

mp 99–100° (lit.⁶ mp 100.5°), in nearly quantitative yield. Similarly, reaction of **1** with 2 equiv of benzophenone gave diol⁷ **2b**, mp 192–193°, in 50% yield, while carbonation with excess solid carbon dioxide produced dicarboxylic acid⁷ **2c**, mp 224–225°, in 74% yield. Next, the dimetalation of *m*-xylene, with *n*-amylsodium–TMEDA, was investigated. This compound had previously been dimetalated⁸ in low yield by heating with *n*-amylsodium in octane for 3 hr. Reaction of *m*-xylene with slightly over 2 equiv of *n*-amylsodium–TMEDA in hexane at room temperature for 2 hr produced the insoluble α,α' -disodio *m*-xylene in quantitative yield, as determined by subsequent quenching with deuterium oxide and quantitative nmr analysis. Treatment of the *m*-xylene dianion with an excess of methyl iodide afforded 1,3-diethylbenzene in excess of 90% yield. Vpc analysis of the crude reaction mixture showed only traces of the monocondensation product 1-ethyl-3-methylbenzene (**3**).

It is particularly interesting to note that 1,4-diazabicyclo[2.2.2]octane⁹ (DABCO) was found to have no catalytic effect on metalations with *n*-amylsodium in hexane. Thus, treatment of *m*-xylene with slightly over 2 equiv of *n*-amylsodium–DABCO followed by excess methyl iodide afforded a mixture of products consisting mainly of *m*-xylene and **3**.

In contrast to organolithium compounds whose complexes with a variety of chelating agents have been studied quite extensively,^{2,10} little is known about complexes involving organometallic compounds of the heavier alkali metals.¹¹ The catalytic effect of TMEDA in metalations with *n*-amylsodium may be attributed to complex formation between the amine and the organosodium reagent similar in nature to that occurring between alkyllithium reagents and tertiary aliphatic amines.^{2,10} Such complex formation would help disperse the large *n*-amylsodium aggregates¹² thereby providing a larger surface area for the metalation reaction to occur.

(6) H. S. Desai and B. D. Tilak, *J. Sci. Ind. Res., Sect. B*, **20**, 22 (1961).

(7) Satisfactory elemental analysis, ir, and nmr spectra were obtained for this new compound.

(8) A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., *J. Amer. Chem. Soc.*, **65**, 1339 (1943).

(9) DABCO was found to be almost as effective in catalyzing metalations with alkyllithium reagents^{2a} as TMEDA.

(10) (a) J. F. Eastham and G. W. Gibson, *J. Amer. Chem. Soc.*, **85**, 2171 (1963); (b) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963); (c) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964); (d) T. L. Brown, R. L. Geteis, D. A. Bafus, and J. A. Ladd, *ibid.*, **86**, 2134 (1964).

(11) C. J. Pedersen (private communication) has found that certain polyethers [C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967)] can form complexes with stabilized organosodium and organopotassium reagents, such as benzylsodium and benzylpotassium, but that the polyether ring is gradually decomposed by the organometallic compounds. It has also been recently reported [report appearing in *Chem. Eng. News*, **49** (24), 31 (1971)] that tetramethyl-1,2-cyclohexanediamine has a chelating effect on α -cumylsodium in cumene.

(12) A. A. Morton, "Solid Organoalkali Metal Reagents," Gordon and Breach, New York, N. Y., 1964, pp 5–6.

The present method, which involves the use of amines as catalysts in metalations with *n*-amylsodium (and presumably with other alkylsodium reagents) presents a significant advance over similar metalations with *n*-amylsodium alone or in the presence of certain other catalysts,¹ since it allows such reactions to proceed at very high yields, mild conditions, and short reaction time.

Acknowledgment. This research was supported in part by a Faculty Research Grant, Western Michigan University.

G. B. Trimitsis,* A. Tuncay, R. D. Beyer

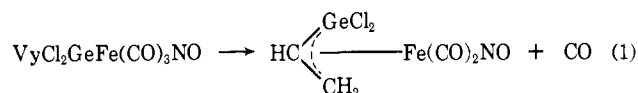
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Received December 10, 1971

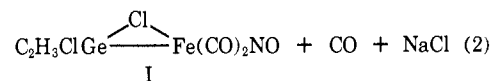
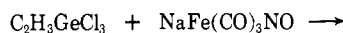
Halogen-Bridged Germanium–Metal Bonds and Germanium-Bridged Metal–Metal Bonds

Sir:

We recently attempted to prepare (vinylchloro-germyl)tricarbonylnitrosyliron, (C₂H₃)Cl₂Ge–Fe(CO)₃NO, hoping to cause a rearrangement to the π -germallyl analog¹



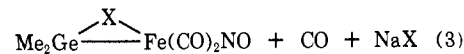
Instead of the expected product, a compound which we formulate as μ -chloro-(vinylchloro-germyl)dicarbonylnitrosyliron (*Fe–Ge*) (I, orange crystals, mp 47–48°) was formed in the reaction between NaFe(CO)₃NO and vinyltrichloro-germane.



To our knowledge this is the first compound of this type, although Graham and coworkers have observed an interaction between a chlorine bound to molybdenum and the tin atom of a similarly bound SnCl₃ group.²

The elemental analyses and mass spectrum support the empirical formula of I. *Anal.* Calcd for C₅H₃GeFeO₄NCl: C, 17.6; H, 0.89; Ge, 21.3; Fe, 16.4. Found: C, 17.8; H, 0.94; Ge, 21.6; Fe, 16.8. The mass spectrum has isotope patterns characteristic of Ge₁Fe₁ at *m/e* 313, 285, 257, and 227 representing the ions C₂H₃Cl₂GeFe(CO)_{*n*}NO⁺ (*n* = 2, 1, 0) and C₂H₃Cl₂GeFe⁺, respectively.

Compounds which we formulate with bridging halogen atoms are also formed in high yield when dimethyldibromogermane and dimethyldichlorogermane are treated with sodium tricarbonylnitrosylferrate (II, X = Cl, yellow needles, mp 55–62° dec; III, X = Br, orange crystals, mp 80–82°).



(1) R. C. Job and M. D. Curtis, submitted for publication.

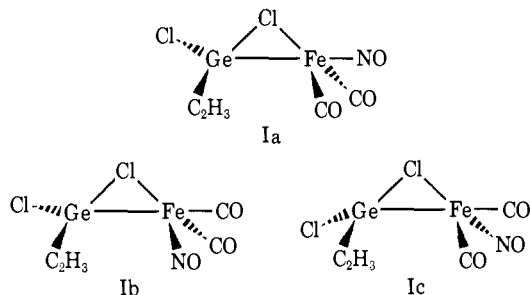
(2) M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Amer. Chem. Soc.*, **90**, 2189 (1968).

The nmr spectrum of I shows a typical vinyl ABC pattern centered around δ 6.2 ppm which is characteristic of uncomplexed vinyl groups. The nmr spectra of II and III each show a single, very sharp, methyl resonance at 1.18 and 1.45 ppm, respectively.

The infrared spectra of $R_3GeFe(CO)_3NO$ compounds show three strong CO stretching bands in the region 2100–1950 cm^{-1} and one strong NO stretch at about 1790 cm^{-1} .³ If it is assumed that the iron is trigonal bipyramidal with the germanium substituent axial,⁴ then these compounds exist in one isomeric form with the NO group in an equatorial position. The ir spectra of the halogen-bridged species, I–III, are quite different and suggest the presence of more than one isomer.

$Me_2ClGeFe(CO)_2NO$ has strong ν_{CO} absorbances at 2082, 2028, 1997, and 1990 cm^{-1} , and strong ν_{NO} peaks at 1797 and 1777 cm^{-1} . The presence of two ν_{NO} peaks suggests the presence of two isomers in which the NO group is "axial" or "equatorial." Each isomer should give two ir-active carbonyl bands for a total of four, as observed.

The spectrum of $C_2H_5Cl_2GeFe(CO)_2NO$ (I) is more complicated since, in this case, there can be a total of three isomers (Ia–c). Isomers Ib and Ic differ only in



having the nitrosyl cis and trans, respectively, to the vinyl group. We thus expect the ν_{CO} and ν_{NO} stretching frequencies of these two isomers to be very similar but rather different from isomer Ia, in which the nitrosyl is "axial." The observed frequencies are 2095, 2074, 2051, 2044, 2022, 2013 cm^{-1} (ν_{CO}), and 1819, 1804 cm^{-1} (ν_{NO}). The expected third nitrosyl band is apparently not resolved. The small differences between the doublets 2051–2044 and 2022–2013 suggest that these frequencies are the symmetric and asymmetric modes of isomers Ib and Ic.

The existence of isomers on the ir time scale, but the presence of single methyl or vinyl resonances in the nmr, indicates that these compounds are fluxional on the nmr time scale at room temperature.

We have attempted to prepare other halogen-bridged germanium–metal bonds by the uv photolysis (low-pressure Hg lamp) of the following compounds: $Me_2ClGeMn(CO)_5$ (mp 71–73°; ν_{CO} 2100 ms, 2035 m, 2005 vs, 1970 w), $Me_2ClGeCo(CO)_4$,⁷ and $Me_2ClGeFe(CO)_2Cp$ (mp 69.5–71.5°; ν_{CO} 2000 vs, 1975 sh, 1962 vs). Upon irradiation, these compounds lose halogen and

(3) A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, C. D. M. Mann, and R. J. O'Brien, *J. Chem. Soc. A*, 736 (1971).

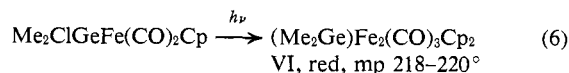
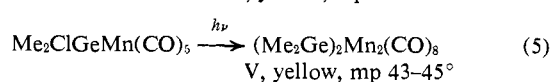
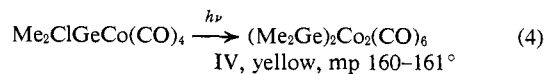
(4) $Fe(CO)_5NO$ is isoelectronic with $Co(CO)_5$, and one expects the germanium or silicon derivatives to have similar structures.^{5,6}

(5) A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 686 (1967).

(6) J. K. Stalick and J. A. Ibers, *J. Organometal. Chem.*, **22**, 213 (1970).

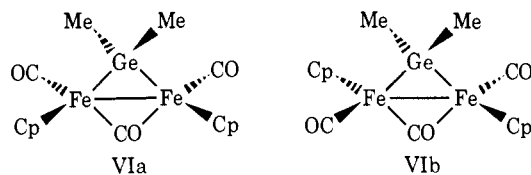
(7) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

form compounds in which a dimethylgermylene (Me_2Ge) group replaces a carbonyl.⁸



The stoichiometry of compounds IV–VI are firmly established by mass spectral and elemental analyses.

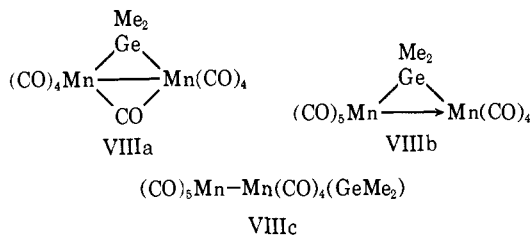
The nmr spectrum of VI shows that this compound was isolated as a 4:1 mixture of cis and trans isomers VIa,b. The cis isomer has nonequivalent methyl groups, whereas these groups are equivalent in the trans isomer (cis, δ 1.5, 1.3 (CH_3), 4.1 (C_5H_5); trans, δ 1.4 (CH_3), 4.3 (C_5H_5) ppm downfield from TMS).



Complexes with single dimethylgermylene groups are produced when bis(metal carbonyl)dimethylgermanes are exposed to uv radiation. The products formed in the photolyses of $Me_2Ge[Co(CO)_4]_2$,⁷ $Me_2Ge[Mn(CO)_5]_2$ (mp 78–79.5°; ν_{CO} 2105 m, 2080 s, 2045 m, 2010–2000 doublet, vs, 1985 s, and 1955 m cm^{-1}), and $Me_2Ge[Fe(CO)_2Cp]_2$ (mp 121–124°; ν_{CO} 2008 w, 1999 m, 1987 s, 1951 w, 1941 s) are, respectively, $Me_2GeCo_2(CO)_7$ (VII) (mp <20°; ν_{CO} 2085 s, 2047 vs, 2024 vs, 2006 vs, 1998 sh, 1971 w, 1844 s), $Me_2GeMn_2(CO)_9$ (VIII) (mp 143–144°; ν_{CO} 2100 w, 2060 ms, 2010 s, 1920 ms, 1835 vw), and $Me_2GeFe_2(CO)_3Cp_2$ (cis ν_{CO} 1980 s, 1941 m, 1788 s; trans ν_{CO} 1955, 1946, 1791 cm^{-1}).

The series, $Co_2(CO)_8$, $(Me_2Ge)Co_2(CO)_7$, and $(Me_2Ge)_2Co_2(CO)_6$, are structurally related by the successive replacement of one and two bridging carbonyl groups by Me_2Ge groups. Adams and Cotton⁹ have shown that IV is fluxional on the nmr time scale at room temperature.

The structures of complexes V and VIII are less certain. Dimanganese decacarbonyl does not have bridging carbonyls, and the ir spectrum of VIII shows only a very weak, broad peak at 1835 cm^{-1} in the bridging CO region. The low intensity of the 1835-



(8) Compounds containing R_2Ge bridging groups have been prepared by other methods: E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Amer. Chem. Soc.*, **90**, 3587 (1968); M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1424 (1969); S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *Chem. Commun.*, 1297 (1969); E. H. Brooks and R. J. Cross, *Organometal. Chem. Rev.*, **6**, 227 (1970).

(9) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **92**, 5003 (1970).

cm⁻¹ peak suggests that Me₂GeMn₂(CO)₈ exists in solution as a mixture of tautomers.

The presence of seven-coordination in VIIIa may render this isomer unstable with respect to the other two which contain the preferred octahedral coordination about manganese. However, at present we are unable to distinguish between isomer VIIIb, with a dative Mn-Mn bond, and VIIIc which has a terminal dimethylgermylene group. A terminal Me₂Ge group would presumably be bound to manganese in much the same way that carbenes are bound to transition metals.¹⁰

The complexity of the ir spectrum of V eliminates the most symmetric structure, *trans,trans*-(Me₂Ge)(CO)₄-Mn-Mn(CO)₄(GeMe₂), but does not allow a choice between less symmetric nonbridged structures or the seven-coordinate structure with two dimethylgermylene bridges.

We are currently extending these studies to include tin derivatives in the hope of obtaining analogous tin complexes.¹¹

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(10) E. Moser and E. O. Fischer, *J. Organometal. Chem.*, **13**, 209 (1969); E. O. Fischer and A. Maasböl, *ibid.*, **12**, P15 (1968).

(11) After submission of this manuscript, Cleland,¹² *et al.*, reported the preparation of Ph₂SnFe₂(CO)₃Cp₂.

(12) A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *J. Organometal. Chem.*, **32**, C15 (1971).

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Received October 19, 1971

The Bishomoconjugative α -Halo Ketone Rearrangement as a Route to Bicyclo[4.2.1]nona-2,4,7-trien-9-one and Barbaralone Derivatives

Sir:

We have examined the behavior of α -bromo ketones of general formula **2** under strongly basic conditions (KO-*tert*-Bu) in a polar aprotic medium (DMSO) at room temperature (25°) and have realized fascinating skeletal rearrangement (termed for simplicity the bishomoconjugative α -halo ketone rearrangement¹) to bicyclo[4.2.1]nona-2,4,7-trien-9-ones (**3**).

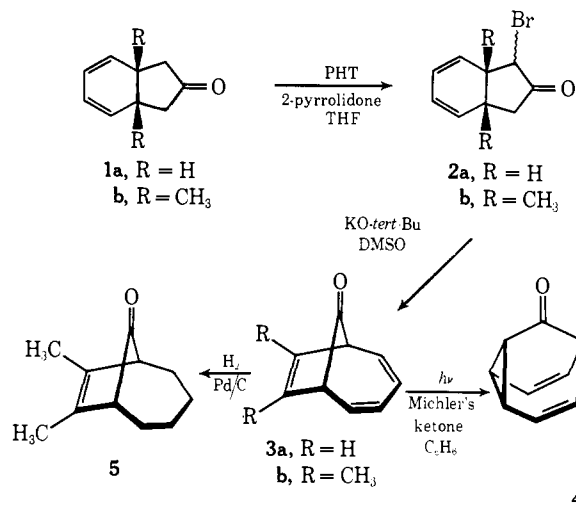
The reaction of **1a** (semicarbazone, mp 186–188° dec²) with pyrrolidone hydrotribromide (PHT, 1 equiv) in anhydrous tetrahydrofuran containing 2-pyrrolidone (1 equiv)³ resulted chiefly in selective α bromination and formation of **2a**. Without purification, **2a** was exposed to the stipulated basic conditions (15 min) and there was obtained ketone **3a** in 10–30% overall yield after vpc isolation. The product was identified by direct comparison with an authentic sample prepared according to the excellent method of Antkowiak, *et al.*;⁴ **3a** is also of

(1) As derived from the presumed intervention of bishomobenzene intermediates. See: (a) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *J. Amer. Chem. Soc.*, **93**, 1047 (1971), and pertinent references cited therein; (b) H. W. Whitlock, Jr., and P. F. Schatz, *ibid.*, **93**, 3837 (1971); (c) D. L. Dalrymple and S. P. B. Taylor, *ibid.*, **93**, 7098 (1971).

(2) All indicated new compounds gave elementary analysis results within 0.3% of theory. The ketones of general structure **1** and **3** are intrinsically unstable and in those instances where derivatives were not prepared, accurate mass measurements were obtained.

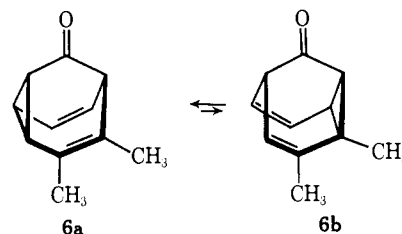
(3) D. V. C. Awang and S. Wolfe, *Can. J. Chem.*, **47**, 706 (1969).

interest in that it undergoes efficient photosensitized (Michler's ketone) isomerization to barbaralone (**4**).⁵ Similar processing of **1b** (semicarbazone, mp 205–206° dec²) afforded **3b** (16% overall) as a low melting solid, semicarbazone mp 212–214° dec.² The structural assignment to **3b** follows convincingly from: (a) its nmr



spectrum in CDCl₃ which displays a four-proton multiplet at δ 5.68–5.97 (olefinic), a two-proton multiplet in the 2.80–3.17 region (bridgehead), and a singlet of area 6 at 1.77 for the methyl groups; (b) the ultraviolet spectrum (isooctane) which is characteristic of this chromophore (λ_{\max} 218 (ϵ 2040), 273 (1910), 283 (1840), and 322 nm (580)); (c) the mass spectrum m/e 160.0885 (calcd 160.0888); (d) its conversion upon direct photolysis (2537 Å, ether) to 1,2-dimethylcyclooctatetraene (85%);^{1a,7} and (e) its selective catalytic hydrogenation to **5** (m/e calcd 164.1201; obsd 164.1199), dinitrophenylhydrazones mp 114–116°.² In the nmr spectrum of **5**, there were displayed two allylic bridgehead protons as a multiplet centered at δ 2.75, a singlet of area 6 at 1.67 for the sp²-bound methyl groups, and a broad eight-proton envelope at 1.35–1.70.⁸

Sensitized irradiation of **3b** as above afforded dimethylbarbaralone **6** (m/e calcd 160.0888; obsd 160.0885). Equilibrium data as derived from nmr spectra of this ketone over the temperature range –80 to +40° established that isomer **6a** is substantially (>85%) pre-



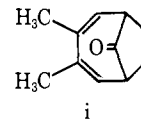
(4) T. A. Antkowiak, D. C. Sanders, J. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, in press; T. A. Antkowiak, Ph.D. Thesis, The Ohio State University, 1968.

(5) Yields of **4** range from 68% to 79%.⁶

(6) We thank Dr. M. J. Broadhurst for this experiment.

(7) Direct photolysis of **3a** has also been found to yield cyclooctatetraene and carbon monoxide.^{4,6}

(8) In particular, this catalytic reduction serves to exclude **i** and re-



lated positional isomers as alternate structural possibilities for **3b**.