# Substituent Effects on the Regioselectivity of C–H Insertion Arising during Stereospecific Intramolecular Cyclization of 7-Norcaranylidenes

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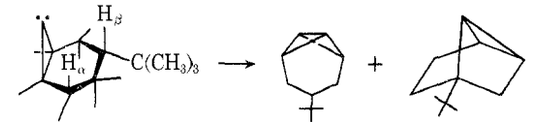
A number of 7,7-dibromo-2-methoxynorcaranes were prepared by addition of dibromocarbene to selected 3-methoxycyclohexenes. The reaction of these dibromides with ethereal methyllithium leads to intramolecular carbenoid insertion with formation of 3-methoxytricyclo[4.1.0.$0^{2,7}$]heptanes and *endo*-2-methoxytricyclo[4.1.0.$0^{3,7}$]-heptanes. The results require that the 7-norcaranylidenes undergo C–H bond insertion *via* that conformation in which the 2-methoxyl substituent is axially disposed. For comparison purposes, the behavior of the *cis*- and *trans*-3-methoxyl- and 3-methyl-7-norcaranylidenes was also examined. To accommodate the high levels of C–$H_\beta$ reactivity in the 2-methoxyl series, it is proposed that neighboring ether oxygen participation gains importance in an effort to offset developing electron deficiency at $C_3$. All insertions are necessarily stereospecific and the role of conformational factors on the regioselectivity of these processes is presented. Electronic effects are also important, the 2-methoxyl group deterring attack at the geminal C–H bond because of its electronegativity influence on the bond nucleophilicity.

The capability of organolithium reagents to produce carbenoid intermediates when allowed to react with *gem*-dihalides has been amply documented in recent years.[2] In the specific instance of 1,1-dibromocyclopropanes, the $\alpha$-bromocyclopropyllithium intermediate or the cyclopropylidene derived therefrom is capable of affording allenes[3] or products of intramolecular capture depending upon the structural elements of the molecule. If a suitably positioned double bond is available, spiropentane formation occurs.[4] In systems where ring opening to an allene is deterred for reasons of excessive product strain and/or lack of a suitable driving force for cyclopropane bond rupture, intramolecular C–H insertion becomes kinetically dominant.[5]

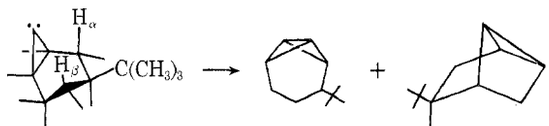
A relevant example is the carbenoid **2**, which has been shown not to experience ring opening to **3** prior to undergoing C–H insertion with formation of **4** and **5**.[5e,6] This finding contrasts markedly with the behavior of dibromide **6**, which reacts with methyllithium to give 1,2-cyclohexadiene (**7**) exclusively;[7] this reactive intermediate undergoes subsequent conversion to dimers and tetramers. Since the related [5.1.0] bicyclic molecule likewise is prone to ring opening (at least partially) with formation of 1,2-cyclooctadiene,[8] it is seen that the reactivity of **2** is somewhat anomalous. As Moore has pointed out,[5e] intermediate **2** is a species which possesses two characteristics not available simultaneously to the [3.1.0] and [5.1.0] bicyclic systems: (1) unlike the higher homolog, conversion to the orthogonal allene is not possible because of the highly strained nature of **3**; (2) unlike the lower homolog, the [4.1.0] carbenoid (the parent 7-norcaranylidene) lacks sufficient ground-state strain to promote ring opening despite the instability of the allene.

As a result of the unique reactivity profile of **2** and 7-norcaranylidenes in general,[5e,f,9] these chemical entities provide a unique opportunity to assess the influence of a number of conventional factors on competitive intramolecular C–H insertion reactions of carbenoids. The situation is illustrated in the case of **2** (shown as **2b** for simplicity in depiction) which very likely exists as a pair of rapidly equilibrating half-chair conformers (**8a** and **8b**).[5e] As with the simpler cyclohexane models, interconversion of these isoenergetic conformational isomers results in interchange of the axial and equatorial environments of the C–H bonds. Inspection of molecular models reveals that all equatorially disposed hydrogens are decidedly too remote from the carbenoid center to permit ready insertion, and therefore that axial C–H bonds are involved during intramolecular cyclization. However, in the parent system, the presumably rapid stereomutation between **8a** and **8b** does not perturb the statistical distribution of one $\alpha$ ($H_5$ in **8a**, $H_2$ in **8b**) and one $\beta$ hydrogen ($H_3$ in **8a**, $H_4$ in **8b**) of axial disposition. Evidence has been obtained[5a] that **2** reacts to give a predominance of **4** over **5** (*ca.* 23:1). Thus there exists a sizable kinetic preference for C–$H_\alpha$ insertion in the structurally unbiased carbenoid.

When the conformation of the 7-norcaranylidene is "fixed" by appropriate *tert*-butyl substitution as in **9** and **10**, the $H_\alpha/H_\beta$ selectivity, equivalent to bicyclobutane *vs.* bicyclopentane formation, undergoes noteworthy modification.[5e] The trans isomer **9** affords a mixture of hydrocarbons **11** and **12** in a ratio of 1:1.5. There is clearly an appreciable enhancement of selectivity toward $H_\beta$ which is believed[5e] to arise primarily from the added inductive contributions of the *tert*-butyl substituent. Cis isomer **10** in contrast undergoes insertion at relative rates such that bicyclobutane production (**13**) again dominates over that of bicyclopentane **14** by a factor of 22. It would appear on this basis that the *tert*-butyl group in **10** does not affect appreciably the conformation adopted by the unsubstituted compound.



9 11 12

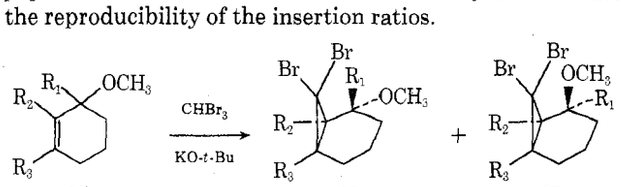


10 13 14

This is of course a rather skeletal assessment of the situation. It appeared that other phenomena which could affect the selectivity of such reactions had to be considered before reasonably accurate mechanistic comprehension of the process was realized. This paper, therefore, describes a study of the regioselectivity of intramolecular C–$H_\alpha$/C–$H_\beta$ carbenoid insertion reactions in 7-norcaranylidenes possessing methoxyl and methyl groups at $C_2$ and $C_3$ (*cf.* 8 for numbering). The perturbations introduced by the electronegative substituent were expected to be rather large yet not necessarily similar in direction to those of the methyl (or *tert*-butyl) substituent, depending upon inductive and resonance contributions which it remained to evaluate.

## Results

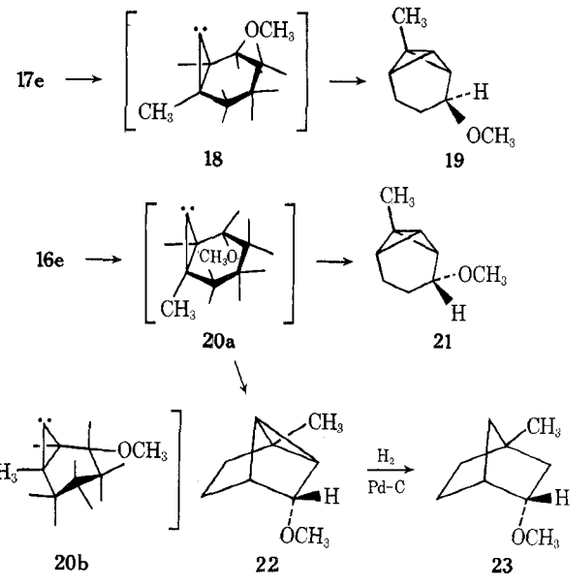
Preparation of the compounds selected for study was effected by a method modeled on the synthesis of dibromide **1**, bolstered by the observation of Seyferth and Mai[10] that high levels of stereoselectivity were realized upon reaction of 3-methoxycyclohexene with phenyl(bromodichloromethyl)mercury. In our hands, treatment of the variously substituted methoxy olefins **15** with dibromocarbene generated from bromoform and potassium *tert*-butoxide likewise gave rise in each case to one major product by far. In no instance was greater than 5% of cis isomers **17** formed. The structural assignments to **16** were made by analogy to those of Seyferth and Mai in the dichloro series and are supported by extensive pmr data (Table I). Of the seven examples studied, three (**16a, 16d,** and **16e**) are of primary importance in the present context. The four deuterated substrates were required for the program described in another paper[11] and are included herein because they demonstrate the reproducibility of the insertion ratios.



15 16 17

**a**, $R_1 = R_2 = R_3 = H$
**b**, $R_1 = D$; $R_2 = R_3 = H$
**c**, $R_1 = R_2 = H$; $R_3 = D$
**d**, $R_1 = R_3 = H$; $R_2 = CH_3$
**e**, $R_1 = R_2 = H$; $R_3 = CH_3$
**f**, $R_1 = D$; $R_2 = H$; $R_3 = CH_3$
**g**, $R_1 = H$; $R_2 = D$; $R_3 = CH_3$

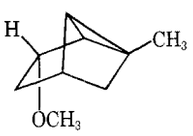
Reaction of **16e–17e** (95:5)[12] with methyllithium in ether at −30° afforded in 68% yield a mixture consisting chiefly of **19** (5%), **21** (67%), and **22** (28%). These products were separated by preparative vpc methods and identified as the compounds indicated on the basis of their spectral properties (Table II) and chemical evidence. For example, the very characteristic pmr features of **22**, particularly the low-



18 19 20a 21 20b 22 23

field quartet ($J_{1,2}$ = 2.5 and $J_{2,3}$ = 7.5 Hz) due to the >CHO– proton, characterizes the substance as an *endo*-2-methoxytricyclo[4.1.0.$0^{3,7}$]heptane derivative.[13] Independent confirmation of structure **22** was derived from catalytic hydrogenation over Pd/C in ethanol at 1 atm exclusively to *endo*-1-methyl-3-methoxynorbornane (**23**). Tricycloheptanes **19** and **21** show complex pmr patterns which are strikingly similar to those of related molecules in the high-field region.[5f,9,14] In particular, both ethers display multiplets (1 H each) at approximately $\delta$ 2.4 and 2.1 assignable to the two dissimilar "wing" protons and in the $\delta$ 1.0 region due to the bridgehead hydrogen. The stereochemistry of **19** and **21** follows from the recognized stereospecificity of such carbenoid insertion reactions;[5e,9b,c] the epimeric relationship of the two isomers is recognized spectroscopically by the great similarity of their pmr spectra except for the $C_1$ methyl singlet signals (in $C_6D_6$) which in **19** appears $\delta$ 0.04 upfield to the corresponding absorption in **21**. As expected for the tricyclo[4.1.0.$0^{2,7}$]heptane nucleus, catalytic hydrogenation of **21** under conditions identical with those utilized for **22** led to the consumption of 1.91 equiv of hydrogen with formation of four products identified as $C_9H_{18}O$ isomers by accurate mass spectral measurements.

These results establish that 7-norcaranylidene **18** undergoes intramolecular insertion chiefly into $H_\alpha$. Clearly it is not possible to rule out completely the $H_\beta$ insertion pathway because of the low concentration of **17e** in the dibromide mixture. However, because **17e** is present to the extent of 5% in the starting material and **19** comprises 5% of the total reaction mixture, internal consistency requires that a high preference for bicyclobutane formation be operative. Such regioselectivity is not encountered with **20,** which is seen to exhibit a $H_\alpha/H_\beta$ selectivity of only 2.4. Strikingly, attack at the C–$H_\alpha$ bond adjoining the methoxyl substituent does not operate.[15] Also, in that half-chair conformation (**20b**) in which the methoxyl group is equatorially disposed, the remaining $H_\alpha$ is likewise oriented in the equatorial plane and consequently lacks adequate proximity for reaction with the carbenoid center. Moreover, were the lone axial $H_\beta$ present in conformation **20b** to undergo intramolecular transfer to $C_7$, ether **24** would result and this is not



24

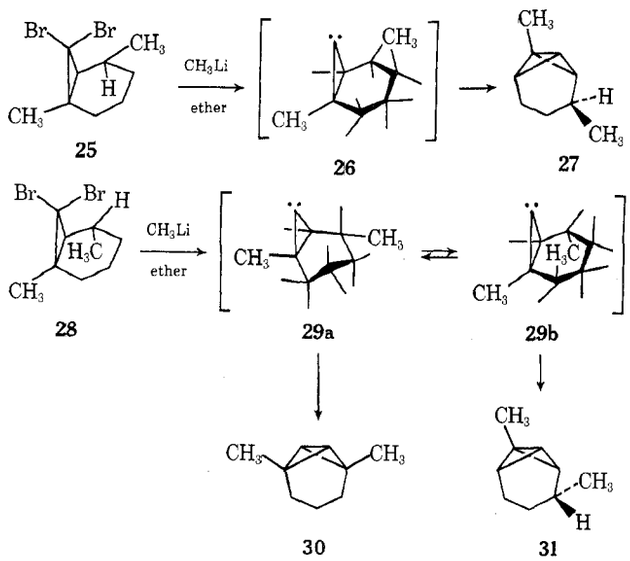
**Table I**
**Physical Data for the 7,7-Dibromo-2-methoxybicyclo[4.1.0]heptanes**

| Compd | Bp, °C (mm) | Pmr, δ (CDCl3, 60 MHz) | Anal. data |
|---|---|---|---|
| **16a** | 97–107 (0.8) | 3.44 (s, 3, $-OCH_3$), 3.44–3.10 (m, 1, >CHO–), and 2.33–1.00 (m, 8)[a] | Calcd for $C_8H_{12}Br_2O$: C, 33.84; H, 4.26. Found: C, 33.79; H, 4.30 |
| **16b** | 97–107 (0.8) | 3.45 (s, 3, $-OCH_3$) and 2.20–0.92 (m, 8) | For $C_8H_{11}D^{79}Br_2O$: calcd *m/e* 282.9319; found 282.9313 |
| **16c** | 90–92 (0.7) | 3.44 (s, 3, $-OCH_3$), 3.44–3.10 (m, 1), and 2.33–1.00 (m, 7) | For $C_8H_{11}D^{79}Br_2O$: calcd *m/e* 282.9319; found 282.9313 |
| **16d** | 96–100 (0.8) | 3.52–3.18 (m, 1), 3.38 (s, 3), 2.25–0.75 (m, 7), and 1.35 (s, 3)[b] | Calcd for $C_9H_{14}Br_2O$: C, 36.27; H, 4.74; Br, 53.62. Found: C, 36.35; H, 4.80; Br, 53.64 |
| **16e** | *c* | | |
| **16f** | *c* | | |
| **16g** | *d* | | |

[a] For **17a** (~3%): δ 3.53 (s, $-OCH_3$). [b] For **17d** (~5%): δ 3.28 (s, $-OCH_3$). [c] See ref 9b. [d] See ref 9c.

seen. These data taken together rule out the possibility that **20** undergoes intramolecular cyclization *via* conformer **20b**. Rather, **21** and **22** must be formed by competitive attack at the two available sites in **20a**.

That the methoxyl substituent is capable of a high level of control of product distribution is seen from the behavior of the related methyl-substituted dibromides **25** and **28**. In this instance,[9b] Zon realized vpc separation of the isomers and treated these substances separately with methyllithium in ether. As with **18**, carbenoid **26** exhibited a high level of regiospecificity for $H_\alpha$ insertion. Intermediate **29** is also characterized by a pronounced specificity for attack at $C-H_\alpha$ bonds. The larger proportion (90%) of bicyclobutane product arising from conformer **29a** indicates that the methyl group is fostering reactivity at $C_2$. Despite this, the assumedly less stable conformer **29b** is able to compete in the product-forming manifold, affording as it does 10% of **31**.

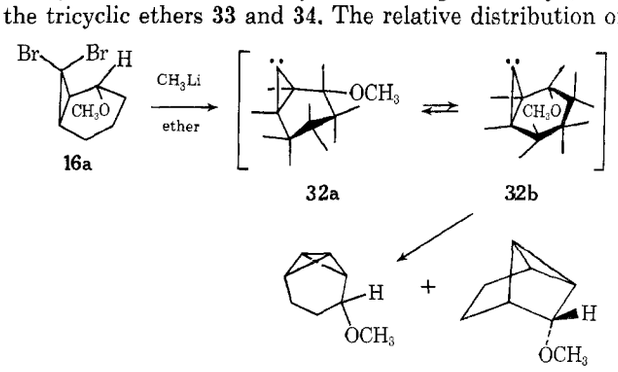



On this basis, it would seem that the cis carbenoid intermediates **18** and **26** compare favorably in their reactivity, perhaps as a consequence of the fact that the $C_2$ substituent is as remote as possible from the carbenoid center and that the remaining $C_2-H$ bond resides trans to $C_7$, thereby rendering it unavailable for insertion. Neither entity gives evidence of $C_3-H_\beta$ attack.

Utilizing the reactivity preferences of parent carbenoid **8** as a model, we see the marked $H_\alpha$ selectivity exhibited by dimethyl derivative **29** to be quite normal. What was somewhat unexpected was that conformer **29b** possesses a sufficient reactivity advantage to compete with **29a** in the product-forming step. If the assumption is allowed that the supportive electronic capabilities of methyl and *tert*-butyl groups are comparable,[16] then the reactivity of **29a** in proceeding to **30** should be about 30-fold more rapid than the **29b** → **31** cyclization. The results show that the partitioning is approximately 9:1 and that **29b** has therefore a somewhat greater reactivity than anticipated. A more important comparison is that of the behavior of the *trans*-2-methoxyl (**20**) and *trans*-2-methyl (**29**) carbenoid intermediates. It is obvious that there are important differences in product distribution, the main ones being that conformer **20b** is unreactive and that **20a** affords considerable $C-H_\beta$ insertion while **29a** and **29b** give no evidence of this. We shall return to these points later in the discussion.

When the deuterated isomer pairs **16f–17f** and **16g–17g** were exposed to methyllithium in ether, behavior nearly identical with that of the unlabeled dibromides was observed (see Experimental Section).

Attention was next turned to the somewhat simpler system **16a–17a** (97:3) which, when treated as before with methyllithium, underwent cyclization to give chiefly (89%) the tricyclic ethers **33** and **34**. The relative distribution of




these products was 23 and 77%, respectively, corresponding to a significant increase in $H_\beta$ reactivity ($H_\alpha/H_\beta$ = 0.30). Structural assignment to **34** followed from its identity with authentic samples.[13a,b,17] The pmr spectrum of **33** is sufficiently similar to those of **19** and **21** to define the molecule

**Table II**
**Physical Data for the Major Products of Carbenoid Insertion**

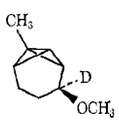
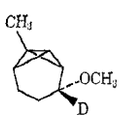
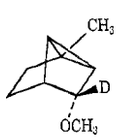
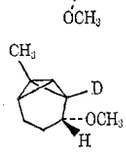
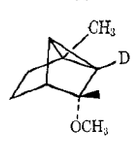
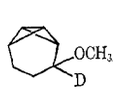
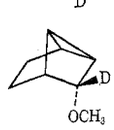
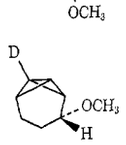
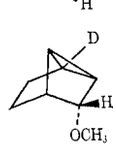
| Starting dibromide | Vpc column employed for separation (°C)[a] | Products | Registry no. | Relative ratio, % | Pmr, δ ($C_6D_6$, 60 MHz) | Anal. data |
|---|---|---|---|---|---|---|
| **16e–17e** (95:5) | C (100) | **19** | | 5 | 3.29–2.99 (m, 1, $H_3$), 3.20 (s, 3, $-OCH_3$), 2.54–2.23 (m, 1, $H_2$ or $H_6$), 2.23–1.93 (m, 1, $H_2$ or $H_6$), 1.81–1.23 (m, 4, methylenes), 1.44 (s, 3, $-CH_3$), and 1.23–0.89 (m, 1, $H_7$) | For $C_9H_{14}O$: calcd *m/e* 138.1045; found 138.1046 |
| | | **21** | | 67 | 3.39–2.99 (m, 1), 3.20 (s, 3), 2.54–2.23 (m, 1), 2.23–1.93 (m, 1), 1.81–1.23 (m, 4), 1.48 (s, 3), and 1.23–0.89 (m, 1) | Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.39; H, 10.18 |
| | | **22** | | 28 | 3.79–3.55 (dd, $J$ = 7.5 and 2.5 Hz, 1, $H_3$), 3.01 (s, 3, $-OCH_3$), 2.71–2.35 (m, 1, $H_3$), 1.99–1.56 (m, 6), and 1.00 (s, 3, $-CH_3$) | Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.07; H, 10.22 |
| **16f–17f** (95:5) | C (100) |  | 51897-63-3 | 3.5 | Spectrum similar to that of **19** with the exception that the absorption due to $H_3$ is lacking and $H_2$ is seen as an apparent quartet ($J$ = 2–3 Hz) | For $C_9H_{13}OD$: calcd *m/e* 139.1107; found 139.1106 |
| | |  | 51897-64-4 | 69.5 | Spectrum similar to that of **21** but with $H_3$ absorption lacking and the appearance of $H_2$ as a triplet ($J$ = 3.5 Hz) | For $C_9H_{13}OD$: calcd *m/e* 139.1107; found 139.1106 |
| | |  | 38452-10-7 | 27 | 3.05 (s, 3), 2.52 (m, 1), 2.39–1.54 (m, 6), and 1.03 (s, 3). | For $C_9H_{13}OD$: calcd *m/e* 139.1107; found 139.1105 |
| **16g** | A (100) |  | 51371-82-5 | 66 | 3.40–3.00 (m, 1), 3.17 (s, 3), 2.08 (br s, 1), 1.85–1.20 (m, 4), 1.49 (s, 3), and 1.13 (br s, 1) | For $C_9H_{13}OD$: calcd *m/e* 139.1107; found 139.1105 |
| | |  | 51371-83-6 | 34 | 3.62 (d, $J$ = 7 Hz, 1), 3.02 (s, 3), 2.50 (v br d, $J \approx 7$ Hz, 1), 2.3–1.4 (m, 5), and 1.02 (s, 3) | For $C_9H_{13}OD$: calcd *m/e* 139.1107; found 139.1105 |
| **16a–17a** (97:3) | A (115) | **33** | | 23 | 3.30–3.00 (m, 1, $H_3$), 3.17 (s, 3, $-OCH_3$), 2.50 (apparent quintet, $J \approx 3$ Hz, 1, $H_2$), 2.37–2.03 (m, 1, $H_6$), and 1.87–0.98 (m, 6) | For $C_8H_{12}O$: calcd *m/e* 124.0888; found 124.0890 |
| | | **34** | | 77 | 3.63 (dd, $J$ = 7.3 and 3.5 Hz, 1, $H_2$), 3.01 (s, 3, $-OCH_3$), 2.74–2.37 (br d, $J \approx 7$ Hz, 1, $H_3$), and 2.22–1.17 (m, 7) | Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 76.89; H, 9.70 |
| **16b–17b** (97:3) | D (62) |  | 51838-75-6 | 24 | 3.17 (s, 3), 2.53 (apparent quartet, $J \approx 3$ Hz, 1), 2.37–2.03 (m, 1), 1.56 (apparent t, $J \approx 3$ Hz, 2), and 2.00–0.95 (m, 4) | For $C_8H_{11}DO$: calcd *m/e* 125.0951; found 125.0949 |
| | |  | 38452-09-4 | 76 | 3.04 (s, 3), 2.57 (br s, 1), and 2.23–1.18 (m, 7) | For $C_8H_{11}DO$: calcd *m/e* 125.0951; found 125.0952 |
| **16c–17c** (97:3) | D (62) |  | 51897-65-5 | 21 | 3.50–3.15 (m, 1, $H_3$), 3.32 (s, 3, $-OCH_3$), 2.70–2.50 (m, 1), 2.37 (v br s, 1), and 2.05–1.10 (m, 5, $H_7$ and methylenes)[b] | For $C_8H_{11}DO$: calcd *m/e* 125.0951; found 125.0952 |
| | |  | 38452-08-3 | 79 | 3.63 (dd, $J$ = 7.0 and 3.7 Hz, 1), 3.03 (s, 3), 2.55 (br d, $J \approx 7$ Hz, 1), and 2.34–1.34 (m, 6) | For $C_8H_{11}DO$: calcd *m/e* 125.0951; found 125.0953 |

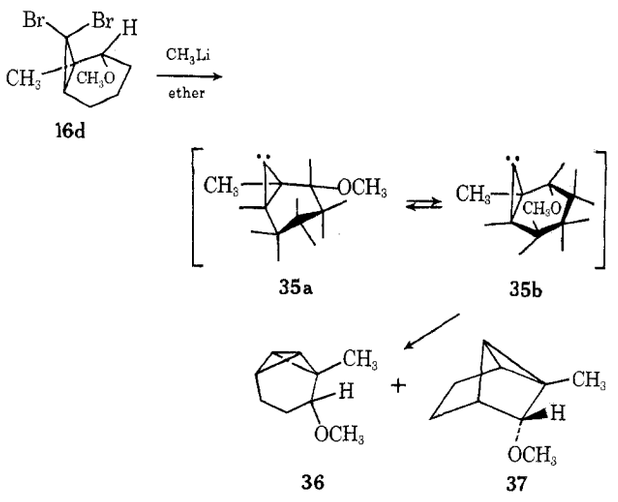
**Table II**
*(Continued)*

| Starting dibromide | Vpc column employed for separation (°C)[a] | Products | Registry no. | Relative ratio, % | Pmr, δ ($C_6D_6$, 60 MHz) | Anal. data |
|---|---|---|---|---|---|---|
| **16d–17d** (95:5) | D (62) | **36** | | 17 | 3.20 (s, 3), 3.30–3.00 (m, 1), 2.21 (apparent quintet, 1), 1.75–1.00 (m, 6), and 1.15 (s, 3) | For $C_9H_{14}O$: calcd *m/e* 138.1045; found 138.1046 |
| | | **37** | | 83 | 3.45 (d, $J$ = 7.0 Hz, 1), 3.07 (s, 3), 2.56 (br d, $J \approx 7$ Hz, 1), 2.20–1.10 (m, 6), and 1.20 (s, 3) | Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.36 |

[a] See ref 37 for identification of the various columns. [b] $CDCl_3$ solvent.

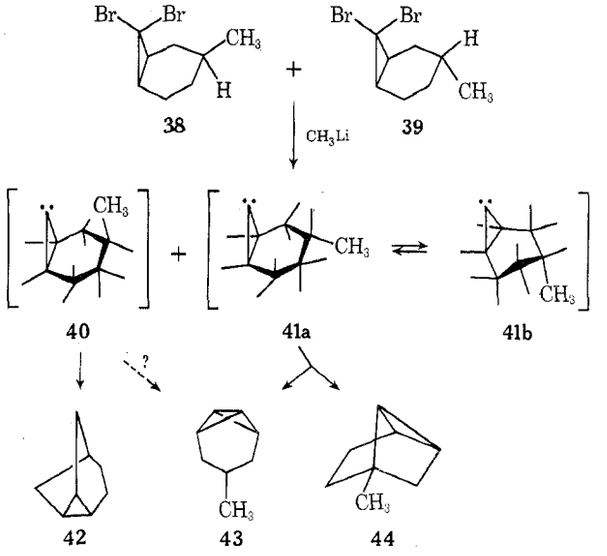
as 3-methoxytricyclo[4.1.0.$0^{2,7}$]heptane. Further corroboration was derived from the differently deuterium-labeled products obtained by cyclization of **16b–17b** and **16c–17c,** which exhibited spectra suitably modified to accommodate the site of isotopic substitution (Table II). The chemical reactivity of **16a** (the product ratio is not expected to be influenced significantly by the presence of 3% of **17a**) indicates again that C–H bond insertion operates only from that carbenoid conformer (**32b**) in which the methoxyl group is axial. Another interesting aspect of this experiment is that C–$H_\beta$ insertion dominates despite the absence of alkyl substitution at $C_3$. We therefore needed some basis on which to rationalize this rather low level of $H_\alpha/H_\beta$ regioselectivity and also to explain the apparent crossover in preferred C–H insertion which obtains upon placement of a methyl group at $C_6$ as in **20a.**

With these goals in mind, dibromide **16d** was prepared (95% purity, the remainder being **17d**) and subjected to the action of methyllithium. One might naively expect that positioning of a methyl group at the bridge position adjacent to the methoxyl function might make it less comfortable than usual for the oxygen-bearing substituent to be equatorially disposed and thereby induce a higher proportion of **35b.** At issue was whether increased alkyl substitution of the cyclopropane ring in this fashion would alter the insertion selectivity of the carbenoid. In actual fact, the cyclization of **16d** gave **36** and **37** with the bicyclopentane heavily

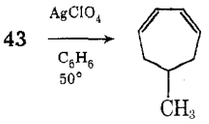



dominating (17:83). The $H_\alpha/H_\beta$ selectivity (0.20) observed for **35b** consequently parallels rather closely that exhibited by **32b** (0.30) but is opposite in direction from the reactivity of **20a** (2.4). We infer from these results that the half-chair conformations adopted by **32b** and **35b** are quite similar. The methyl group in **35b** may cause some distortion in a way which moves $H_3$ toward the $C_7$ carbenoid center, but the impact of this conformational change is not felt because the methoxyl substituent inhibits competitive insertion into the $C_2$–H bond. If the same twisting effect operates in **20a,** the $C_5$ carbon is compressed closer to $C_7$ and an enhanced selectivity of insertion into the C–$H_\alpha$ bond can be expected to result. We of course do not have a way of assaying this conformational interpretation directly, but note only that dimethyl carbenoid **29b** gives every indication of operating under similar control ($H_\alpha$ insertion only).

Insofar as the reactivity consequences of $C_3$ substitution are concerned, the behavior of the inseparable mixture of cis and trans dibromides **38** and **39** (57:43)[5e] serves to denote the effect of methyl substitution. When treated with methyllithium, the three hydrocarbons **42** (60%), **43** (28%), and **44** (12%) were obtained. Tricyclo[2.2.2.$0^{2,6}$]octane(**42**)

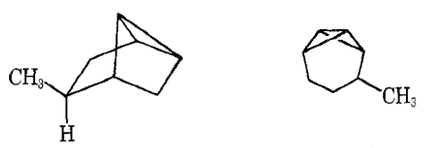



was identified on the basis of its pmr features and the identity of its infrared spectrum and melting point with those of the known compound.[18] Structural assignment to **43** is founded chiefly upon its characteristic pmr spectrum and facile Ag(I)-catalyzed rearrangement[19] to 6-methyl-1,3-cycloheptadiene (**45**). Tricyclic system **44** displays a sharp methyl singlet at δ 1.12 and a multiplicity pattern for the remaining protons very similar to that of **12.**[5e,20] Accordingly, the methyl-substituted carbon must be tertiary, an observation which requires carbenoid insertion into the C–H bond formerly at that site.




45

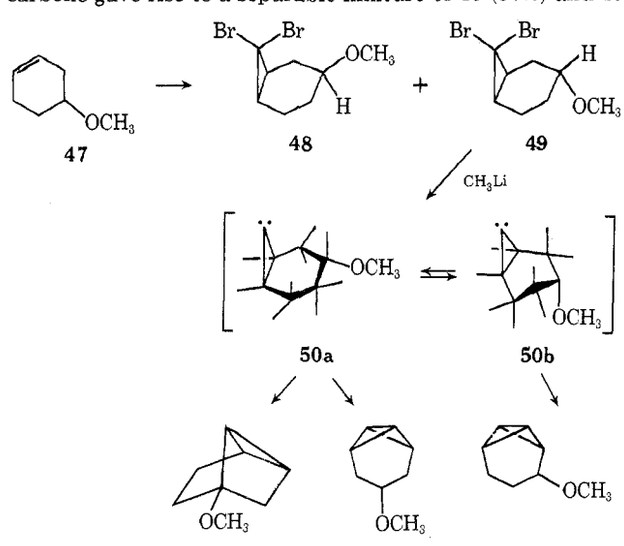
An interesting aspect of these product studies is that the major hydrocarbon is derived from intramolecular insertion of the cis carbenoid into its methyl group. Although this process enjoys a threefold statistical advantage over comparable pathways, it requires the intervention of the destabilized conformation **40**. No reaction from that conformational isomer of **40** possessing an equatorially oriented methyl substituent (leading to **46a** or **46b**) was detected.




**46a** **46b**

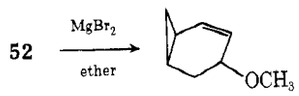
That **40** undergoes no $H_\alpha$ insertion cannot be stated unequivocally. However, mass balance considerations necessitate that if this transformation operates it be quite inefficient. All of the products from trans carbenoid **41** are accounted for in a straightforward way in terms of its more stable conformer **41a**. In marked contrast to the cis series, where the axial methyl conformer commands a large kinetic advantage, **41b** is not a significant product-determining intermediate. Assuming that all of **43** arises directly from **41a**, its $H_\alpha/H_\beta$ reactivity profile is seen to be 2.3. This result shows that **41a** exhibits, as a result of suitable methyl labeling, a tenfold greater capability for $H_\beta$ insertion than parent carbenoid **8**. The directing effect of methyl is not, however, as large as that of *tert*-butyl, where $H_\beta$ insertion now actually predominates (compare **9** for which $H_\alpha/H_\beta$ = 0.66[5e]).

Reaction of 4-methoxycyclohexene (**47**) with dibromocarbene gave rise to a separable mixture of **48** (37%) and **49**




**47** **48** **49** **50a** **50b** **51** **52** **53**

(63%). Exposure of **48** to methyllithium led to consumption of the dibromide without formation of volatile products isomeric with the carbenoid formulation. Under identical conditions, **49** was transformed into a mixture of **51** (71%), **52** (22%), and **53** (7%). Identification of **51** was based on its pmr spectrum, which lacks a >CHO– signal and can otherwise be accommodated only by the indicated tricyclic formulation (see Experimental Section). Ethers **52** and **53** proved inseparable under the many vpc conditions examined. However, treatment of this isomer mixture with a small amount of ethereal magnesium bromide resulted in essentially exclusive rearrangement of **52** to **54**. The recov-

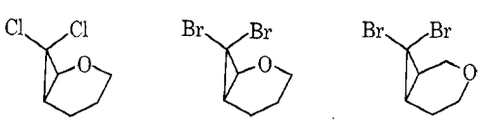



**54**

ered unreacted **53** proved identical with an authentic sample.[9b] In agreement with its 2-norcarene structure, **54** exhibits two widely separated olefinic absorptions at $\delta$ 6.10–5.90 and 5.75–5.55. The low-field signal due to $H_2$ is an expected multiplet,[21] but the presence of a methoxyl group at $C_4$ causes the $H_3$ absorption to appear as a doublet with $J$ = 10 Hz. The absence of spin–spin interaction between $H_3$ and $H_4$ denotes an approximate 90° dihedral angle relationship between these protons. Such geometry could be attained by adoption by the trans isomer of a pseudo-boat conformation, or as a consequence of the cis isomer in a pseudo-chair conformation. Consequently, the stereochemistry of **54** remains a moot question. Notwithstanding, the location of the methoxyl substituent at $C_4$ in this norcarene requires the precursor tricycloheptane to be **52**. Consequently, intermediate **50a** is characterized by an $H_\alpha/H_\beta$ reactivity ratio of 0.31 while **50b** cyclizes chiefly with bicyclobutane formation ($H_\alpha$ insertion).

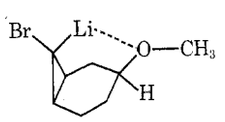
## Discussion

In contrast to carbenoid systems of less novel structure, 7-norcaranylidenes are seen to exhibit a richly varied reactivity pattern which is highly sensitive to conformational and substituent effects. As one example, we cite the mandatory requirement for transfer of axial hydrogen such that insertions necessarily occur with retention of configuration. Perhaps the most unique transformation, the conversion of **38** to tricyclic hydrocarbon **42**, establishes that axially oriented 3-methyl groups also are sufficiently proximate to $C_7$ to allow for ready C–H insertion. Insofar as the inability of the related methoxyl derivative **48** to achieve intramolecular cyclization is concerned, it is recognized that ether oxygen confers a marked stabilizing effect on $\alpha$-haloalkyllithium compounds. Köbrich[2a,22] and others,[23] for instance, have reported extensively on the chemical properties of tetrahydrofuran-stabilized lithium carbenoids. The fact that the 2-oxabicycloheptyl systems **55** and **56** undergo halo-




**55** **56** **57**

gen–metal exchange predominantly at the endo site upon reaction with methyllithium at low temperatures to afford *stable* lithium carbenoids similarly attests to a stabilizing coordinative interaction. The behavior of **57** appears entirely analogous.[24,25] We rationalize on this basis that the cis-oriented methoxyl oxygen in **48** directs the course of the exchange reaction[26] to provide **58**, which because of intra-




**58**

molecular solvation of lithium by neighboring oxygen is deterred from further reaction of the customary type.

The question now arises as to why the several *trans*-2-methoxyl substituted carbenoids studied, *i.e.*, **20**, **32**, and

**35,** exhibit the proclivity for C–H insertion only from that conformation in which the group at $C_2$ is oriented axially.[27] This finding attests to the greater reactivity of the axial conformer, but unfortunately provides no information on the question of which conformer enjoys greater relative stability. Since carbenoids and carbenes are, generally speaking, unstable energetic species and the reactions in which they engage rather strongly exothermic,[2b] the competing transition states for C–$H_\alpha$ and C–$H_\beta$ insertion might be expected[28] to be somewhat insensitive to product stability and governed to a greater extent by other factors such as proximity considerations, angle distortions, C–H bond nucleophilicities, and the like. However, it need not follow that precisely the same mechanism operates during the course of $H_\alpha$ and $H_\beta$ insertion. Owing to geometric restrictions, both types of hydrogen must experience intramolecular abstraction by way of triangular transition states[29] rather than *via* theoretically favored linear approach.[30] If the assumption is now made that biradicals subsequently intervene, then the causative factors underlying the prototypical preferential $H_\beta$ abstraction within **32b** ($H_\alpha/H_\beta$ = 0.30) to the exclusion of $H_\alpha$ abstraction within **32a** seeks explanation. Dreiding molecular models show that the proximity of $C_7$ to $H_\alpha$ and $H_\beta$ in either conformer is rather closely balanced; consequently, to focus attention on steric factors is unwarranted.

The recognized ability of oxygen and other heteroatoms to stabilize an incipient free radical is now universally attributed to delocalization factors which give rise to polar contributions.[31] That such polar effects are important in carbene chemistry has been amply documented, especially for ether oxygen,[32] and is further substantiated in 7-norcaranylidene systems by the behavior of **50a.** Thus, to the

$$R_2\dot{C}-\ddot{O}-R' \longleftrightarrow R_2\ddot{\underset{-}{C}}-\dot{\overset{+}{O}}-R'$$

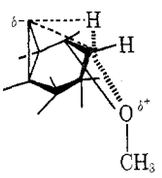
extent that factors which stabilize free radicals also stabilize the transition state in a hydrogen atom transfer reaction,[33] $H_\alpha$ abstraction by **32a** should be favored. However, such reactivity is not encountered.

A possible rationalization is that oxygen resonance stabilization can only fully materialize when the geminal C–H bond is extensively broken. Should $H_\alpha$ abstraction in 7-norcaranylidenes proceed along a reaction coordinate wherein the transition state is reached early *without extensive C–H bond stretching,* C–H bond nucleophilicities would be expected to become the dominant controlling reactivity factor. $H_\alpha$ insertion adjacent to a methoxyl group would thereby be disfavored. On the basis of electronegativity considerations alone, the following $H_\alpha$ reactivity order is expected. The behavior of all 7-norcaranylidenes exam-

$$H-\overset{|}{\underset{|}{C}}-\text{alkyl} > H-\overset{|}{\underset{|}{C}}-H > H-\overset{|}{\underset{|}{C}}-OCH_3$$

ined to date conform to this working hypothesis, the apparent frustration of thermodynamics arising because of the reactant-like nature of the activated complex, where cationic effects are less prevalent than inductive influences.

We can account for the role played by the axial 3-methoxyl group in promoting high levels of $H_\beta$ insertion by assuming that such transition states arrive later in the reaction profile. Greater C–H bond stretching and a decreased resemblance of the transition state to the reactant now obtain. It is known from studies on the solvolysis of ether oxygen-containing sulfonate esters that the capability of divalent oxygen to function as a neighboring group in carbonium ion reactions operates at a high level.[34] This is particularly so when three-membered cyclic oxonium ions are produced as intermediates. Given that the carbenoid center in 7-norcaranylidenes is electrophilic in character, the act of C–$H_\beta$ insertion will incur in its transition state a significant quantity of electron deficiency in the carbon atom bearing the hydrogen. The ability of methyl and *tert*-butyl groups to supply electron density to the carbon under siege and thereby modify the normal reactivity order has already been commented upon. Given this electronic state of affairs and the conformation now recognized to be favored for such reactions, it is entirely possible that C–$H_\beta$ reactivity is enhanced by "backside" assistance provided by the axial methoxyl substituent. As represented in **59,** the development of epioxonium characteristics by trans diaxial involvement of methoxyl oxygen could reasonably increase the normal levels of C–$H_\beta$ nucleophilicity. Interestingly, carbenoids in which the methoxyl group is equatorial and unable to participate in this way exhibit little or no propensity for C–$H_\beta$ insertion. This anchimeric assistance by neighboring methoxyl is reminiscent of the effects encountered in radical-chain halogenations of certain alkyl bromides and chlorides where anomalously high reactivity and product stereochemistry control have been attributed to intervention of bridged free-radical intermediates involving the $\sigma$-bonded halogen atom.[35] Finally, the $H_\alpha/H_\beta$ reactivity order encountered in the cyclization of **50b** is restored to a value greater than unity presumably as a result of assistance by the neighboring axial 4-methoxyl of hydrogen abstraction at both sites (not necessarily to equal extents). The product distribution is commensurate with this analysis.[36]




**59**

## Experimental Section

All boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and proton magnetic resonance spectra were recorded with Varian A-60A and Joelco MH-100 instruments. Apparent splittings are given in all cases. Mass spectra were obtained with a AEI-MS9 instrument at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

**Preparation of the 3-Methoxycyclohexenes. Generalized Procedure.** A solution of 75.0 g (0.67 mol) of 2-methylcyclohex-1-en-3-ol in 170 ml of anhydrous dimethylformamide was added dropwise under nitrogen to a mechanically stirred suspension of sodium hydride (56.4 g, 1.34 mol) in the same solvent (450 ml). After complete addition, the mixture was stirred for 1.5 hr at 40° and cooled in an ice bath before a solution of methyl iodide (400 g, 2.8 mol) in dimethylformamide (100 ml) was added at a rate such as to keep the temperature below 15°. The resulting slurry was stirred overnight at 25°, water (300 ml) was introduced with ice cooling, and the entire mixture was shaken with pentane (750 ml) and more water (900 ml) after being transferred to a separatory funnel. The separated aqueous layer was extracted with pentane (400 ml) and the combined pentane layers were washed with water (3 × 150 ml) before drying. Solvent was removed by distillation at atmospheric pressure. Distillation of the residue gave 73.0 g (86%) of **15d** as a colorless, fragrant oil, bp 91–100° (92 mm). Preparative vpc (column A,[37] 94°, 60 ml/min He) afforded analytically pure material: pmr $\delta_{TMS}$ ($CDCl_3$) 5.70–5.45 (m, 1, olefinic), 3.65–3.45 (m, 1, >CHO–), 3.36 (s, 3, $-OCH_3$), 1.75 (br s, 3, $-CH_3$), and 2.25–1.35 (m, 6, methylenes).

*Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.06; H, 11.32.

**Dibromocarbene Additions. Typical Procedure.** A solution

of 56 g (0.5 mol) of 3-methoxy-1-cyclohexene[38] in 100 ml of pentane was added to a mechanically stirred suspension of potassium *tert*-butoxide (60.5 g, 0.54 mol) in pentane (750 ml) which was precooled and maintained at −30° under a nitrogen atmosphere. A solution of bromoform (126.5 g, 0.5 mol) in pentane (100 ml) was then introduced to this suspension during 3 hr while keeping the reaction mixture at −30°. Following complete addition, the mixture was stirred at room temperature for 5 hr and hydrolyzed by the addition of water (250 ml). The separated organic layer was washed with water (250 ml), dried, and concentrated. Short-path vacuum distillation of the residue gave 92 g (65%) of a pale yellow oil, bp 97–107° (0.8 mm). The nmr spectrum of this material indicated that it contained 7% unchanged methoxycyclohexene and **16a–17a** (97:3). *Preparative vpc purification (column B, 132°, 70 ml/min He) gave an analytically pure sample (see Table I).*

**Prototypic Cyclization Procedure.** A magnetically stirred solution containing 20 g (0.07 mol) of **16a–17a** (97:3) in 125 ml of anhydrous ether was precooled to −10° and maintained at approximately this temperature under a nitrogen atmosphere during dropwise addition of a solution of methyllithium in ether (50 ml of 1.6 *M*, 0.08 mol) over a 2-hr period. Upon complete addition, the orange reaction mixture was stirred at room temperature for 1 hr before cooling to 5° and cautious addition of water (125 ml). The separated organic layer was washed with saturated aqueous sodium chloride solution (125 ml), dried, and carefully concentrated. Bulb-to-bulb distillation of the residue at 60° (1 mm) gave 4 g (46%) of a colorless liquid, vpc analysis of which (column A,[37] 115°, 60 ml/min He) indicated it to contain two major components (89% of total multicomponent mixture) in a relative ratio of 77:23. These products were separated and purified by preparative vpc techniques and characterized spectroscopically (Table II).

*endo*-**1-Methyl-3-methoxynorbornane (23).** A magnetically stirred suspension of 10% Pd on carbon (14 mg) in absolute ethanol (6 ml) was treated with hydrogen (1 atm) until uptake ceased. A solution of **22** (44 mg, 0.3 mmol) in absolute ethanol (4 ml) was injected and rapid uptake of hydrogen was noted. After 30 min, 1.08 equiv of hydrogen was consumed and the mixture was stirred for an additional 1 hr, filtered, diluted with water (6 ml), and then washed four times with 0.75-ml portions of pentane. Preparative vpc isolation of the sole detectable product (column D,[37] 100°, 120 ml/min He) in the combined pentane washings led to collection of 9.5 mg (22%) of **23:** pmr $\delta_{TMS}$ ($C_6D_6$) 3.62 (d of t, $J_{2exo,3exo}$ = 9.5, $J_{2endo,3exo}$ = 4.5, $J_{3exo,4}$ = 4.5 Hz, 1, exo $H_2$),[39] 3.08 (s, 3, $-OCH_3$), 2.23 (br s, 1, $H_4$), 2.13–1.00 (m, 8), and 1.02 (s, 3, $-CH_3$).[39]

*Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.25; H, 11.49.

**Hydrogenation of *syn*-3-Methoxy-1-methyltricyclo-[4.1.0.0$^{2,7}$]heptane (21).**[40] A 99-mg sample of **21** in absolute ethanol (10 ml) containing 10% Pd on carbon (32 mg) was reduced in essentially the same manner as described above. The consumption of 1.91 equiv of hydrogen was realized in 30 min. Preparative vpc (column D,[37] 100°, 75 ml/min He) led to collection of the four components: A (20 mg), B (5 mg), and a mixture (owing to their proximate retention times) of C and D (5 mg). These were identified as $C_9H_{18}O$ isomers by accurate *m/e* measurements and by pmr data: for A, $\delta_{TMS}$ ($C_6D_6$) 3.21 (s, 3, $-OCH_3$), 2.85–2.30 (m, 1, >CHO–), 2.30–1.85 (m, 1), 1.85–0.80 (m, 7), 1.09 (br s, 3, $-CH_3$), and 0.91 (br s, 3, $-CH_3$); for B, $\delta_{TMS}$ ($C_6D_6$) 3.21 (s, 3, $-OCH_3$), 3.20–2.75 (m, 1, >CHO–), 2.20–0.70 (m, 8), and 0.90–0.70 (m, 6, two $-CH_3$); for C + D, $\delta_{TMS}$ ($C_6D_6$) 3.22 and 3.18 (two s of approximately equal intensity, 3, two $-OCH_3$), 3.45–2.80 (m, 1, >CHO–), 2.20–0.70 (m, 8), and 1.00–0.70 (m, 6, two $-CH_3$).

**Cyclization of *cis*- and *trans*-7,7-Dibromo-3-methylnorcarane (38 and 39).** Treatment of 10.0 g of a 57:43 mixture of **38** and **39**[5e] dropwise with 25 ml of 1.6 *M* methyllithium in 50 ml of ether at −20° as described above gave a pale yellow liquid, vpc analysis (column A,[37] 80°, 70 ml/min) of which showed three components in the ratio 12:28:60.

The major component was identified as **42:** mp 87–89° (lit.[18] mp 91–92°); major infrared peaks correspond to those reported;[18] nmr $\delta_{TMS}$ ($CDCl_3$) 2.00–1.60 (m, 9, including sharp s at 1.60), 1.60–1.20 (m, 2), and 0.80–0.50 (m, 1); for $C_8H_{12}$ calcd *m/e* 108.0938 (found 108.0940).

The middle peak was characterized as **43:** pmr $\delta_{TMS}$ ($CDCl_3$) 2.35–2.10 (m, 2), 1.60–1.25 (m, 6), and 1.00–0.65 (m, 4, including d centered at 0.87, $J$ = 7 Hz, 3); $\nu_{max}$ (neat) 3100, 3000, 2958, 2920, 2860, 1455, 1150, 1065, 988, and 920 cm$^{-1}$; for $C_8H_{12}$ calcd *m/e* 108.0938 (found 108.0940).

*Anal.* Calcd for $C_8H_{12}$: C, 88.92; H, 11.18. Found: C, 88.90; H, 11.22.

The minor product was formulated as **44:** pmr $\delta$ 2.10–1.60 (m, 4), 1.60–1.20 (m, 5), and 1.12 (s, 3); $\nu_{max}$ (neat) 3060, 3050, 2950, 2930, 2862, 1455, 1380, 1333, 1285, 1260, 1230, 797, 770, and 730 cm$^{-1}$; for $C_8H_{12}$ calcd *m/e* 108.0938 (found 108.0940).

*Anal.* Calcd for $C_8H_{12}$: C, 88.92; H, 11.18. Found: C, 88.98; H, 11.18.

**Ag(I)-Catalyzed Rearrangement of 43.** To 50 mg of 43 dissolved in 500 μl of dry benzene was added 500 μl of a 0.1790 *N* silver perchlorate–benzene solution. After this solution was heated to 50° for 12 hr, saturated brine was added and the product was extracted with pentane. Vpc analysis (column A,[37] 70°) revealed essentially total conversion to **45:** $\lambda_{max}$ ($C_2H_5OH$) 249 nm; pmr $\delta_{TMS}$ ($CDCl_3$) 5.90–5.50 (m, 4), 2.40–1.90 (m, 4), 1.80–1.59 (m, 1), and 1.10–0.85 (m, 3); for $C_8H_{12}$ calcd *m/e* 108.0938 (found 108.0940).

*cis*- **and** *trans*-**7,7-Dibromo-3-methoxynorcarane (48 and 49).** 4-Methoxycyclohexene (**47**),[41] bp 129°, was prepared in 77% yield by pyrolysis of 4-methoxycyclohexyl acetate at 490°. Reaction of 30.0 g of this alkene and 33 g of potassium *tert*-butoxide in 75 ml of pentane at −20° with 76 g of bromoform in 20 ml of pentane as previously described afforded 40.3 g (53%) of an isomeric mixture, bp 129–131° (3 mm).

*Anal.* Calcd for $C_8H_{12}Br_2O$: C, 33.83; H, 4.26. Found: C, 33.56; H, 4.25.

The cis and trans isomers were separated on column E[37] (150°, 100 ml/min) and the ratio was seen to be 37:63: for **48,** pmr $\delta_{TMS}$ ($CDCl_3$) 3.30 (br, s, 4), 2.20–1.70 (m, 6), and 1.60–1.30 (m, 2), for $C_8H_{12}Br_2O$ calcd *m/e* 281.9256 (found 281.9261); for **49,** $\delta_{TMS}$ ($CDCl_3$) 3.28 (br s, 4), 2.20–1.70 (m, 6), and 1.60–1.30 (m, 2), for $C_8H_{12}Br_2O$ calcd *m/e* 281.9256 (found 281.9261).

**Cyclization of 48–49.** Exposure of a solution composed of 10.0 g of the dibromide mixture in 50 ml of ether with 25 ml of 1.6 *M* methyllithium in ether at −40° for 30 min according to the predescribed method gave a product which could be separated into two components (ratio 71:29) on column D[37] (50°, 60 ml/min). The first component was collected and amounted to 591 mg. Pmr analysis showed the second peak (267 mg) to be comprised of two methyl ethers (ratio *ca.* 3:1). Separation of these isomers could not be achieved on any of the many columns examined.

The more rapidly eluted component was identified as **51:** $\nu_{max}$ (neat) 3040, 2940, 2910, 2860, 2825, 1460, 1445, 1320, 1280, 1250, 1050, and 890 cm$^{-1}$; pmr $\delta_{TMS}$ ($CDCl_3$) 3.27 (s, 3), 2.40–2.05 (m, 2), 2.00–1.65 (m, 2), and 1.65–1.30 (m, 5).

*Anal.* Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.47; H, 9.74.

Characterization of the remaining two products was achieved after selective magnesium bromide promoted rearrangement (*vide infra*). When the purified isomeric dibromides **48** and **49** were individually allowed to react with ethereal methyllithium, **48** was not converted to any of the above three products; no volatile substances were seen. In contrast, trans isomer **49** gave rise to **51–53** in the same ratios realized for the mixture.

**Reaction of 52–53 with Ethereal Magnesium Bromide.** A mixture of **52–53** (32 mg, *ca.* 3:1) was allowed to stand overnight in the presence of 1.5 ml of 0.1 *M* ethereal magnesium bromide. After quenching with water, the organic layer was separated, dried, and carefully concentrated. Vpc analysis on column D[37] (65°, 60 ml/min) revealed that the major component had chiefly undergone isomerization to a substance with longer retention time (ratio 2.5:1). Preparative scale isolation gave pure **53,** the pmr spectrum of which was identical with that of an authentic sample.[9b]

The major peak of longer retention time was characterized as norcarene **54:** $\nu_{max}$ (neat) 3030, 2920, 2860, 2820, 1450, 1320, 1100, 800, and 700 cm$^{-1}$; pmr $\delta_{TMS}$ ($C_6D_6$) 6.10–5.90 (m, 1), 5.75–5.55 (d, $J$ = 10 Hz, 1), 3.60–3.30 (m, 1), 3.16 (s, 3), 2.50–2.20 (m, 1), 1.70–1.30 (m, 1), 1.20–0.80 (m, 2), and 0.80–0.10 (m, 2); for $C_8H_{12}O$ calcd *m/e* 124.0888 (found 124.0890).

*Anal.* Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.00; H, 9.83.

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**Registry No.**—**15a,** 2699-13-0; **15b,** 38445-64-6; **15c,** 38445-63-5; **15d,** 38445-61-3; **16a,** 38445-66-8; **16b,** 38445-69-1; **16c,** 38445-68-0; **16d,** 38580-52-8; **16e,** 38445-67-9; **16f,** 38445-70-4; **16g,** 51326-30-8; **17a,** 51897-58-6; **17b,** 51897-59-7; **17c,** 51897-60-0; **17d,** 51838-95-0; **17e,** 51349-28-1; **17f,** 51838-96-1; **19,** 42403-40-7; **21,** 42403-41-8; **22,** 51349-29-2; **23,** 51838-97-2; **33,** 51838-69-8; **34,** 38452-05-0; **36,** 51838-70-1; **37,** 38452-06-1; **38,** 51897-61-1; **39,** 51897-62-2; **42,** 285-43-8; **43,** 51838-71-2; **44,** 51838-72-3; **45,**

38511-91-0; **47,** 15766-93-5; **48,** 51838-98-3; **49,** 51838-99-4; **51,** 51838-73-4; **52,** 51838-74-5; **53,** 51838-69-8; **54,** 38996-47-3; 2-methylcyclohex-1-en-3-ol, 20461-30-7.

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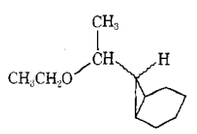


i

(16) This hypothesis is supported qualitatively by the reactivity of the 2-methyl-7,7-dibromobicyclo[4.1.0]heptanes.[5f]

(17) We thank Dr. Tanida for providing us with a copy of the pmr spectrum of **34.** High-resolution pmr analysis revealed that each component of the doublet of doublets due to $H_2$ is further split ($J \simeq 0.5$ Hz) by long-range coupling.

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(37) The following Al columns were employed herein: A, 12 ft × 0.25 in. 5% OV-11 on 60/80 mesh Chromosorb G; B, 5 ft × 0.25 in. 3% SE-30 on 100/120 mesh Varaport No. 30; C, 12 ft × 0.25 in. 5% Carbowax 20 M on KOH-washed 60/80 mesh Chromosorb P; D, 2 ft × 0.25 in. 12% OV-11 on 80/100 mesh Chromosorb W; E, 6 ft × 0.25 in. 10% UCON 50 HB 2000 Polar on 60/80 mesh Chromosorb G.

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