cm^{-1} peak suggests that Me$_2$GeMn$_2$(CO)$_9$ 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 Me$_2$Ge 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*-(Me$_2$Ge)(CO)$_4$-Mn–Mn(CO)$_4$(GeMe$_2$), 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.

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(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 Ph$_2$SnFe$_2$(CO)$_3$Cp$_2$.

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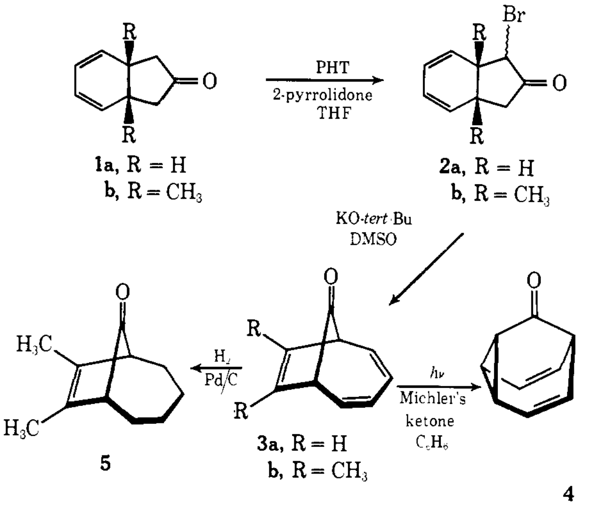
The Bishomoconjugative α-Halo Ketone Rearrangement as a Route to Bicyclo[4.2.1]nona-2,4,7-trien-9-one and Barbaralone Derivatives

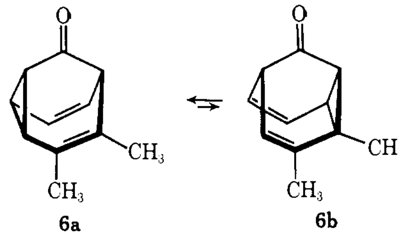
Sir:

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 rearrangement[1]) to bicyclo[4.2.1]nona-2,4,7-trien-9-ones (**3**).

The reaction of **1a** (semicarbazone, mp 186–188° dec[2]) 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 interest in that it undergoes efficient photosensitized (Michler's ketone) isomerization to barbaralone (**4**).[5] Similar processing of **1b** (semicarbazone, mp 205–206° dec[2]) 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 CDCl$_3$ 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), dinitrophenylhydrazone 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 sp^2-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-



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(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).

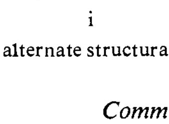
(4) T. A. Antkowiak, D. C. Sanders, J. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, in press; T. A. Antkowiak, Ph.D. Thesis, The Ohio State University, 1968.

(5) Yields of **4** range from 68[4] 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]

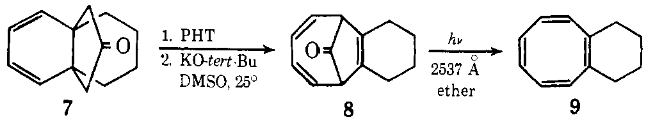
(8) In particular, this catalytic reduction serves to exclude i and related positional isomers as alternate structural possibilities for **3b**.



i

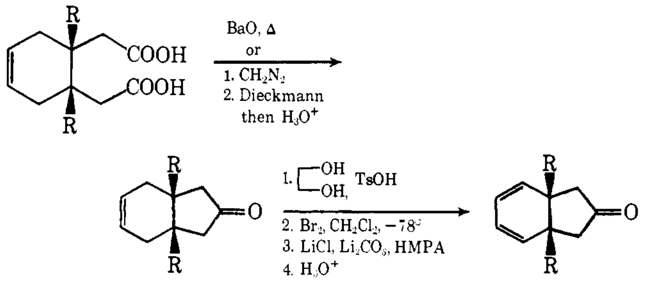
ferred over **6b**. Our data again attest to the substantial preference of a methyl substituent for bonding to sp^2- rather than sp$^{2.3}$-hybridized carbon.[9,10]

Selective bromination of **7**[2] with PHT and direct reaction of the α-bromo ketone with base led to the isolation of **8** (*m/e* calcd 186.1044; obsd 186.1042) in 24% yield after preparative vpc. This substance was shown to possess extended conjugation by the ultraviolet spectrum [$\lambda_{\max}^{\text{isooctane}}$ 217 sh (ϵ 2590), 273 (1410), 283 (1380), and 318 nm (390)] and a strained carbonyl group (1780 cm^{-1}). These spectral features in combination with the nmr data [$\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.75 (m, 4, olefinic), 2.82–3.07 (m, 2, bridgehead), 1.85–2.35 (m, 4, allyl), and 1.67 (br s, 4, methylenes)] and the ready photodecarbonylation to **8**[1a,7] support the structural assignment.

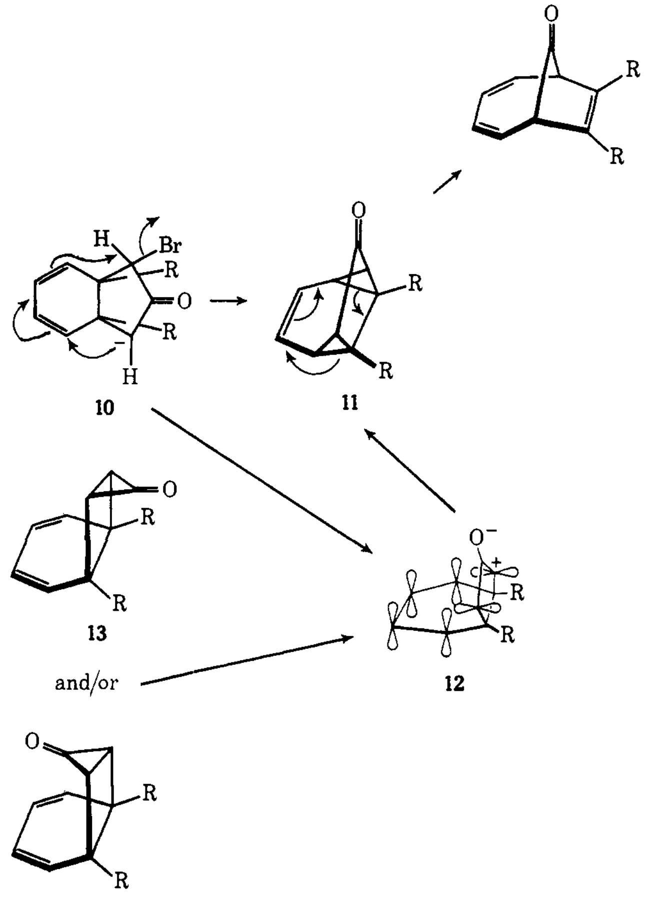


7 **8** **9**

The general method of synthesis of ketones **1a**, **1b**, and **6** is outlined below. In each of the rearrangements studied, no secondary products were detected. The bicyclo[4.2.1]nonatrienones were frequently contaminated, however, with small amounts of residual starting material as a result of incomplete bromination.[11]



With regard to mechanism, the bishomoconjugative α-halo ketone rearrangement is most plausibly rationalized in terms of a dicyclopropyl ketone intermediate of general formula **11**.[1] This strained species may result from: (a) intramolecular [4 + 3] cycloaddition of symmetrical oxyallyl zwitterion **12**, a process which could be concerted since oxyallyl is an electrophilic 2π fragment;[12] (b) vinylogous S$_N$2′ intramolecular displacement of bromide ion by the enolate anion (*cf.* arrows in **10**); and (c) prior generation of cyclopropanones **13** and/or **14** and their direct or indirect (*via* **12**) conversion to **11**.



10 **11** **12** **13** **14**

Although combined experimental evidence presently does not permit a definitive distinction between these alternatives, the *direct* conversion of **13** and **14** to **11** appears least likely for several reasons. Granted that cyclopropanone and its simple derivatives are decidedly cyclic in nature,[13] theoretical and thermodynamic considerations suggest that significant concentrations of the corresponding planar acyclic oxyallyls may exist in mobile equilibrium with the three-membered ring.[14] This concept gains credence from past studies of the Favorskii rearrangement which have demonstrated that the use of polar media (which should promote zwitterion formation) leads to significant losses of stereochemistry.[15] Such findings have led to the current belief that the detailed nature of the Favorskii process as it relates to the generation of specific intermediates will vary with reaction conditions.[16] In the present instance, not only should solvation by DMSO favor **12** over **13** and **14**, but the severe ring strain associated with the bicyclopentanone part structure in the latter molecules will certainly demand relief, particularly in view of the gain in resonance energy which can be acquired in proceeding to **12**. Also, only **14** would presumably be capable of intramolecular cycloaddition since inside approach to the bicyclopentane flap appears necessary.[17] But overlap of the cyclopropyl bond in **14** with the diene p orbitals is significantly inferior to that existing in **12**.[18]

From the synthetic viewpoint, utilization of the bishomoconjugative α-halo ketone rearrangement should permit access to bicyclo[4.2.1]nonatrienones and barbaralones whose preparation could not previously be realized.

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(9) J. C. Barborak, S. Chari, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 5275 (1971).

(10) G. Schroder and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **6**, 414 (1967); L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 5296 (1969).

(11) Attempts to improve this situation by utilization of somewhat greater than 1 mol equiv of PHT were not successful. All yields quoted herein do not reflect the quantity of starting ketone recovered which ranged from 10 to 25%.

(12) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(13) (a) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *ibid.*, **90**, 1072 (1968); (b) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(14) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(15) H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965), and pertinent references cited therein.

(16) N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **87**, 3258 (1965).

(17) P. G. Gassman, *Accounts Chem. Res.*, **4**, 128 (1971).

(18) The electron density of oxyallyl has been calculated: J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

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1,2-Alkyl Shift, from Carbon to Positive Nitrogen, in Simple, Open-Chain *N*,*N*-Dichloroalkylamines

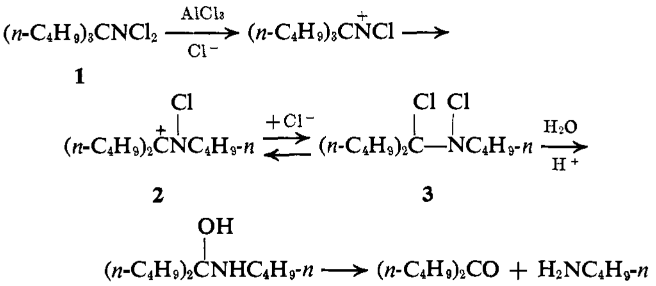
Sir:

1,2-Alkyl shifts from carbon to carbon[1a] and from carbon to oxygen[1b] involving electron-deficient species are well established for uncomplicated alkyl structures. However, apparently no analogous situation has been observed for rearrangement from carbon to positive nitrogen arising from an *N*-halamine. Examples in this category which are reported[2,3] contain mono-, bi-, or tricyclic units characterized by some degree of strain, usually quite appreciable. The Stieglitz rearrangement,[2] believed to fit in this general class, entails migration of an aryl group.

We now present the first examples of 1,2-alkyl shift from carbon to electron-deficient nitrogen generated from simple, open-chain *N*-halamines. The reactions proceeded quite cleanly in high yields. Treatment of *N*,*N*-dichlorotri-*n*-butylcarbinamine (**1**) with aluminum chloride gave a rearranged product which was converted to *n*-butylamine (84% yield) and di-*n*-butyl ketone (94% yield) on exposure to aqueous acid. Similarly, *N*,*N*-dichlorodi-*n*-butyl-*sec*-butylcarbinamine formed *sec*-butylamine (51% yield) and *n*-butylamine (46% yield), along with di-*n*-butyl ketone (55% yield) and *n*-butyl *sec*-butyl ketone (43% yield).

By analogy to prior mechanistic interpretations,[2,3] the reaction is thought to take place according to the indicated pathway (Scheme I).

Scheme I



In the absence of catalyst, rearrangement was negligible. There is little basis for comment concerning the synchronous *vs.* stepwise nature of the migration. Rearranged product might be in the form of either **2** or **3**. The similarity in the ratio of *sec*-butylamine:*n*-butylamine (1.1) to the ratio of di-*n*-butyl ketone:*n*-butyl *sec*-butyl ketone (1.3) from *N*,*N*-dichloro-di-*n*-butyl-*sec*-butylcarbinamine supports the proposed scheme, as does the close correspondence in yields of *n*-butylamine and di-*n*-butyl ketone from **1**. The order of migratory aptitudes, *sec*-butyl:*n*-butyl = 2.2 (statistically corrected), is also in keeping with the mechanistic approach.

Our investigation of the open-chain types is continuing. The indicated procedure was followed. **1** was obtained by chlorination[4] (1 hr) of tri-*n*-butylcarbinamine.[5] A mixture of crude **1** (~0.025 mol) and aluminum chloride (0.05 mol) in 60 ml of methylene chloride was stirred at −30° for 1.5 hr. After addition of concentrated hydrochloric acid, solvent was removed *in vacuo*. Steam distillation gave ketone product in the volatile fraction. Extraction of the residue with methylene chloride provided minor amounts of starting amine hydrochloride and intractable solid. The aqueous acid portion was made basic and distilled into acid for the isolation of *n*-butylamine.

Di-*n*-butyl-*sec*-butylcarbinamine, bp 75.5° (0.28 mm), prepared according to the procedure[5] for the tri-*n*-butyl analog, was characterized by ir and nmr spectra and elemental analyses.

Yields are based on the *N*,*N*-dichloramine with the assumption of minor contamination by *N*-chloramine.

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(1) (a) Y. Pocker, *Mol. Rearrangements, 1963–1964*, 1 (1963); (b) P. A. S. Smith, *ibid.*, 457 (1963).

(2) P. G. Gassman, *Accounts Chem. Res.*, 3, 26 (1970).

(3) P. Kovacic, J.-H. Liu, E. M. Levi, and P. D. Roskos, *J. Amer. Chem. Soc.*, **93**, 5801 (1971); P. Kovacic, M. K. Lowery, and P. D. Roskos, *Tetrahedron*, **26**, 529 (1970).

(4) See procedure for 1-*N*,*N*-dichloroaminoadamantane: P. Kovacic and P. D. Roskos, *J. Amer. Chem. Soc.*, **91**, 6457 (1969).

(5) N. Sperber, D. Papa, and E. Schwenk, *ibid.*, **70**, 3091 (1948); N. Sperber and R. Fricano, *ibid.*, **71**, 3352 (1949).

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