Analogous products have been obtained from acetone and from 2-butanone in slightly lower yields. In these cases products **2** and **3** (R = CF_3)[2] from the acetylene and carbon disulfide alone were also obtained. With 2-butanone, alkylation occurred exclusively at the methylene group. Aliphatic aldehydes such as propionaldehyde and isobutyraldehyde gave analogous products in 28 and 29% yield along with **2** and **3**.

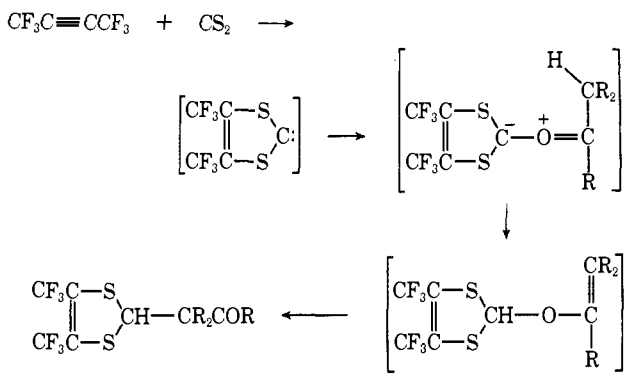
Dimethyl acetylenedicarboxylate reacted similarly with carbon disulfide and aldehydes and ketones. Slightly higher temperatures (120–140°) were needed and yields have generally been lower.

This reaction is not general for compounds with acidic hydrogen. Ethyl malonate and malononitrile were not alkylated. In these cases products **1**, **2**, and **3** were obtained.

In none of these reactions have products derived from nucleophilic attack of the 1,3-dithiolium carbene at the carbonyl group been found. The absence of a general reaction for acidic hydrogen compounds indicates that a direct insertion of the carbene into a CH bond is an unlikely mechanism. Reaction of the carbene with the enol form of the aldehyde or ketone also appears unlikely because of the low concentration of enol under the essentially neutral reaction conditions.

The most likely mechanism for the alkylation reaction is given in Scheme I. That the dithiolium carbene is generated under the reaction conditions is

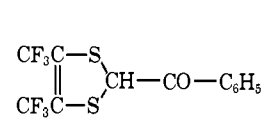
Scheme I



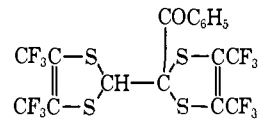
demonstrated by the fact that products derived from it and the acetylene are also obtained in many of the reactions. Although in many cases the carbene reacts as a nucleophile the carbon atom still has a vacant orbital and the potential for electrophilic reaction. Electrophilic attack at the carbonyl oxygen would lead to the enol ether. The initial dipolar ion need not be an antiaromatic species. The negative charge could overlap with the d orbitals of sulfur and not enter into the π system of the dithiolium ring. Under the neutral reaction conditions the more stable enol would be formed and this would lead to the orientation observed with 2-butanone and 2,4-pentanedione. The isomerization of the enol ether to the observed product could occur by either a homolytic or a heterolytic process.

Hexafluoro-2-butyne reacted with carbon disulfide and benzaldehyde to give **17** and **18**. Cinnamaldehyde reacted analogously as did other aromatic aldehydes. It is believed that **18** is formed from **17** by the type of reaction discussed above for aldehydes and ketones.

(2) The numbering of compounds is the same as in ref 1.



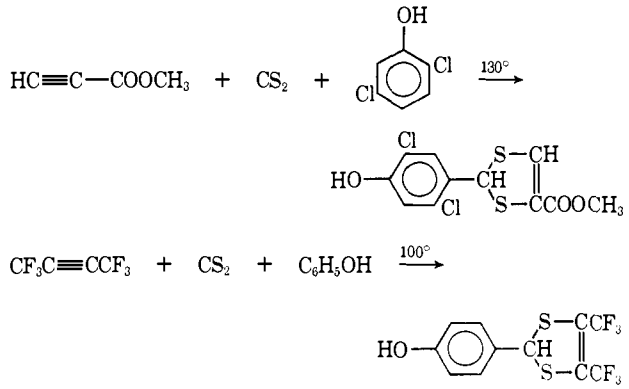
17



18

The mechanism of formation of **17** is not known, but a likely possibility would be nucleophilic attack of the 1,3-dithiolium carbene at the carbonyl carbon followed by a hydride shift.

Another type of alkylation reaction was observed with acetylenes, carbon disulfide, and phenols. This reaction evidently results from formation of the 1,3-



dithiolium carbene, protonation to give the corresponding cation, and a Friedel–Crafts type alkylation of the phenol (or phenolate ion). In some cases the addition of acid (such as trifluoroacetic acid) is needed to suppress the addition of the phenol to the acetylene.

The thermal carbon disulfide–acetylene reaction permits the investigation of a wide variety of reactions of a carbene which is probably unencumbered with solvent or other complexing materials.

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Stereochemistry of the Alkylation of Cobalt(I)

Sir:

In the first reported alkylations of vitamin B_{12s},[1] the reactions were formulated as additions to a cobalt hydride. Later it was proposed that B_{12s} is a nucleophilic Co(I) species and the alkylations are SN2 processes.[2] Recent evidence has shown that B_{12s} and the related cobaloxime(I) react with alkylating agents *via* bimolecular processes.[3] The variation in rate upon changing the alkylating agent is similar to that of known SN2 reactions. However, the mechanism cannot be considered established until the stereochemical fate of the reacting carbon is known.

We wish to report that the reaction of cobaloxime(I) with typical alkylating agents (epoxides, bromides, and

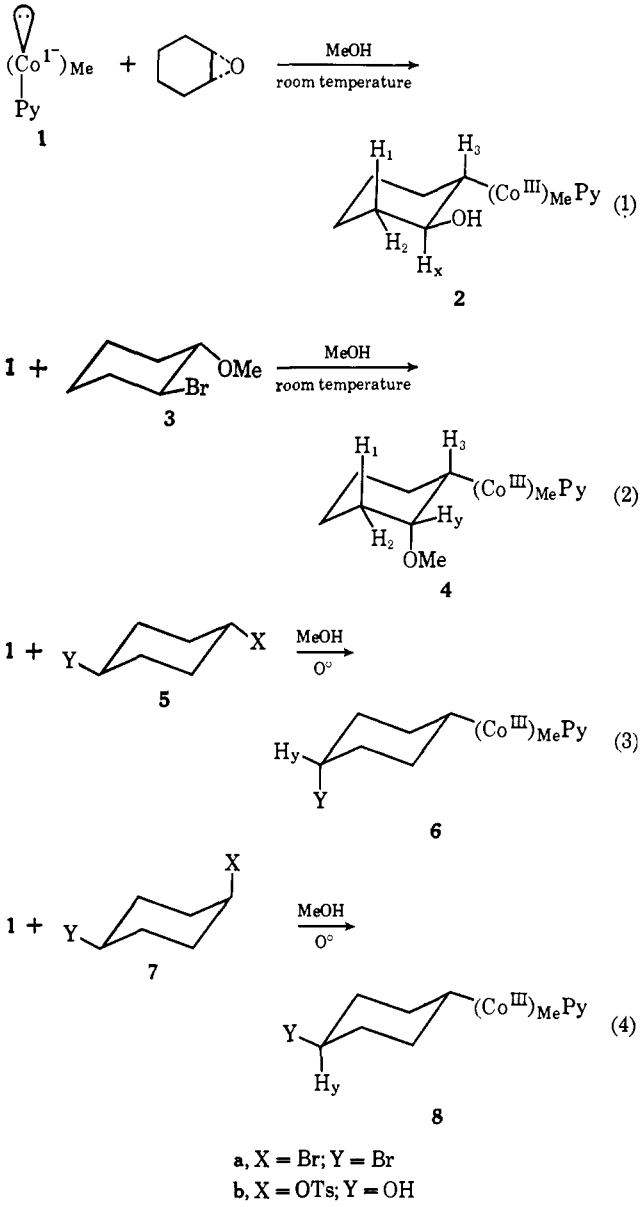
(1) (a) O. Müller and G. Müller, *Biochem. Z.*, 336, 299 (1962); (b) O. Müller and G. Müller, *ibid.*, 337, 179 (1964), (c) A. W. Johnson, L. Mervyn, N. Shaw, and E. L. Smith, *J. Chem. Soc.*, 4146 (1963).

(2) G. N. Schrauzer, R. I. Windgassen, and J. Kohnle, *Chem. Ber.*, 98, 3324 (1965).

(3) G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, 91, 3341 (1969).

tosylates) proceeds with inversion of configuration at carbon, unambiguously establishing the SN2 nature of this process.

Methanol solutions of pyridine[bis(dimethylglyoximato)]cobalt(I) (**1**)[4] were added, under nitrogen, to both 1,2- and 1,4-disubstituted cyclohexanes[6] to give substituted cyclohexylcobaloximes[7] (eq 1–4). The ir



spectra of the products confirm their gross structure but were of little use in assigning stereochemistry. The structures of **2**, **4**, **6**, and **8** were assigned on the basis of 100-MHz nmr spectra. For example, in deuteriochloroform **2** gave: δ 13.3 (broad s, 2 H, O–*H*··O), 8.7–7.1 (m, 5 H, Py), 2.90 (m, 1 H, O–C–*H*), 2.18 (s), and 2.14 (s) superimposed on a broad multiplet, 2.4–0.8 (total 22 H, ligand, hydroxyl, and ring protons). The

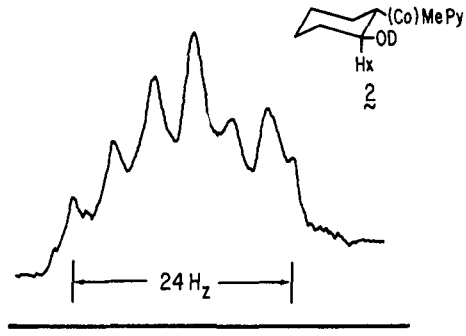
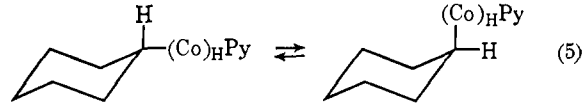


Figure 1. Nmr spectrum (100 MHz) of H_x from compound **2**; solvent $CDCl_3$, time average 61 scans, 1 Hz/sec.

nmr spectrum of **4** shows ($CDCl_3$): δ 13.3 (broad s, 2 H, O–*H*··O), 8.7–7.1 (m, 5 H, Py), 3.30 (s, 1 H, O–C–*H*), 3.16 (s, 3 H, OCH_3), 2.10 (s, 12 H, ligand CH_3), and 1.9–1.0 (m, 9 H, ring H).

To facilitate the structural determinations of the substituted cyclohexylcobalt compounds, the conformational preference ($-\Delta F$ for eq 5) was investigated. In the nmr spectrum of cyclohexylpyridine[bis(dimethylglyoximato)]cobalt(III), the α proton appears under the



resonances of the ligand methyl protons and two of the four β protons. In order to circumvent this difficulty, β,β,β′,β′-tetradeuteriocyclohexylpyridine(bisglyoximato)cobalt(III) was prepared. Its nmr spectrum was determined (pyridine-d_5–methylene chloride, 1:1) at 33° and intermediate temperatures to −88°. No change was observed in the shapes of the methine or other cyclohexyl proton resonances over this temperature range. This absence of a significant difference between the spectra under time-average and slow-exchange conditions[8] indicates the material exists primarily in one form (cobalt equatorial; *vide infra*).

From analysis of the nmr spectra of the H_x and H_y protons of **2** and **4** based on the known[8] behavior of axial and equatorial protons in substituted cyclohexanes, the configurations are assigned as follows. Expansion of the H_x signal of **2** (δ 2.90) reveals the multiplet shown in Figure 1. The corresponding proton in **4** (δ 3.30) appears as a broad singlet (11-Hz total width). The splitting pattern of H_x can only be explained by structure **2** while that of H_y indicates structure **4** with the conformations shown predominating. In **2**, the splitting pattern could vary from six ($J_{1,X} = J_{3,X} \neq J_{2,X}$) to eight lines ($J_{1,X} \neq J_{3,X} \neq J_{2,X}$). Since axial–axial coupling constants are larger (8–14 Hz) than axial–equatorial or equatorial–equatorial (1–7 Hz)[9] the pattern will be broad. The splitting in **4** may be complex but is not observed because the coupling constants are small.

(4) Trivial name: cobaloxime(I).[5] Compound **1** was prepared by sodium borohydride reduction of the Co(II) complex.[5]

(5) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968), and references therein.

(6) Prepared by standard routes. **3**: A. Iovchev, *Bulgar. Akad. Nauk.*, **2**, 67 (1965) (*Chem. Abstr.*, **64**, 11067 (1967)); **5a**, **7a**: C. A. Grob and W. Bauman, *Helv. Chim. Acta*, **38**, 594 (1955); **5b**, **7b**: L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 320 (1949).

(7) Satisfactory elemental analyses were obtained for all new compounds.

(8) (a) F. R. Jensen and B. H. Beck, *J. Am. Chem. Soc.*, **90**, 3251 (1968); (b) F. R. Jensen and C. H. Bushweller, *ibid.*, **91**, 3223 (1969); (c) C. H. Bushweller, Ph.D. Thesis, University of California, Berkeley, 1966; (d) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Am. Chem. Soc.*, **91**, 344 (1969).

(9) N. H. Bhacca and N. D. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco Calif., 1964, p 51.

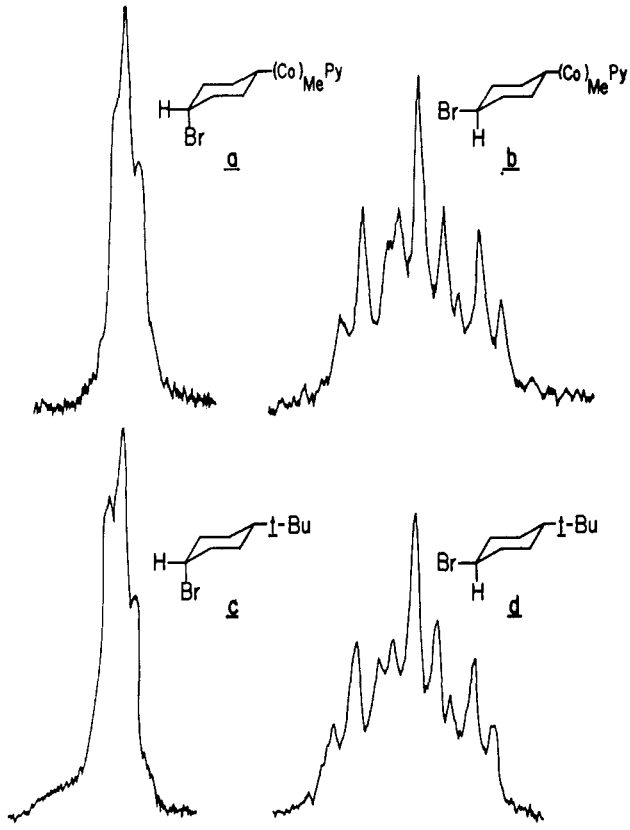


Figure 2. Nmr spectra (100 MHz) of the H_y–C–Br proton resonances in: (a) (*cis*-4-bromocyclohexyl)pyridine[bis(dimethylglyoximato)]cobalt(III); (b) the corresponding *trans*-cyclohexylcobalt compound; (c) *cis*-4-bromo-*t*-butylcyclohexane; and (d) *trans*-4-bromo-*t*-butylcyclohexane. The solvent was $CDCl_3$, 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 SN2 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

(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).