the expense of **8**. In separate experiments the ability of the intermediates to undergo the reverse reactions was explored. Decreasing the temperature did not give rise to any reverse reactions. However, addition of more HCl to a solution containing **4a** did provide a reverse reaction to **2a** and **2b** (3:1). The other reactions, of course, do not revert under these conditions.

Reaction of Compound 1 with 1 Equiv of HCl. In an nmr tube 0.2 ml of methylene chloride was cooled to -85° and dry HCl gas (0.1 mmol) was then dissolved at this temperature. Subsequently a pre-cooled (-85°) solution of 16 mg (0.1 mmol) of **1** in 0.3 ml of methylene chloride was introduced and the reaction mixture was stirred with a rod. The pmr spectrum at -85° , taken 5 min after preparation showed the peaks of **4a** and peaks at δ 3.22 (q, $J = 6$ Hz, 1 H), 1.67 (s, 6 H), 1.39 (s, 3 H), 0.95 (s, 6 H), and 0.72 (d, $J = 6$ Hz, 3 H) (**4b**). Compounds **4a** and **4b** were present in almost equal amounts. After 1 hr at -85° pmr indicated only **4a** to be present. On warming the same reactions were observed as in the case with 2 equiv of HCl; here, however, the reaction rates were much slower.

Reaction of Compound 1 with 0.5 Equiv of HCl at -95° . A solution of 32 mg (0.2 mmol) of **1** in 0.4 ml of methylene chloride in an nmr tube was cooled to -95° (a solid separated). Dry HCl gas (0.1 mmol) was introduced from a syringe and the reaction mixture was stirred (the precipitate dissolved in part). The pmr spectrum of this mixture taken at -90° 5 min after preparation showed **1** (50%), **4a** (10%), and **4b** (40%). The spectrum remained unchanged on standing for 1 hr at -90° . On warming to -60° **4b** isomerized slowly to **4a**.

Reaction of Compound 1 with 0.5 Equiv of HCl at -115° . A solution of 32 mg (0.2 mmol) of **1** in 0.4 ml of vinyl chloride was prepared by liquifying vinyl chloride at -50° in an nmr tube and subsequently introducing **1** with stirring. The resulting solution was cooled to -115° and dry HCl gas (0.1 mmol) was introduced. The pmr spectrum of this solution taken at -105° 10 min after preparation showed the presence of **1** and **4b**. Compound **4a** could not be detected.

Quenching of Intermediates. Quenching of intermediates in the reactions of **1** with varying quantities of HCl in methylene chloride was performed by pouring these solutions into 5% sodium methoxide in methanol. A twofold excess of sodium methoxide was used, calculated on the basis of the quantity of acid. The quenching reagent was cooled to the same temperature as the solution to be quenched, and, with vigorous stirring, the solutions were mixed. Then the reaction mixtures were allowed to warm to room temperature, water was added, and the resulting mixtures were extracted with pentane. Washing with water, drying over anhydrous sodium sulfate, and evaporating the solvent yielded crude products. Quenching at -70° of a solution of ions **2a** and **2b** afforded the ethers **3a** and **3b** in a 3:1 ratio as evidenced by the pmr spectrum.^{7d} Quenching at -85° of a solution of **4a** prepared in a reaction of **1** with 2 equiv of HCl in methylene chloride provided **3a** only. Various quenchings at -90° of solutions of **4a** and **4b** (and **1**) prepared from reaction of **1** with 0.5 equiv of HCl at temperatures between -60 and -115° provided mixtures of the ethers **3a** and **3b** in ratios varying from 10:1 to 10:7. Quenching of a solution of **6**, prepared in a reaction of **1** with 2 equiv of HCl at -40° , yielded a crude product which showed major peaks in the pmr spectrum at δ 3.14, 1.00, 0.88 (s, each 6 H), 1.02 (d, $J = 7$ Hz, 3 H), and 0.78 (d, $J = 7$ Hz, 3 H) (90% of the proton count, **13** in CCl_4). Attempted purification was not successful; **13** decomposed into 1 equiv of methanol and 1 equiv of **14** (which was identified by its pmr, ir, and mass spectra^{7c}).

endo,endo-Methyl-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl Isothiocyanate (5a). Under nitrogen with stirring 75 ml of methylene chloride, 0.8 g (10 mmol) of dry sodium thiocyanate, and 0.8 g (5 mmol) of **1** were cooled to -80° . Dry HCl gas (140 mmol) was introduced over 2 hr with stirring. Subsequently the reaction mixture was carefully neutralized by adding triethylamine in methylene chloride at the same temperature. Cooling was stopped and the reaction mixture was stirred overnight and then poured into water. The organic layer was separated and washed four times with water and twice with a saturated aqueous sodium chloride so-

lution and stored overnight over sodium bicarbonate. Evaporating the solvent yielded 1.0 g of a yellow semisolid. Crystallization from hexane afforded 0.74 g (3.4 mmol, 67%) of slightly yellow **5a** (mp $66-68^\circ$): pmr (CCl_4) δ 3.03 (q, $J = 6$ Hz, 1 H), 1.63 (s, 6 H), 1.25 (s, 3 H), 0.98 (s, 6 H), 0.78 (d, $J = 6$ Hz, 3 H); ir (*inter alia*) absorption at 2175 cm^{-1} ($-\text{NCS}$); mass spectrum, $M^+ m/e$ 221, base peak m/e 163, $M - \text{SH } m/e$ 188. Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NS}$: C, 70.54; H, 8.66; N, 6.33; S, 14.49. Found: C, 70.19; H, 8.66; N, 6.28; S, 14.58.

A thiourea derivative of **5a** was obtained as an oil by treatment with *tert*-butylamine at 20° for 6 days: pmr (CCl_4) δ 6.31 (s, broad, 1 H), 5.53 (s, broad, 1 H), 3.15 (q, $J = 6$ Hz, 1 H), 1.70 (s, 6 H), 1.57 (s, 9 H), 1.32 (s, 3 H), 1.05 (s, 6 H), 0.77 (d, $J = 6$ Hz, 3 H); ir (*inter alia*) absorptions at 3430 (N-H), 1530, 1490, 1270, 1225, and 1195 cm^{-1} .

endo,endo-Methyl-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl Isocyanate (5b). Under nitrogen with stirring 75 ml of methylene chloride, 0.65 g (10 mmol) of dry sodium cyanate, and 0.8 g (5 mmol) of **1** were cooled to -80° . Dry HCl gas (55 mmol) was introduced and the reaction mixture was stirred for 4.5 hr at -80° . Neutralization at -80° was performed by adding dropwise and with stirring 10 ml of triethylamine in 10 ml of methylene chloride. Cooling was stopped and the reaction mixture was left standing overnight. The reaction mixture was diluted with twice its volume of hexane and was filtered. The filtrate was evaporated to leave 1.05 g of a slightly yellow oil which contained 62% of **5b** (by pmr). The product was distilled using a Kugelrohr apparatus (bp $50-60^\circ$, 0.05 mm, the distillate was received at -70°). Pmr (CCl_4) indicated 80% purity after distillation: δ 3.00 (q, $J = 6$ Hz, 1 H), 1.63 (s, 6 H), 1.18 (s, 3 H), 0.91 (s, 6 H), 0.73 (d, $J = 6$ Hz, 3 H). Several minor peaks amounting to ca. 20% of the proton count were noted: ir (*inter alia*) absorption at 2270 cm^{-1} ($-\text{NCO}$).

The *tert*-butylurea derivative of **5b** was prepared by treatment with *tert*-butylamine for 15 min at 20° . The crude product was recrystallized from aqueous ethanol, mp $194.5-195.5^\circ$. Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}$: C, 73.33; H, 10.86; N, 10.06. Found: C, 73.10; H, 10.83; N, 9.73.

endo,endo-Methyl-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl Azide (5c). Under nitrogen with stirring 75 ml of methylene chloride, 0.65 g (10 mmol) of dry sodium azide, and 0.8 g (5 mmol) of **1** were cooled to -80° . Dry HCl gas (140 mmol) was introduced and the reaction mixture was stirred for 4 hr at -80° . Neutralization at -80° was performed by adding dropwise and with stirring 30 ml of triethylamine. Cooling was stopped and the reaction mixture was allowed to stand overnight. It was diluted with twice its volume of hexane and was filtered. The filtrate was evaporated to leave 1.03 g of a pale yellow oil which consisted of 70% **5c** (by pmr). The product was distilled (bp 30° , 0.05 mm, the distillate was received at -70°): pmr (CCl_4) δ 3.13 (q, $J = 6$ Hz, 1 H), 1.64 (s, 6 H), 1.22 (s, 3 H), 0.90 (s, 6 H), 0.70 (d, $J = 6$ Hz, 3 H), no impurity peaks were noted except for one at δ 2.10 (2% of the proton count, perhaps compound **10**); ir (*inter alia*) absorption at 2130 cm^{-1} ($-\text{N}_3$).

When the experiment was performed at -150° , using vinyl chloride as the solvent and 7.5 mmol of HCl, mainly starting material **1** and a few per cent of product **5c** were obtained.

Reaction of Compound 6 with FHSO_3 . A solution of **6** prepared from **1** and 2 equiv of HCl in methylene chloride in an nmr tube, as described above, was treated with 0.5 ml of FHSO_3 at -80° . The pmr spectrum of the lower (FHSO_3) layer at -80° indicated the presence of **7b**. The pmr spectrum of the ion **7b** was observed up to room temperature, at which time rearrangement to **11** occurred.

Reaction of Compound 8 with SbF_5 . Compound **8**^{10c,11} was added to a mixture of 0.2 ml of SbF_5 and 0.3 ml of SO_2 in an nmr tube at -60° . The reaction mixture was stirred with a rod and the pmr spectrum was recorded 8 min later after addition of **8**. The pmr spectrum indicated the presence of **11** only.

Reaction of Hexamethyl(Dewar benzene) Epoxide 15 with $\text{HCl}-\text{CH}_2\text{Cl}_2$ (1:2 v/v). Hexamethyl(Dewar benzene) epoxide **15**¹⁵ (51 mg, 0.3 mmol) in 0.3 ml of methylene chloride in an nmr tube was cooled to -80° and dry HCl gas was introduced at this temperature until the total volume of the solution was 0.5 ml. The pmr spectrum at -70° showed peaks at δ 2.15 (s, 6 H), 1.62 (s, 9 H), and 1.39 (s, 3 H) (**2c**). The same spectrum was obtained using **16**¹⁵ as precursor.

Reaction of Compound 15 with HCl. Hexamethyl(Dewar benzene) epoxide **15**¹⁵ (35 mg, 0.2 mmol) was dissolved in 0.4 ml of methylene chloride. The solution was cooled and HCl was introduced until the pmr spectrum indicated that 60% of **15** had reacted to give **2c**. On warming to -40° the pmr signals of **17**¹⁵ and **16**^{6,15} appeared together with other peaks. At room temperature the pmr spectrum indicated **15** (15%), **16** (10%), and **17** (20%). A number of other peaks were also present in the spectrum. These other peaks were also noted in the pmr spectrum of a solution obtained on room temperature treatment of a solution of **17**¹⁵ in methylene chloride with a stream of HCl gas.

Reaction of Compound 1 with 2.2 Equiv of Bromine.²² A methylene chloride solution of 13 mg (0.08 mmol) of **1** diluted to 0.3 ml was cooled to -70° in an nmr tube. At this temperature 29 mg (0.18 mmol) of bromine diluted to 0.2 ml with methylene chloride was introduced and the mixture was agitated with a rod. The pmr spectrum at -70° of the solution showed peaks at δ 2.25 (s, 6 H), 2.06 (s, 3 H), 1.63 (s, 6 H), and 1.57 (s, 3 H) (**2d**).

Reaction of Compound 1 with 1.2 Equiv of Bromine. A methylene chloride solution of 81 mg (0.5 mmol) of **1** diluted to 0.3 ml was cooled to -70° in an nmr tube. At this temperature 96 mg (0.6 mmol) of bromine diluted to 0.2 ml with methylene chloride was introduced and the mixture was stirred with a rod. The pmr spectrum at -70° of the yellow solution showed peaks at δ 2.39 (s, 6 H), 2.03 (s, 3 H), 1.80 (s, 3 H), and 1.70 (s, 6 H) (**2d**). On warming the solution to -40° the peaks disappeared and peaks appeared at δ 4.30 (q, $J = 7$ Hz, 1 H), 4.20 (s, 2 H), 1.90 (broad s, 6 H), 1.82 (broad s, 3 H), 1.31 (d, $J = 7$ Hz, 3 H), and 1.14 (s, 3 H) (**20**). On warming to room temperature no further changes in the pmr spectrum were observed within 30 min. The pmr spectrum indicated no remaining **1**, **20** amounting to 90%. The solvent was evaporated to leave 160 mg of a yellow liquid. Spectra were taken within 1 hr after preparation. After that time a brown color developed and the mass spectrum indicated the presence of dimeric and polymeric material: mass spectrum m/e 320, 322, and 324 (1:2:1) (corresponding to $C_{12}H_{18}Br_2$); $uv \lambda_{max}^{pentane}$ 278 nm. The pmr spectrum in benzene shows hyperfine structure on the olefinic methyl and methylene proton signals.

By using less than 1 equiv of bromine at -70° pmr signals in addition to those of **1** and **2d** were observed at δ 1.89, 1.25, and 1.06.²²

Reaction of Highly Diluted 1 with Bromine. Compound **1** (32 mg, 0.2 mmol) was dissolved in 2 l. of methylene chloride. The solution was cooled to -20° and 32 mg of bromine was introduced with stirring. After 30 min the solvent was evaporated and the pmr spectrum of the residue was recorded. The spectrum was identical with that obtained in the 1 *M* reaction described above.

Kinetics of the Formation of 20 from 2d. Solutions of ion **2d** (0.2 and 2 *M*) were prepared from the equivalent amounts of **1** and bromine at -80° in nmr tubes. After placement of the tubes in the nmr probe (precooled -40°), the intensities of the pmr signals of **2d** and **20** were recorded as a function of time. Straight first-order plots were obtained over at least two half-lives for cation **2d**.

Reactions of Compound 1 with Chlorine (General). Methylene chloride solutions of chlorine were prepared and stored in an all-glass apparatus at or below 0° in dim light. Standardization of these solutions was accomplished by adding known aliquots to aqueous potassium iodide, the liberated iodine being titrated with standard sodium thiosulfate solution. Restandardization of the chlorine solutions after 1 week showed no change in concentration.

Reaction of Compound 1 with 2.3 Equiv of Chlorine. Hexamethyl(Dewar benzene) (**1**) (9.6 mg, 0.059 mmol) was dissolved in 0.10 ml of methylene chloride in an nmr tube. The resulting solution was cooled to -80° (a white precipitate was noted). To this mixture was added 0.15 ml of precooled (-80°) 0.90 *N* chlorine solution (0.135 mmol of chlorine). The resulting yellow solution was vigorously agitated at -80° and, immediately thereafter, the pmr spectrum was taken. At -65° pmr indicated only ion **2e**: δ 2.35 (s, 6 H), 1.98 (s, 3 H), 1.73 (two coincident s, 9 H). After 15 min a small amount of dichloride **25a** had formed (5%). After warming

to -45° , **2e** further isomerized to **25a**: δ 1.57 (s, 6 H), 1.33 (s, 6 H), 1.11 (s, 6 H). After 6 min at -45° the maximum amount of **25a** was noted, **25a** (46%) and **2e** (54%). On warming to -40° the pmr spectrum of **25a** disappeared leaving only the spectrum of **2e**, but with the peaks now somewhat shifted: δ 2.27 (s, 6 H), 1.93 (s, 3 H), 1.68 (s, 6 H), 1.63 (s, 3 H). Weak broad absorption occurred in the region of δ 1.0–2.0, perhaps due to decomposition products of **25a**. Recooling the sample to -65° did not change this spectrum.

Reaction of Compound 1 with 1.4 Equiv of Chlorine. Solutions of **1** (16.0 mg, 0.096 mmol) and chlorine (0.135 mmol) in methylene chloride were allowed to react at -80° as in the preceding experiment. The pmr spectrum for the resulting colorless solution taken at -65° 15 min after mixing indicated three species: **2e** (85%), **25a** (5%), and **1** (10%). After 30 min at this temperature the ratio of products was **2e** (70%), **25a** (20%), and **1** (10%). The tube contents were warmed to -40° , **2e** (40%) and **25a** (60%). Little or no **1** remained. On further warming to -20° , the tube contents turned purple. The spectrum indicated no remaining **2e** or **25a** but, instead, the dichloride **26**: δ 4.27 (s, 2 H), 4.15 (q, $J = 7$ Hz, 1 H), 1.88–1.75 (s, 6 H and broad s, 3 H), 1.13 (s, 3 H), 1.10 (d, $J = 7$ Hz, 3 H). Other unassigned peaks were noted at 2.23, 2.20, and 1.42–1.00 (five small peaks). The peaks at 2.33 and 2.20 amounted to ca. 25% of the proton count.

Reaction of Compound 1 with 0.6 Equiv of Chlorine. Solutions of **1** (17 mg, 0.106 mmol) and chlorine (0.06 mmol) in methylene chloride were allowed to react at -70° as in the preceding experiments. The pmr spectrum at -63° showed **2e** (27%), **25a** (5%), and unreacted **1** (68%). On warming to -20° , the spectrum of **2e** disappeared while that of **25a** increased. Due to the close proximity of peaks only a semiquantitative estimate of **25a** (40%) and unreacted starting material (60%) could be made. After the colorless reaction solution had sat at room temperature overnight, the spectrum of **25a** had been replaced by that of **26** (45%) and unidentified materials (5%); **1** was also still present (50%).

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