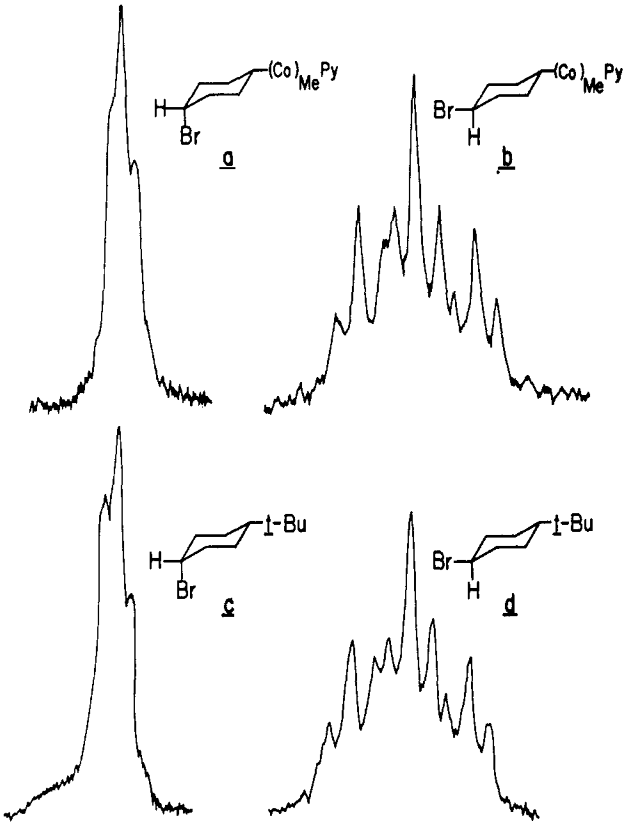

Figure 2. Nmr spectra (100 MHz) of the H_y–C–Br proton resonances in: (a) (*cis*-4-bromocyclohexyl)pyridine[bis(dimethylglyoximato)]cobalt(III); (b) the corresponding *trans*-cyclohexylcobalt compound; (c) *cis*-4-bromo-*t*-butylcyclohexane; and (d) *trans*-4-bromo-*t*-butylcyclohexane. The solvent was $CDCl_3$, the temperature was 33°, and the spectra for the cobalt compounds were enhanced utilizing a Varian C-1024 time-averaging computer.

Although the number of coupled protons differs (replacement of an equatorial proton by cobalt), the H_x multiplet of **2** bears similarities to the axial *H*-C–OR proton in the low-temperature nmr spectrum of equatorial trideuteriomethoxycyclohexane.[8b,c] The magnitudes of the coupling constants are similar and the gross shapes of the peaks show resemblances.

From these spectra, it is concluded that **2** is a *trans* compound formed by reaction of **1** with *cis* starting material and that **4** is a *cis* compound formed from *trans* starting material.

Inspection of the nmr spectrum of crude **4** reveals the presence of a small amount (<10%) of a second compound [δ 3.12 (s), 2.78 (broad m)] which appears to be the *trans* isomer from the upfield position and peak width of the *H*-C–OR proton. Compound **4** is not converted into this material under reaction or work-up conditions. It is possible that a second, minor mechanistic pathway is operating in the reaction of **1** with **3** due to steric hindrance to approach of the nucleophile.

The nmr spectra of **6** and **8** were analyzed in a similar manner and provide compelling evidence for the assignments. In Figure 2 are presented the *H*-C–Br nmr proton resonances for compounds **6a**, **8a**, and *cis*- and *trans*-4-*t*-butylcyclohexyl bromides. The near-identity of the splitting patterns and axial and equatorial chemical shift differences for the 4-methine protons in the cobalt and *t*-butyl derivatives indicate similar structures and identical conformations for the two sets of compounds. The equatorial resonances exhibit small but definite splitting and the axial resonances show large splittings characteristic of those expected for the X part of an A_2B_2X pattern. The observed spectra for **6a** and **8a** require that the cobalt moiety is in the equatorial position.

The *H*-C–Y (Y = Br, OH) proton splitting patterns of the 4-substituted cyclohexylcobalt compounds (**6** and **8**) more closely resemble those of the corresponding 4-substituted *t*-butylcyclohexyl compounds than those observed in the low-temperature (slow inversion on the nmr time scale) spectrum of monosubstituted cyclohexanes;[8c] *i.e.*, the cobalt moiety and the *t*-butyl group similarly affect the splitting pattern in the 4 position, possibly as a result of analogous ring deformations. These considerations lead to the conclusion that the cobalt grouping in these compounds has a very large preference—comparable to or greater than that of the *t*-butyl group—for the equatorial position.

The above results demonstrate that cobaloxime(I) (**1**) reacts with alkylating agents with inversion of configuration at the carbon center. This observed stereochemistry coupled with earlier kinetic results[3] conclusively establishes the S_N2 nature of these reactions. From the reported similarity between the chemistry of **1** and vitamin B_{12s},[5] one may assume reactions of the latter also proceed by this mechanism.[10]

(10) Support of this research by the National Institutes of Health under GM 15373 is gratefully acknowledged.

(11) National Institutes of Health Postdoctoral Fellow, 1969–1970.

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A 1,2-Methyl Shift to a Vinyl Cation

Sir:

Vinyl cations as possible intermediates in organic reactions have been receiving increasing attention in recent years,[1] and a number of analogies could be established between them and their saturated counterparts with one notable exception: to our knowledge there is no report in the literature[2] which describes a 1,2-methyl shift to a vinyl cation, although this type of reaction is a common feature in the chemistry of saturated carbonium ions.

In the course of our work on electrophilically induced cyclodimerizations of allenic and acetylenic hydrocarbons *via* vinyl cations as intermediates,[3] we recently had occasion to examine the reaction of hydrogen chloride with *t*-butylacetylene (**1**). The reactions were carried out with neat mixtures of *t*-butylacetylene and anhydrous hydrogen chloride in the liquid phase at ambient temperatures. For this purpose, the reactants were condensed into a thick-walled glass reactor at the

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(1) For a recent summary of pertinent references see S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 2115 (1969).

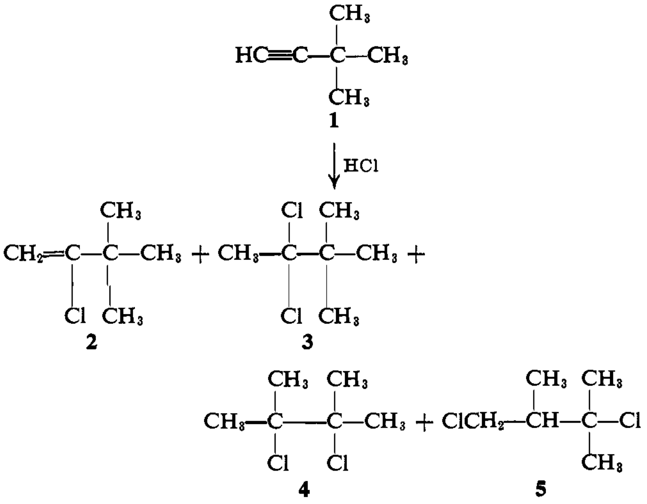
(2) In a presentation at the Chemiedozententagung at Karlsruhe, 1969, M. Hanack mentioned that the solvolysis of 2 by silver acetate may also be accompanied by a partial 1,2-methyl shift to a vinyl cation. To our knowledge, this work has not been published. 1,2-Phenyl migration to a vinyl cation, on the other hand, has been observed previously by W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, **89**, 1960 (1967).

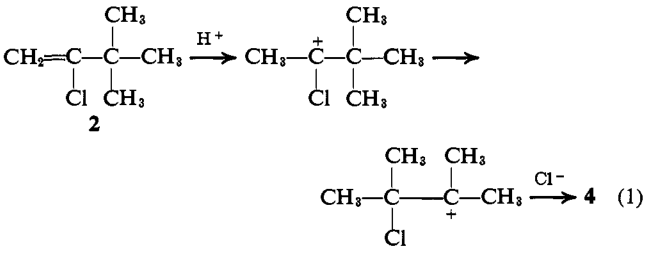
(3) For a brief summary see K. Griesbaum, *Angew. Chem.*, **81**, 966 (1969); *Angew. Chem. Intern. Ed. Engl.*, **8**, 933 (1969).

temperature of liquid air, and, after closing the reactor, the mixture was allowed to warm to room temperature.

Analysis of the crude adduct mixtures by glpc showed that the reaction of equimolar amounts of HCl and *t*-butylacetylene produced four instead of the anticipated two adducts. Separation of such a mixture by preparative glpc afforded all four adducts in a spectroscopically pure form. Three components could be readily identified. They were 2-chloro-3,3-dimethyl-1-butene (**2**),[4] 2,2-dichloro-3,3-dimethylbutane (**3**),[4] and 2,3-dichloro-2,3-dimethylbutane (**4**).[5] The identification of these products is based on a comparison of their nmr spectra with those of independently synthesized authentic compounds.

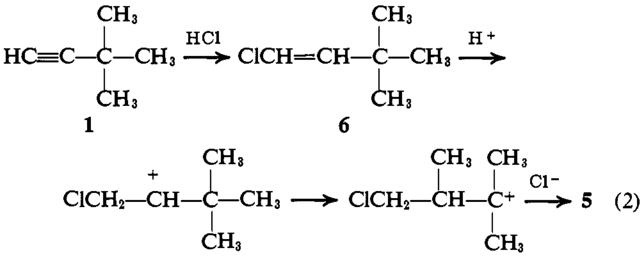
The fourth component analyzed correctly for a diadduct of HCl and *t*-butylacetylene and showed the nmr spectrum depicted in Figure 1 which, on the basis of spin–spin decoupling experiments, was ascribed to the structure of 1,3-dichloro-2,3-dimethylbutane (**5**). This structure assignment could be further substantiated by the fact that the same adduct was also formed in the addition of excess HCl to 2,3-dimethylbutadiene under the conditions of this work (*vide infra*). These results show that the reaction of HCl with *t*-butylacetylene produces not only the normal adducts **2** and **3**, but also appreciable quantities (Table I) of the adducts **4** and **5**, having a rearranged carbon skeleton. *A priori* this result could be compatible both with a methyl shift to a vinyl cation and with neopentyl-type rearrangements. Thus, the formation of **4** could be envisioned by a migration in the second addition step of HCl to **1** (eq 1)





$$\underset{\textbf{2}}{CH_2{=}\underset{Cl}{C}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3} \xrightarrow{H^+} CH_3{-}\overset{+}{\underset{Cl}{C}}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3 \longrightarrow CH_3{-}\overset{CH_3}{\underset{Cl}{C}}{-}\overset{CH_3}{\underset{+}{C}}{-}CH_3 \xrightarrow{Cl^-} \textbf{4} \quad (1)$$

and the formation of diadduct **5** by a series of two anti-Markovnikov additions to **1** and a concurrent methyl migration during the second addition step (eq 2).



$$\underset{\textbf{1}}{HC{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3} \xrightarrow{HCl} \underset{\textbf{6}}{ClCH{=}CH{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3} \xrightarrow{H^+} ClCH_2{-}\overset{+}{C}H{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3 \longrightarrow ClCH_2{-}\overset{CH_3}{C}H{-}\overset{CH_3}{\underset{CH_3}{C^+}} \xrightarrow{Cl^-} \textbf{5} \quad (2)$$

Model experiments demonstrated, however, that these reactions (eq 1 and 2) could not be responsible for the formation of **4** and **5**, respectively. Reaction of HCl with authentic **2**[4] produced no detectable amounts of **4** but only the Markovnikov adduct **3**. Reaction of HCl with authentic **6**,[6] on the other hand, did lead to a product in which the presence of **5** was indicated by glpc analysis. However, the reaction was very slow. Starting with an equimolar mixture of **1** and **6** and using a 5-fold excess of HCl, more than 95% of **6** was recovered after all of **1** had been converted. Hence, if **6** were an intermediate in the addition of HCl to **1**, its concentration should build up during the reaction; yet this was not observed.

These results lead us to the conclusion that the formation of the rearrangement products **4** and **5** is indeed due to a 1,2-methyl shift to the positive center of the vinyl cation **7** with the concurrent formation of the resonance-stabilized allylic cation **8**. The derivation of **4** and **5** from this cation **8** is straightforward (see Scheme I).

At first glance this proposed reaction path might seem to be in conflict with the results of the reaction of excess HCl with *t*-butylacetylene. For, while it might be anticipated that excess HCl leads to an accelerated trapping of the vinyl cation **7**, the opposite effect was observed (Table I). Starting with a reactant ratio of 1:1, rearrangement occurred to the extent of 31%; with a 5-fold excess of HCl, rearrangement increased to 51% and with a 10-fold excess of HCl, rearrangement increased to 64%. We think that this may be explained by the increasingly polar medium which is provided by the excess of liquefied hydrogen chloride and which may promote the rearrangement reaction. In order to

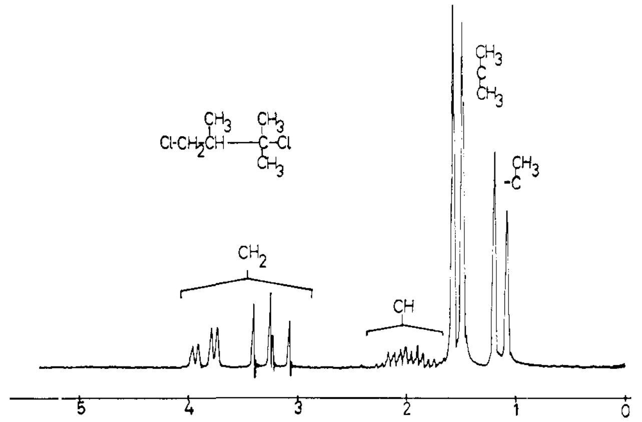


Figure 1. Nmr spectrum of the isolated 1,3-dichloro-2,3-dimethylbutane (**5**).

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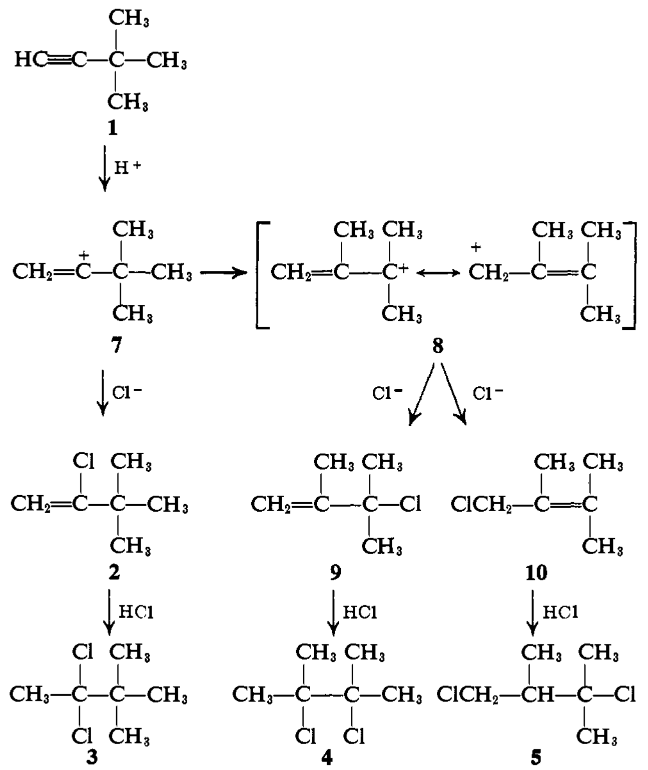
[4] Preparation according to a procedure by P. D. Bartlett and L. J. Rosen, *J. Amer. Chem. Soc.*, **64**, 543 (1942).

[5] Preparation according to a procedure by F. Couturier, *Ann. Chim. Phys.*, 26 (6), 433 (1892).

[6] A. P. Meshcheryakov and L. V. Petrova, *Izv. Akad. Nauk SSSR*, **8**, 1488 (1964).

Scheme I



clarify this question, attempts are underway to assess the effect of solvent polarity upon the extent of the rearrangement.

Table I. Product Distribution in the Addition of Hydrogen Chloride to *t*-Butylacetylene

Molar ratio of HCl:1	Relative amounts of components 2-5 in crude adduct mixture,[a] mol %			
	2	3	4	5
1	42	27	5	26
5	4	44	18	34
10		36	22	42

[a] The components 2-5 comprised >90% of the total adduct mixture. Minor amounts of yet unidentified by-products were formed when low ratios of HCl:1 were applied.

No evidence was obtained for the presence of 2,3-dimethylbutadiene in the crude adduct mixtures, although its formation could be envisaged by loss of a proton from **8**. Its intermediacy can, however, not be negated by this finding, since it could be shown that the reaction of excess HCl with 2,3-dimethylbutadiene, under the conditions described above, leads also predominantly to the diadduct **5** rather than **4**.[7] The question of the intermediacy of dimethylbutadiene[8] is, however, a secondary one as its formation would also require a 1,2-methyl shift to the vinyl cation **7**.

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(7) This is quite in contrast to the previously reported reaction of aqueous HCl with 2,3-dimethylbutadiene, where the thermodynamically more stable adduct **9** was the predominant reaction product: L. F. Hatch and G. E. Journeay, *J. Amer. Chem. Soc.*, **75**, 3712 (1953).

(8) This question was raised by one of the referees and is therefore dealt with here.

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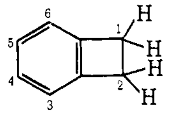
Benzocyclobutene Radical Anion

Sir:

We have been studying ring strain effects on spin densities in strained aromatic radical anions.[1,2] We wish to report some of our observations regarding the benzocyclobutene (BCB) radical anion.[3]

Reduction of BCB with a potassium mirror at −70° in dimethoxyethane immediately yielded the 69-line spectrum shown in Figure 1. The spectrum is readily interpreted in terms of the interaction of the electron with four sets of two equivalent nuclei. The hyperfine coupling constants are given in Table I.

Table I. Hyperfine Splitting Constants of Benzocyclobutene Radical Anion



Position	−70°	−10°	20°
Methylenes	5.20 G (2 H) 5.70 G (2 H)	5.40 G (4 H)	5.30 G (4 H)
4,5	1.45 G (2 H)	1.42 G (2 H)	1.40 G (2 H)
3,6	7.55 G (2 H)	7.28 G (2 H)	7.24 G (2 H)
Potassium		0.18 G	0.20 G

However, as the temperature was raised certain lines broadened, and when the temperature was raised to −10° the spectrum collapsed to the one shown in Figure 1. At the same time, the hyperfine coupling constants gradually changed to the values shown in Table I. One additional feature was the appearance of metal splitting at approximately −45°. The metal hyperfine splitting gradually increased as the temperature was raised. At −10°, the spectrum can be interpreted in terms of two sets of two equivalent nuclei and one set of four equivalent nuclei. We have observed this spectrum up to +20° and found it to be completely reversible with the low-temperature spectrum. The hyperfine coupling constants at −10° are given in Table I.

The alternating line-width effect can be associated with some exchange process. The nuclei with coupling constants of $a_H = 5.70$ G and $a_H = 5.20$ G are being interchanged and in the fast-exchange limit collapse to one set of equivalent nuclei with a splitting constant of 5.40 G. A diagram of the spin states shows that upon exchange of the quantum numbers for these two sets of nuclei all but 27 lines should broaden, as is observed. Replacement of one of the methylene protons with a deuterium yields a low-temperature spectrum which can only be simulated as a mixture of two species. The mixture was a 1:1 composition in which one species has a nucleus of splitting constant 5.20 G replaced by a deuterium atom and the second species has one of the nuclei of 5.70-G splitting constant replaced with a deuterium atom. As the temperature is raised to −10°, the spectrum collapses to one which has

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(1) R. D. Rieke, C. F. Meares, and L. I. Rieke, *Tetrahedron Lett.*, 5275 (1968).

(2) R. D. Rieke, W. Rich, and T. Ridgway, *ibid.*, 4381 (1969).

(3) A preliminary report on this work was presented at the 165th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN 152.