Reaction of 23 with Pentafluorophenylcopper Tetramer. Three separate weighed aliquots of a mixture of **23** and tetrahydrofuran were diluted with chloroform and a small amount of pentafluorophenylcopper tetramer (*ca.* 5 mg) was added. An immediate exothermic reaction took place with the simultaneous evolution of nitrogen. An internal standard (2,2,4-trimethylpentane) was then added and the solution analyzed by vpc on a 10 ft $\times$ $^1/_8$ in. 20% D.C. Silicone Fluid No. 200 on 60–80 Chromosorb P column at 75°. The yield of 2,5-dimethyl-2,4-hexadiene (**22**), which was the only product, was 48% based on the tosylhydrazone precursor of **23**. Prior to the analytical run a preparative scale reaction was run and the product was collected and shown to be identical in all respects with an authentic sample.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

Transition Metal Complex Promoted Rearrangements. Tricyclo[4.1.0.0^{2,7}]heptane and 1-Methyltricyclo[4.1.0.0^{2,7}]heptane[1]

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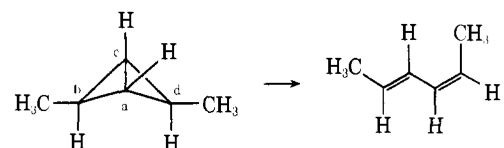
Abstract: The transition metal complex promoted isomerization of tricyclo[4.1.0.0^{2,7}]heptane (**5**) and 1-methyltricyclc[4.1.0.0^{2,7}]heptane (**13**) has been studied in detail. Derivatives of copper, iridium, mercury, palladium, platinum, rhodium, ruthenium, tin, and zinc were found to readily bring about the rearrangement of **5** to norcarene, 3-methylenecyclohexene, or 1,3-cycloheptadiene. Similarly, certain transition metal derivatives readily isomerize **13** to methylated derivatives of norcarene, 3-methylenecyclohexene, 1,3-cycloheptadiene, or bicyclo[3.2.0]hept-6-ene. The yields and nature of the products formed were shown to be very dependent on the nature of the metal, the ligands attached to the metal, and the presence of the methyl group on **13**. Mechanistically, it appears that the transition metal promoted isomerization of these highly strained tricyclic molecules occurred *via* a stepwise process. A mechanism is proposed which involves initial attack of the transition metal complex at the bridgehead of the bicyclo[1.1.0]butane moiety to cleave a side bond of the bicyclo[1.1.0]butane portion of the molecule. This mechanistic scheme utilizes the transition metal complex as a highly selective Lewis type acid which generates a cyclopropylcarbinyl type cation in cleaving the aforementioned side bond. Consistent with this mechanistic scheme were experiments in which some initially generated intermediate was trapped by nucleophilic solvent. An overall mechanistic picture is presented which provides a reasonable explanation of the processes which lead to each of the observed products.

Since the first reported synthesis of bicyclo[1.1.0]butane and its derivatives, numerous workers have investigated its thermal isomerization to 1,3-diene derivatives.[3] The mechanism of this rearrangement has been discussed in detail,[4,5] and has been shown to involve a conrotatory mode of ring opening of one cyclopropane ring concomitant with a disrotatory mode of ring opening of the other cyclopropane ring. For example, *exo,exo*-2,4-dimethylbicyclo[1.1.0]butane (**1**) gives 93% of *cis,trans*-2,4-hexadiene (**2**) and *endo,exo*-2,4-dimethylbicyclo[1.1.0]butane (**3**) gives 95% of *trans,trans*-2,4-hexadiene (**4**).[4c] The formation of **2**, for example, may be viewed as occurring by cleavage of either of the opposite pairs of side bonds (a–b and c–d, or a–d and b–c) followed by conrotatory rotation of one pair of developing orbitals and disrotatory rotation of the other set of orbitals to give the observed



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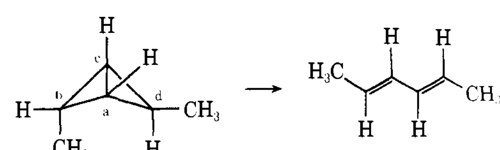
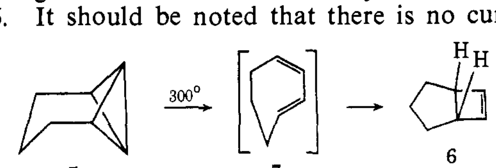


3 **4**

stereochemistry. The thermal opening of tricyclo[4.1.0.0^{2,7}]heptane (**5**) has been reported[4b] to give bicyclo[3.2.0]hept-6-ene (**6**). It was suggested that *cis,-trans*-1,3-cycloheptadiene (**7**) was initially formed. It was further postulated that **7** was very unstable due to the strain of the trans double bond and thus underwent rapid ring closure under the thermolysis conditions to give **6**. It should be noted that there is no currently



5 **7** **6**

(1) Paper XXXIV of a series on The Chemistry of Bent Bonds. For the preceding paper in this series see P. G. Gassman, G. R. Meyer, and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7741 (1972).

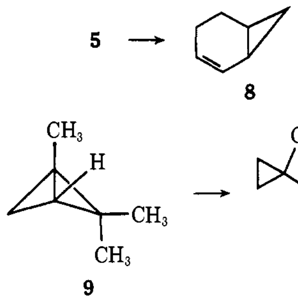
(2) National Science Foundation Trainee, 1968–1972.

(3) For a detailed listing of references to the thermal cleavage of bicyclo[1.1.0]butanes, see P. G. Gassman, G. R. Meyer, and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7741 (1972).

(4) (a) K. B. Wiberg and J. M. Lavinish, *ibid.*, **88**, 5272 (1966); (b) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968); (c) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

(5) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). In particular, see pp 810–814.

available convincing evidence that the center bond of the bicyclo[1.1.0]butane skeleton is ever cleaved in a purely thermal reaction to produce 1,3-butadiene derivatives. Opening of the bicyclobutane moiety has been affected by acids and results in the formation of vinylcyclopropane derivatives as in the isomerization of **5** to give 2-norcarene (**8**)[6] and of **9** to give **10**.[7]

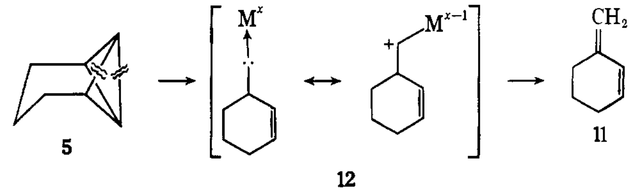


In view of our interest in the chemistry of strained ring systems and our successful utilization of transition metal compounds to effect isomerization of quadricyclane,[8] bicyclo[2.1.0]pentane,[9] and simple bicyclo-[1.1.0]butane[10] derivatives, we investigated the reactions of transition metal compounds with the rigid, highly strained tricyclo[4.1.0.0^{2,7}]heptane ring system.

Results

Although the bicyclo[1.1.0]butane nucleus has a strain energy of *ca.* 64 kcal/mol,[11] temperatures of 150–300° and activation energies in excess of 40 kcal/mol[3d,3g] appear necessary for a reasonable rate of isomerization. We have found that bicyclobutane derivatives can be isomerized to give diene derivatives below room temperature by treatment with transition metal compounds.[10,12] When an acetonitrile solution of **5**[6] was treated with 4 mol % of rhodium dicarbonyl chloride dimer, a rapid exothermic reaction occurred to give 3-methylenecyclohexene (**11**) in 98% yield after 15 min. This material was identical in all respects with an authentic sample of **11** prepared *via* the Wittig reaction of 2-cyclohexenone with methylenetriphenylphosphine.[13,14]

The formation of **11** differs markedly from the thermal[4b] and silver ion[15,16] catalyzed transformations of **5**. Our isomerization requires a hydrogen migration whereas the thermal and silver ion catalyzed rearrangements do not (*vide post*). The isomerization of **5** to **11** may be viewed as occurring *via* cleavage of one

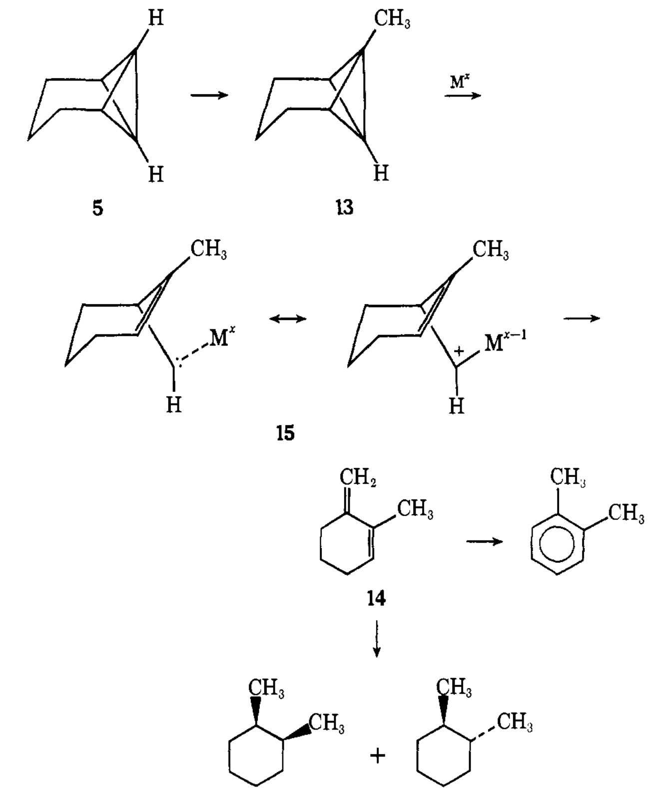


side bond and the central bond of the bicyclobutane nucleus to give the intermediate **12**, which may be represented as either the metal-bonded carbene complex or its resonance structure, the metal-bonded carbonium ion. The intermediate **12** could then experience hydrogen migration with loss of M^X to give **11**. This prototypal mode of ring cleavage amounts to a *formal* retrocarbene reaction.

In order to gain some insight into the nature of the proposed intermediate **12**, we decided to study the effect of an alkyl substituent at the bridgehead position. 1-Methyltricyclo[4.1.0.0^{2,7}]heptane (**13**) was prepared by the method of Closs and Closs,[17] through formation of the anion of **5** with the *n*-butyllithium–tetramethylethylenediamine 1:1 complex in ether, and methylation of the anion with methyl iodide. When a chloroform solution of **13** was treated with 5 mol % of rhodium dicarbonyl chloride dimer, a rapid exothermic reaction occurred to yield 96% of 2-methyl-3-methylenecyclohexene (**14**). The structure proof of **14** was based on its characteristic spectral data [nmr τ 4.37 (1 H, m), 5.17 (1 H, br s), and 5.30 (1 H, br s); ir 6.09, 6.22 (conjugated diene), and 11.28 μ (terminal methylene); uv λ_{max}^{hexane} 234 nm (ϵ 16,200)]. In addition, **14** was catalytically hydrogenated to give a mixture of *cis*- and *trans*-1,2-dimethylcyclohexane and dehydrogenated to give *o*-xylene. We feel that cleavage of a side and central bond of the bicyclobutane moiety in **13** occurred to give the proposed transition metal complexed carbene–transition metal bonded carbonium ion hybrid **15**. Hydrogen shift with loss of M^X would then produce **14**. The isomerization showed amazing stereospecificity in that only the side bond attached to the unsubstituted bridgehead carbon was cleaved (in addition to the central bond of the bicyclo[1.1.0]butane moiety). This specificity parallels our observations on the reaction of 1,2,2-trimethylbicyclo[1.1.0]butane (**9**) with rhodium dicarbonyl chloride dimer.[10a,18]

We next turned our attention to the role of the metal derivative and attempted to determine what effect different transition metal compounds might have upon the mode of isomerization of the strained bicyclo-[1.1.0]butane portion of **5** and **13**. The conditions used for these reactions and the results are shown in Table I. From the table it can be seen that derivatives of some

(6) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).
(7) L. Skattebøl, *Tetrahedron Lett.*, 2361 (1970); W. R. Moore, K. B. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970).
(8) P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Amer. Chem. Soc.*, **90**, 7271 (1968); P. G. Gassman and D. S. Patton, *ibid.*, **90**, 7276 (1968).
(9) P. G. Gassman, T. J. Atkins and J. T. Lumb, *Tetrahedron Lett.*, 1643 (1971); P. G. Gassman and E. A. Armour, *ibid.*, 1431 (1971).
(10) (a) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970); (b) P. G. Gassman and F. J. Williams, *Tetrahedron Lett.*, 1409 (1971); (c) P. G. Gassman, G. R. Meyer, and F. J. Williams, *Chem. Commun.*, 842 (1971); (d) P. G. Gassman and F. J. Williams, *ibid.*, 80 (1972); (e) P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, **93**, 5897 (1971).
(11) For recent discussions of strain in polycyclic molecules see R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968); N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); P. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970); S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *ibid.*, **92**, 3109 (1970); N. C. Baird, *Tetrahedron*, **26**, 2185 (1970).
(12) For preliminary reports of part of the work presented in this manuscript, see P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 1042 (1971); P. G. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971); P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 4597 (1971).
(13) G. Wittig and U. Schoellkopf, *Org. Syn.*, **40**, 66 (1960).
(14) We wish to thank Mr. H. R. Drewes for preparing the authentic sample of **11**.
(15) L. A. Paquette, R. P. Henzel, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 7002 (1970); L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93**, 1288 (1971).
(16) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971).
(17) G. L. Closs and L. E. Closs, *ibid.*, **85**, 2022 (1963).
(18) P. G. Gassman and F. J. Williams, *ibid.*, **94**, 7733 (1972).



5 13 15 14

Table I. Metal-Promoted Isomerizations of Tricyclo[4.1.0.0^{2,7}]heptane (5)

Catalyst	Conditions (temp (°C), time, solvent)	% yield of products^a 8	11	16
$AgBF_4$	(*Ca.* 40, "minutes," $CDCl_3$)^c			100
ZnI_2	25, 16 hr, Et_2O		11	88
$HgBr_2$	50, 48 hr, Et_2O		8	85
$[Rh(CO)_2Cl]_2$	25, 15 min, CH_3CN		98	
$[Ir(CO)_3Cl]_2$	25, 14 hr, $CHCl_3$		91	
$[(\pi\text{-}CH_2{:}CHCH_2)PdCl]_2$	25, 30 min, $CHCl_3$		94	
$(C_6H_5CN)_2PdCl_2$	25, 20 hr, CH_3CN		69	
$[C_6F_5Cu]_4$	25, 2 hr, $CHCl_3$		74	
$((C_6H_5)_3P)_2Rh(CO)Cl$	65, 48 hr, CH_3CN	5	92	
$[Ru(CO)_3Cl_2]_2$	25, 40 hr, CH_3CN	12	44	
PtO_2	65, 48 hr, CH_3CN	24	62	
$SnCl_2\cdot 2H_2O$	60, 24 hr, $CHCl_3$	40		
$AlCl_3$	(ether)^d	*b*		

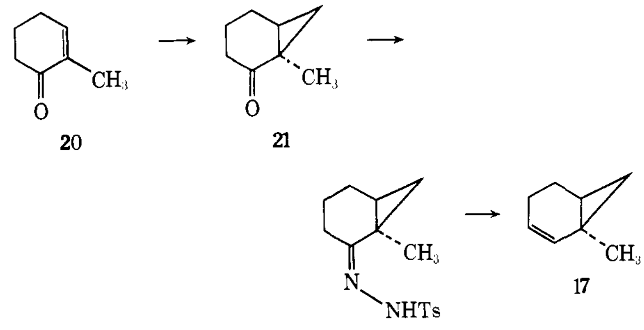
^{a} All yields reported from this laboratory represent the average of at least two runs. ^{b} Yield not reported. ^{c} References 15 and 16. ^{d} Reference 6.

11 different metals have been used to effect the isomerization of **5** and that these derivatives gave varying proportions of three different products: **8**,[19] **11**, and 1,3-cycloheptadiene (**16**).[19] Surprisingly, stannous chloride and aluminum chloride gave the "normal" acid-catalyzed product, 2-norcarene (**8**), but the known Lewis acids, zinc iodide and mercuric bromide, gave mixtures of **11** and **16**. The formation of **16** as the major product in these reactions closely parallels the silver ion catalyzed rearrangement of **5**.[15,16] The behavior of iridium tricarbonyl chloride dimer, (π-allyl)palladium chloride dimer, bisbenzonitrile–palladium chloride, and pentafluorophenylcopper tetramer[20] simulated that of rhodium dicarbonyl chloride dimer. However, none of the complexes which mimic rhodium dicarbonyl chloride dimer appear to be as reactive nor as quantitative. *trans*-Chlorocarbonylbis(triphenylphosphine)-rhodium(I), ruthenium tricarbonyl dichloride dimer, and platinum oxide give products which form a connecting link between the products formed in the presence of zinc iodide and mercuric bromide, and those formed in the presence of alumunum chloride or mineral acid.

The results from the transition metal complex promoted isomerizations of 1-methyltricyclo[4.1.0.0^{2,7}]-heptane (**13**) are shown in Table II. Again, a range of products was obtained depending on the metal derivatives used. Treatment of an ethereal solution of **13** with 7 mol % of stannous chloride in a sealed tube at 60° for 24 hr afforded 53% of the expected protic acid catalyzed product, 1-methyl-2-norcarene (**17**). The structure proof of **17** was based on comparison with an authentic sample prepared from the reaction of 2-methyl-2-cyclohexenone (**20**)[21] with dimethylsulfoxonium methylide,[22] which afforded 1-methyl-2-norcaranone (**21**) in 76% yield. Treatment of **21** with *p*-toluenesulfonylhydrazine gave **22**

Table II. Metal-Promoted Isomerizations of 1-Methyltricyclo[4.1.0.0^{2,7}]heptane (**13**)

Catalyst	Conditions (temp (°C), time, solvent)	% yield of products^a 17	14	18	19
$[Rh(CO)_2Cl]_2$	25, 15 min, $CHCl_3$		96		
$[Ir(CO)_3Cl]_2$	25, 14 hr, $CHCl_3$		93		
$[(\pi\text{-}CH_2{:}CHCH_2)PdCl]_2$	25, 30 min, $CHCl_3$		93		
$[C_6F_5Cu]_4$	25, 6 hr, $CHCl_3$		56		
ZnI_2	25, 16 hr, Et_2O			48	12
$HgBr_2$	60, 24 hr, Et_2O			24	42
$SnCl_2\cdot H_2O$	60, 24 hr, Et_2O	53			



20 21 22 17

which was treated with 2 equiv of methyllithium[23] to give a 54% yield of **17**.

The reactions of **13** with zinc iodide and mercuric bromide resembled the recently published silver ion catalyzed rearrangement[15,16] of **13**. The two products which were obtained were 2-methyl-1,3-cycloheptadiene (**18**) and 6-methylbicyclo[3.2.0]hept-6-ene (**19**). Their structures were established through in-

(19) The structure was conclusively established by comparison with an authentic sample.

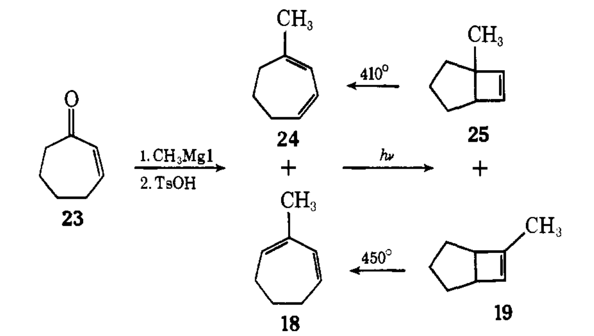
(20) We wish to thank Dr. William Sheppard of the DuPont Co. for supplying us with a sample of this catalyst.

(21) E. W. Warnhoff, D. G. Martin, and W. S. Johnson, *Org. Syn.*, 37, 8 (1957).

(22) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

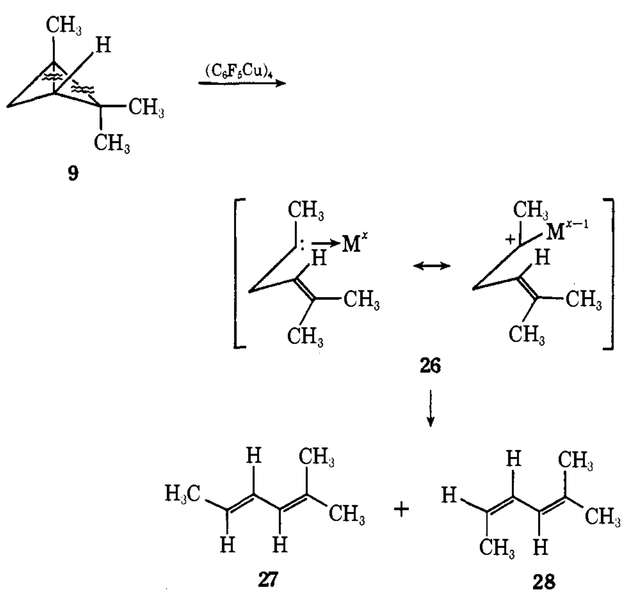
(23) R. H. Shapiro and M. J. Heath, *ibid.*, **89**, 5734 (1967); W. J. Dauben, M. E. Larber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *ibid.*, **90**, 4762 (1968); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

dependent synthesis. The reaction of 2-cycloheptenone (**23**) with methylmagnesium iodide followed by de-



hydration with *p*-toluenesulfonic acid gave a 2:1 mixture of **24** and **18**, respectively, in 66% combined yield. Photolysis of a mixture of **24** and **18** gave a 24% yield of a mixture of **25** and **19**, which was separated by preparative vpc. The structural correlation of **18** with **19** was unequivocally established by pyrolysis of **19** at 450° to give only **18**. Similarly, **25** gave only **24** on pyrolysis at 410°.

As in the case of **5**, iridium tricarbonyl chloride dimer, (π-allyl)palladium chloride dimer, and pentafluorophenylcopper(I) tetramer gave the same product as rhodium dicarbonyl chloride dimer in the transition metal complex promoted isomerization of **13**. Interestingly, although **13** bears a structural resemblance to 1,2,2-trimethylbicyclo[1.1.0]butane (**9**) (one bridgehead carbon atom of the bicyclo[1.1.0]butane moiety has a methyl substituent and the other has a hydrogen), their reactions with pentafluorophenylcopper(I) differed markedly. Treatment of **9** with the aryl copper compound[10b,18] resulted in products arising from cleavage of the side and central bonds in the manner indicated below to give the proposed intermediate species **26**.



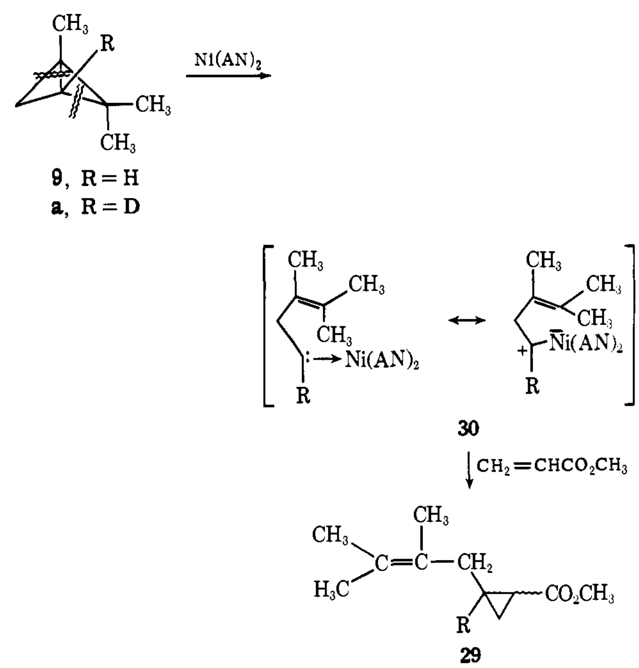
Treatment of **13** with $(C_6F_5Cu)_4$, however, gave **14** which arose from cleavage of a different side bond and the central bond. This mode of cleavage would be best explained in terms of the intermediate **15** in which the metal is attached to the carbon atom *not* bearing the methyl group. Apparently, transition metal complex promoted isomerizations of the bicyclo[1.1.0]butane nucleus are as sensitive to the nature of the ring system as they are to the nature of the transition metal complex.

Discussion

Since the discovery that transition metal compounds promote the facile rearrangement of a wide variety of strained ring compounds[24] many mechanisms have been proposed to account for the products obtained. In our studies of the reactions of simple bicyclo[1.1.0]butane derivatives we have proposed the formation of a transition metal complexed carbene–transition metal bonded carbonium ion hybrid as is depicted by structures **12** and **15**.[10,12,18] This intermediate would arise *via* cleavage of a side and central bond of the bicyclo[1.1.0]butane moiety. Evidence in support of this proposal in relation to simple methylated bicyclo[1.1.0]butanes has been presented in an accompanying paper.[18] Additional evidence in support of the formation of this intermediate has recently appeared in the form of intramolecular[10e] and intermolecular[25] trapping of the carbenoid species.[25a]

(24) For leading references see footnotes 1, 15, 16, 18, 26, and 27, and T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6519 (1969); P. E. Eaton and S. A. Cerefice, *Chem. Commun.*, 1494 (1970); J. Wristers, L. Bener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7491 (1970).

(25) R. Noyori, T. Suzuki, Y. Kumagai and H. Takaya, *ibid.*, **93**, 5894 (1971). When bicyclo[1.1.0]butane derivatives **9** and **9a** were

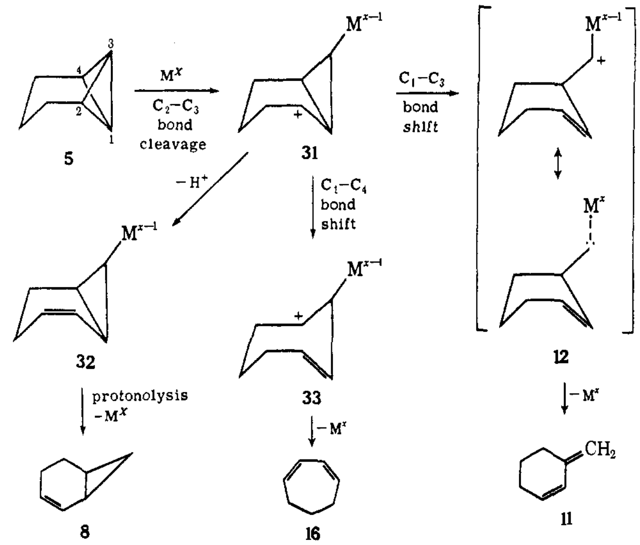


treated with bis(acrylonitrile)nickel(0) in the presence of methyl acrylate, adducts of the type **29** and **29a** were formed. This reaction can be viewed as occurring *via* cleavage of a side and central bond in **9** in the manner shown to give 30, which can then undergo addition to give the cyclopropane derivatives represented by **29**. The formation of these adducts may therefore be viewed as the result of a *formal* intramolecular retrocarbene reaction followed by an intermolecular carbene addition. The complex and unusual properties of the intermediate generated in this reaction are evident from its facile addition to the electron-deficient double bond of the acrylate ester, and its failure to add to the other olefins present in solution. This indicates that the metal complexed intermediate generated in the nickel(0) promoted rearrangement has some nucleophilic character. This indicates to us that in the nickel(0) studies back donation of electrons may make the "carbenoid" intermediate take on properties similar to ylides.

(25a) Note Added in Proof. Subsequent to the submission of this manuscript, two independent reports of the observation of a metal-complexed carbene intermediate in a metal-catalyzed rearrangement of a bicyclo[1.1.0]butane derivative have appeared [S. Masamune, M. Sakai, and N. Darby, *Chem. Commun.*, 471 (1972); W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **94**, 3669 (1972)]. We

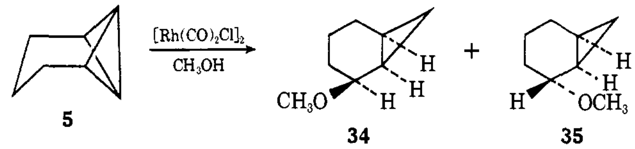
The data presented in Table I show that there is a gradual crossover of products for the metal derivatives used. We feel that the entire range of products can be explained in terms of the mechanism shown in Scheme I,[26] which details a stepwise bond cleavage process for

Scheme I

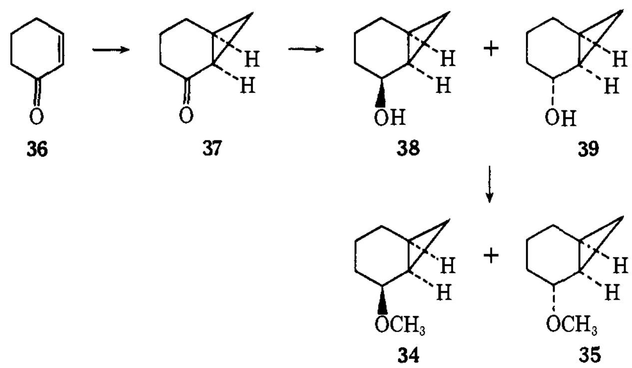


the bicyclo[1.1.0]butane nucleus. In this mechanism, the various transition metal derivatives act as *highly specific* Lewis acids. Initial attack of the transition metal derivative would produce the cyclopropylcarbinyl cation **31** *via* cleavage of the C_2–C_3 bond. All of the observed products can be adequately explained on the basis of the intermediacy of **31**. Subsequent cleavage of the C_1–C_3 bond would produce the hybrid intermediate **12** represented by the resonance contributors shown. A hydrogen shift from C_4 to C_3 and loss of M^X at this point would produce **11**. Loss of a proton from **31** would give **32** which on protonolysis[27] of the carbon–metal bond would give **8**.[28] 1,3-Cycloheptadiene (**16**) could be viewed as arising by cleavage of the C_1–C_4 bond in **31** to give the homoallylic cation **33**, which upon loss of M^X would give **16**.

In order to add substance to our hypothesis, we attempted to trap **31** by running the reaction in a more nucleophilic solvent. Treatment of **5** with rhodium dicarbonyl chloride dimer in methanol[29,29a] resulted in the formation of a 75% isolated yield of a 4:1 mixture of the methyl ethers **34** and **35**. This is the same ratio of ethers as was found in the methanolysis of **5** catalyzed



by sulfuric acid.[30] The structures were conclusively proven by spectral comparison with authentic samples synthesized by a modification of the procedure used by Dauben and Berezin.[31] 2-Cyclohexenone (**36**) was treated with dimethylsulfoxonium methylide[22] to give



37, which was reduced with lithium aluminum hydride to give a 30:70 mixture of **38** and **39**, respectively. Methylation of the mixture of these alcohols with sodium hydride–methyl iodide afforded a mixture of **34** and **35** in 85% yield.

When a methanolic solution of **5** was treated with 1 mol % of (π-allyl)palladium chloride dimer or 6 mol % of zinc iodide, again rapid addition of methanol occurred to give essentially the same mixture of **34** and **35**. This indicates to us that the transition metal compounds can behave as very specific Lewis acid catalysts. Furthermore, the trapping of a carbonium ion type intermediate by nucleophilic solvent tends to be consistent with our hypothesis that the multiple bond cleavages promoted by transition metal derivatives are stepwise processes which lead, *in some instances*, to an

were pleased to see that both of these groups interpreted their low-temperature nmr spectral data in a manner consistent with our initial postulate.

(26) In some respects there is a similarity between the stepwise mechanism which we are proposing for the rearrangement of 5 and that which has been suggested for the metal-catalyzed rearrangement of tri-*tert*-butylprismane [K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **93**, 1270 (1971)]. Both mechanisms use the transition metal catalyst as an electron acceptor. For an additional discussion see J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971).

(27) For a recent discussion of the mechanism of such protonolysis processes, see: T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **93**, 1049 (1971).

(28) This is the pathway taken in the "normal" protic acid catalyzed reaction of 5.

(29) Control experiments demonstrated that the dimer could be recovered unchanged from methanol and that the addition of enough sodium methoxide to make the reaction mixture strongly basic did not stop the reaction. Hence, it would appear that the observed reaction was not due to the formation of some new catalyst from methanol and rhodium dicarbonyl chloride dimer nor by generation of a Brønsted acid in the solution. It should be noted that we have not rigorously established that the reactive species is rhodium dicarbonyl chloride dimer in methanol. In principle, a rapid equilibrium between the rhodium(I) complex, methanol, and some new complex could exist. If removal of the methanol should shift such a hypothetical equilibrium back to the starting rhodium(I) complex, a new complex (in equilibrium) would have gone undetected.

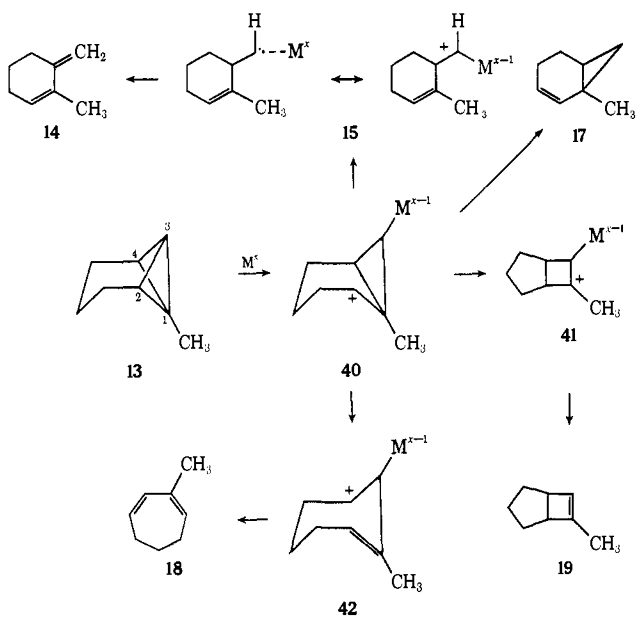
(29a) Note Added in Proof. Subsequent to the submission of this paper, it has been suggested that our results were due to old $[Rh(CO)_2Cl]_2$ and that freshly prepared $[Rh(CO)_2Cl]_2$ in methanol converted 5 into 11 [W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, 94, 3669 (1972)]. It was also stated that the formation of ethers is a side reaction due to impurities and that "a metal cyclopropylcarbinyl cation is not involved in the rearrangement of bicyclobutane 1" (5). We have reinvestigated this aspect of our study and have found that an acidic media can be generated from methanol, $[Rh(CO)_2Cl]_2$, and 5. However, the results obtained in our laboratory show that the overall process is more complex than either we or Dauben anticipated. Although we conclude now that 34 and 35 can be formed in an acid-catalyzed process under our conditions, we wish to note that we cannot accept either a portion of Dauben and Kielbania's experimental results or mechanistic conclusions relative to that aspect of our investigation involving methanol. Our detailed study of this complex chemistry [P. G. Gassman and R. Reitz, unpublished work] will be the subject of a future report. In relation to the present paper we wish to note that the formation of 34 and 35 neither detracts from nor supports our overall mechanistic picture.

(30) (a) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970); (b) Masamune and coworkers have observed similar results with silver ion in methanol (M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971)).

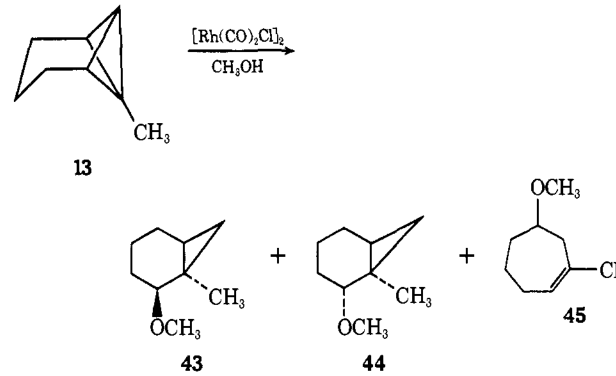
(31) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

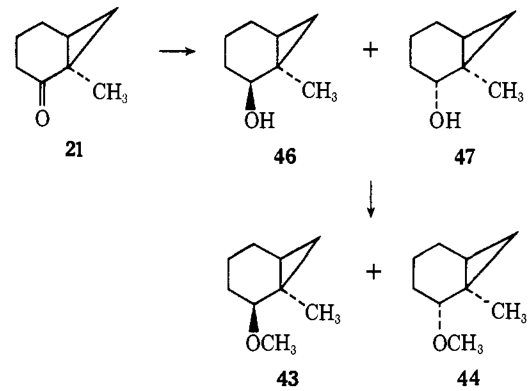
intermediate which can be represented by resonance hybrids such as **12**.

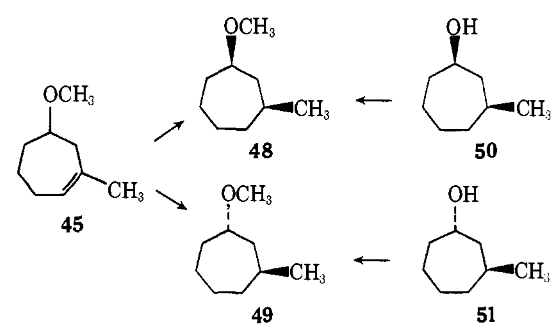
Table II lists the products observed in the reaction of various transition metal derivatives with **13**. The metal derivatives which converted **5** to **11** have been previously discussed, and evidence was presented in support of **12** as an intermediate in this isomerization. Similar arguments can be utilized in support of the intermediacy of the resonance hybrid **15** in the isomerization of **13** to **14**. The formation of the "expected" acid-catalyzed product, **17**, may be viewed in the same manner as the formation of **8**. However, the formation of **18** and **19** when zinc iodide or mercuric bromide was used as the reaction initiator deserves some mechanistic comment. Initial attack of the complex on **13** would be expected to lead to the cleavage of the C_2–C_3 bond to give the cyclopropylcarbinyl cation **40**. Cleavage of the C_1–C_3 bond would lead to formation of **15** and subsequently to **14**, while proton loss and protonolysis of the carbon–metal bond of **40** would produce **17**. Alternatively, **40** could undergo a shift of the C_1–C_4 bond to give the homoallylic cation **42**. Upon loss of the metal ion, **42** would give **18**. A cyclopropylcarbinyl–cyclobutyl cation rearrangement of **40** would produce the tertiary cation **41**,[32] which would yield **19** upon loss of M^x. It is presumably the added stability of the tertiary cation **41** which differentiates the formation of **19** from **13** from the lack of formation of any bicyclo[3.2.0]heptane derivative from **5**.



Evidence consistent with a stepwise mechanism similar to that proposed for the rearrangement of **5** was obtained by treatment of a methanolic solution of **13** with 1 mol % of rhodium dicarbonyl chloride dimer. The trapping of the carbonium ion type intermediate **40** was substantiated by the formation, in 82% isolated yield, of an 80:10:10 mixture of *exo*-2-methoxy-1-methylnorcarane (**43**), *endo*-2-methoxy-1-methylnorcarane (**44**), and 4-methoxy-2-methylcycloheptene (**45**). The structures of **43** and **44** were conclusively proven by independent synthesis in the following manner. Reduction of **21** with lithium aluminum hydride afforded a 5:1 mixture of **46**[33] and **47**. Methylation of the mixture of alcohols with sodium hydride–methyl iodide yielded a mixture of **43** and **44**. The structure of **45**[34] was based upon its spectral data [ir (CCl_4 solution) 8.98, 9.10, and 9.21 μ; nmr ($CDCl_3$) τ 4.40 (1 H, t, J = 7 Hz), 6.71 (3 H, s), 7.0 (1 H, m), 7.6–9.0 (11 H, br m containing a 3 H s at τ 8.29)], and by reduction of **45** to give a 3:2 mixture of **48** and **49**, which were prepared independently by methylation of **50** and **51**, respectively.[35]







The experimental data presented in the main body of this paper provide strong support for our mechanistic postulate. In general, this postulate provides a unified picture of the overall patterns of reactions which derivatives of tricyclo[4.1.0.0^{2,7}]heptane can follow in transition metal complex promoted rearrangements. These concepts appear to apply equally well to sim-

(32) Alternately, **41** could be formed by homoallylic participation of the double bond in **42**. A multistep mechanism which involved initial cleavage of the central bond of **13** could also be constructed to explain the origin of **19**.

(33) We wish to thank Professor W. Dauben for supplying us with the ir spectrum of authentic **46**.

(34) Compound **45** could also be obtained by treatment of the mixture of **46** and **47** with *p*-toluenesulfonyl chloride in pyridine followed by refluxing the crude product in methanol.

(35) Prepared according to the method of W. Hückel and O. Honecker, *Justus Liebigs Ann. Chem.*, **678**, 10 (1964).

ple methylated derivatives of bicyclo[1.1.0]butane.[18]

In view of the ease with which our mechanistic picture provides a clear insight into the route from starting materials to products, we feel it is of interest to compare our mechanistic theory with the various different mechanisms which have been proposed for the silver ion catalyzed rearrangement of **5**[15,16,36] and **13**.[37-40] The silver ion catalyzed rearrangement of **5** was initially suggested to proceed *via* a concerted cleavage of only side bonds.[15] As additional evidence bearing on the mechanism of this rearrangement began to appear,[10a,12,16] the concerted mechanism was abandoned in favor of a complete "argento carbonium ion" mechanism.[37] It is interesting to note that this "argento carbonium ion" represents one extreme of the transition metal complexed carbene–transition metal bonded carbonium ion hydrid which we proposed[12] as an intermediate in the formation of conjugated dienes from bicyclo[1.1.0]butane derivatives. More recently, the "argento carbonium ion" mechanism for the silver ion promoted isomerization of derivatives of tricyclo-[4.1.0.0^{2,7}]heptane has been dramatically altered to a mechanism which bypasses argento carbonium ions in certain instances.[38] This change[38] brings the postulated mechanism for the silver ion promoted rearrangements of **5** and **13** to a stage where it shows marked resemblance to our mechanistic picture[12] of the transition metal complex promoted rearrangements of **5** and **13**.[41]

In summary, we feel that the data we have presented now offer a more unifying concept for the reactions of bicyclo[1.1.0]butane derivatives with transition metal complexes and lend support to the hypothesis that the transition metal complex promoted rearrangements of highly strained polycyclic systems, such as **5** and **13**, are stepwise processes in which the transition metal complex acts as a very specific type of Lewis acid. The specificity of the metal complex, *i.e.*, why different metals and even different ligands on the metal effect a crossover in the mechanistic pathways, is a question which remains to be answered and which is currently under investigation in our laboratories.[42]

Experimental Section

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord as neat liquids, in solution in carbon tetrachloride or chloroform, or as powdered solids in potassium bromide disks. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60-A spectrometer and are reported in τ units relative to tetramethylsilane (τ = 10.00) as the internal standard. Exact mass determinations were obtained on an MS-9 high resolution mass spectrometer.

General Procedures. Two procedures were used to determine the products from the reactions of **5** and **13** with the various transition metal derivatives.

A. To a solution of *ca.* 2 mmol of **5** or **13** in 1 ml of solvent under nitrogen was added *ca.* 5 mol % of the transition metal derivative and the mixture was stirred *at 25°* for the described time. The volatile products were then vacuum transferred and the products were separated from solvent by preparative vpc on a 10 ft × $^1/_4$ in. 20% D.C. Silicone Fluid No. 200, 1000 cs on 60–80 Columpak column at 80°.

B. A mixture of *ca.* 2 mmol of **5** or **13** in 1 ml of solvent was heated in a sealed tube with *ca.* 5 mol % of the transition metal derivative at the desired temperature for a prescribed period of time. The tube was cooled and opened and the contents were vacuum transferred. The products were isolated as in procedure A.

All yields reported in these reactions were determined by vpc *vs.* an internal standard and represent the average of at least two runs. The yields were determined on a 10 ft × $^1/_8$ in. 20% D.C. Silicone Fluid No. 200, 1000 cs on 60–80 Columpak at 80°, and are corrected for detector response. Both preparative and analytical analyses were obtained on an F&M Model 810 gas chromatograph.

All products were identified *via* comparison with authentic samples.

Tricyclo[4.1.0.0^{2,7}]heptane (5). This compound was prepared by the method of Moore, *et al.*[6]

Reaction of 5 with Zinc Iodide. Procedure A. A 202.4-mg (2.15 mmol) sample of **5**, 2 ml of anhydrous ether, and 44.6 mg (0.14 mmol, 6.5 mol %) of anhydrous zinc iodide gave 11% of 3-methylenecycloheptene (**11**) and 88% of 1,3-cycloheptadiene (**16**) after stirring for 16 hr.

Reaction of 5 with Mercuric Bromide. Procedure B. A 142.1-mg (1.51 mmol) sample of **5**, 2 ml of anhydrous ether, and 50.1 mg (0.139 mmol, 9 mol %) of mercuric bromide gave 8% of **11** and 85% of **16** after 48 hr at 50°.

Reaction of 5 with Rhodium Dicarbonyl Chloride Dimer. Procedure A. A 265-mg (2.8 mmol) sample of **5**, 1 ml of acetonitrile, and 29 mg (0.075 mmol, 4 mol %) of rhodium dicarbonyl chloride dimer gave 98% of **11** after 15 min. Using chloroform as solvent under the same conditions we obtained 97% of **11**.

Reaction of 5 with Iridium Tricarbonyl Chloride Dimer. Procedure A. A 23.4-mg (0.25 mmol) sample of **5**, 0.25 ml of chloroform, and 7 mg (0.012 mmol, 5 mol %) of iridium tricarbonyl chloride dimer yielded 91% of **11** after 14 hr.

Reaction of 5 with (π-Allyl)palladium Chloride Dimer. Procedure A. A 153.0-mg (1.63 mmol) sample of **5**, 1 ml of chloroform, and 7.3 mg (0.02 mmol, 1.2 mol %) of (π-allyl)palladium chloride dimer produced 94% of **11** after 30 min.

Reaction of 5 with Bis(benzonitrile)palladium Chloride. Procedure A. A 148.7-mg (1.58 mmol) sample of **5**, 1 ml of acetonitrile, and 32.3 mg (0.079 mmol, 5 mol %) of bis(benzonitrile)palladium chloride gave 69% of **11** after 20 hr.

Reaction of 5 with Pentafluorophenylcopper Tetramer. Procedure A. A 158.0-mg (1.68 mmol) sample of **5**, 1 ml of chloroform, and 32.1 mg (0.035 mmol, 2 mol %) of pentafluorophenylcopper tetramer gave 74% of **11** after 2.5 hr.

Reaction of 5 with *trans*-Chlorocarbonylbis(triphenylphosphine)-rhodium(I). Procedure B. A 174-mg (1.86 mmol) sample of **5**, 1 ml of acetonitrile, and 62 mg (5 mol %) of *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) gave 92% of **11** and 5% of 2-norcarene (**8**) after 48 hr at 65°.

Reaction of 5 with Platinum Oxide. Procedure B. A 155-mg (1.65 mmol) sample of **5**, 1 ml of acetonitrile, and 18 mg (5 mol %) of platinum oxide yielded 62% of **11** and 24% of **8** after 48 hr at 65°.

Reaction of 5 with Stannous Chloride. Procedure B. A 148.9-mg (1.59 mmol) sample of **5**, 1 ml of chloroform, and 40.2 mg (0.18 mmol, 11 mol %) of stannous chloride dihydrate gave 40% of **8** after 24 hr at 60°.

1-Methyltricyclo[4.1.0.0^{2,7}]heptane (13).[17] To a magnetically stirred solution of 5.15 g (44.4 mmol) of dry tetramethylethylenediamine (TMEDA) in 10 ml of anhydrous ether was added 60 ml of 0.74 *N* *n*-butyllithium in ether (44.4 mequiv) and the mixture was stirred for 20 min under nitrogen. *Via* a syringe, 3.00 g (31.9 mmol) of **5** was added dropwise and the solution was stirred for 5 hr at 25°; 6.00 g (42 mmol) of methyl iodide was slowly added while

(36) Our first indication of the ease with which silver ion could facilitate the rearrangement of **5** came completely by accident when G. D. Richmond, who was studying cycloaddition reactions of **5**, attempted to purify **5** by chromatography on a 10% silver nitrate on alumina column, only to find that **5** rapidly rearranged under these conditions. In contrast, tricyclo[4.1.0.0^{3,7}]heptane was stable to chromatography on the same column (G. D. Richmond, Ph.D. Thesis, The Ohio State University, 1968).

(37) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 2335 (1971).

(38) L. A. Paquette and S. E. Wilson, *ibid.*, **93**, 5934 (1971).

(39) M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971).

(40) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

(41) Although the latest mechanism[38] for the silver ion promoted rearrangement of **5** and **13** is starting to approach very close to our proposed[12] mechanistic process, there are still numerous differences. We are currently carrying out experimental work designed to eliminate further these differences of opinion.

(42) We feel that a possible source of the specificity may be related to the strength of the various carbon–metal "bonds" formed in the first step of the rearrangement process.

cooling the reaction mixture in ice and the mixture was then stirred for 3.5 hr at 25°. The solution was poured onto ice, the layers were separated, and the aqueous phase was extracted with 40 ml of ether. The combined organic layers were washed with three 50-ml portions of water and 50 ml of saturated salt solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration. After careful distillation of the ether at atmospheric pressure, vacuum distillation of the residue through a 10-cm Vigreux column afforded 5.30 g of a hydrocarbon mixture, bp 56–65° (190 mm). Pure **13**, 2.12 g (61%), was obtained after removal of the *n*-octane impurity by preparative vpc on a 10 ft × $^1/_4$ in. 15% Carbowax 1500–3% KOH on 60–80 Chromosorb G column at 50°.

Reaction of 13 with Rhodium Dicarbonyl Chloride Dimer. Procedure A. A 56-mg (0.53 mmol) sample of **13**, 0.5 ml of chloroform, and 9 mg (0.023 mmol, 5 mol %) of rhodium dicarbonyl chloride dimer, after 15 min reaction time, gave 96% of 2-methyl-3-methylenecyclohexene (**14**): ir (CCl_4 solution) 3.21, 3.40, 6.09, 6.22, 6.96, and 11.28 μ; nmr (CCl_4) τ 4.37 (1 H, m), 5.17 (1 H, br s), 5.30 (1 H, br s), 7.5–8.1 (4 H, m), 8.21 (3 H, d, J = 1.5 Hz), 8.2–8.6 (2 H, m); uv λ_{max}^{hexane} 234 nm (ϵ 16,200); *m/e* calcd for C_8H_{12}, 108.0938; found, 108.0937.

Reaction of 13 with Iridium Tricarbonyl Chloride Dimer. Procedure A. A 156.4-mg (1.44 mmol) sample of **13**, 1 ml of chloroform, and 44 mg (0.7 mmol, 5 mol %) of iridium tricarbonyl chloride dimer gave 93% of **14** after 14 hr.

Reaction of 13 with (π-Allyl)palladium Chloride Dimer. Procedure A. A 104.4-mg (0.96 mmol) sample of **13**, 0.5 ml of chloroform, and 4.8 mg (0.013 mg, 1.4 mol %) of (π-allyl)palladium chloride dimer gave 93% of **14** after 30 min.

Reaction of 13 with Pentafluorophenylcopper Tetramer. Procedure A. A 161.1-mg (1.49 mmol) sample of **13**, 1 ml of chloroform, and 24.4 mg (0.026 mmol, 1.8 mol %) of pentafluorophenylcopper tetramer yielded 56% of **14** after 6 hr.

Reaction of 13 with Zinc Iodide. Procedure A. A 167.4-mg (1.42 mmol) sample of **13**, 2 ml of anhydrous ether, and 42.0 mg (0.13 mmol, 9 mol %) of dry zinc iodide gave 48% of 2-methyl-1,3-cycloheptadiene (**18**) and 12% of 6-methylbicyclo[3.2.0]hept-6-ene (**19**) after 16 hr.

Reaction of 13 with Mercuric Bromide. Procedure B. A 143-mg (1.32 mmol) sample of **13**, 2 ml of anhydrous ether, and 25 mg (0.069 mmol, 5.25 mol %) of mercuric bromide produced 24% of **18** and 42% of **19** after 24 hr at 60°.

Reaction of 13 with Stannous Chloride. Procedure B. A 188-mg (1.74 mmol) sample of **13**, 1 ml of anhydrous ether, and 28.1 mg (0.125 mmol, 7 mol %) of stannous chloride dihydrate gave 53% of 1-methyl-2-norcarene (**17**) after 24 hr at 60°.

Hydrogenation of 14. In a 15-ml round-bottomed flask equipped with a magnetic stirrer and serum cap was placed 15 mg of 5% palladium-on-carbon and 59 mg of **14**. The flask was charged with 10 cm^3 of hydrogen gas *via* a syringe and the solution was stirred at 25°. At three 0.5-hr intervals additional 10-cm^3 portions of hydrogen gas were added and the solution was stirred overnight under a positive hydrogen pressure. The solution was centrifuged and the supernatant liquid was found to contain a mixture of 43% of *trans*-1,2-dimethylcyclohexane, 24% of *cis*-1,2-dimethylcyclohexane, and 33% of *o*-xylene *via* vpc analysis. The components were isolated by preparative vpc at 90° on a 10 ft × $^1/_4$ in. 20% D.C. Silicone Fluid No. 200, 1000 cs on 60–80 Columpak column, and characterized by spectral comparison to authentic samples.

2-Methyl-1,3-cycloheptadiene (18). Methylmagnesium iodide was prepared in the usual manner from 3.65 g (0.15 g-atom) of magnesium turnings and 21.3 g (0.15 mol) of methyl iodide in a total volume of 125 ml of anhydrous ether in a 300-ml three-necked flask equipped with a magnetic stirrer, addition funnel, reflux condenser, and drying tube. A solution of 10.8 g (0.0983 mol) of 2-cycloheptenone (**23**) in 20 ml of anhydrous ether was slowly added over 1.5 hr and the mixture was stirred for an additional hour at 25°. The mixture was poured onto ice–saturated ammonium chloride solution and the layers were separated. The aqueous layer was extracted with two 50-ml portions of ether and the combined organic layers were washed with saturated salt solution and dried over anhydrous magnesium sulfate. After filtration, distillation of the solvent afforded 11.0 g (89%) of crude alcoholic product.

The crude alcoholic product was dissolved in 25 ml of benzene in a 50-ml flask equipped with a Dean-Stark trap and the solution was refluxed with 0.5 g of *p*-toluenesulfonic acid for 75 min. The reaction solution was diluted with an equal volume of ether and washed with 25-ml portions of water, saturated sodium carbonate solution, and saturated salt solution, and was dried over anhydrous magnesium sulfate. The solution was filtered and the solvents were carefully removed by distillation. Vacuum distillation of the residue through a short-path column afforded 6.95 g (66%) of a 2:1 mixture of 1-methyl-1,3-cycloheptadiene (**24**) and **18**, bp 73–78° (60 mm).[43] Pure samples of **24** and **18** were obtained by preparative vpc on a 10 ft × $^1/_4$ in. 15% Carbowax 1500–3% KOH on 60–80 Chromosorb G column. Spectral properties of **18** were: ir (CCl_4 solution) 6.06 and 6.20 (w) μ; nmr ($CDCl_3$) τ 4.11–4.49 (3 H, m), 7.5–8.4 (9 H, m, containing 8.19 (3 H, s)). Spectral properties of **24** were: ir (CCl_4 solution) 6.06 and 6.16 (m) μ; nmr ($CDCl_3$) τ 4.2–4.5 (3 H, m), 7.45–7.83 (4 H, m), 7.90–8.36 (5 H, m, containing 8.16 (3 H, s)).

6-Methylbicyclo[3.2.0]hept-6-ene (19). A solution of 4.00 g (0.037 mol) of a 2:1 mixture of **24** and **18** in 350 ml of olefin-free pentane was irradiated for 2 hr at 0° in a quartz photolysis apparatus equipped with a Vycor filter using a Hanovia high-pressure mercury lamp. The solution was dried over anhydrous magnesium sulfate and filtered. The pentane was removed by distillation and the residue was vacuum transferred. Preparative vpc of the crude material on a 10 ft × $^1/_4$ in. 20% D.C. Silicone Fluid No. 200, 1000 cs on 60–80 Columpak column, afforded 486 mg of 6-methylbicyclo[3.2.0]hept-6-ene (**19**) and 554 mg of 1-methylbicyclo[3.2.0]-hept-6-ene (**25**) (26% combined yield). In order to unequivocally establish the structural relationships, pure **25** was pyrolyzed at 410° in the vapor phase to give **24** and pure **19** was pyrolyzed at 450° to give **18**. Spectral properties of **19** were: ir (CCl_4 solution) 6.10 μ (m); nmr ($CDCl_3$) τ 4.45 (1 H, m), 6.97 (2 H, br d), 8.0–9.3 (9 H, m containing a 3 H d (J = 1.5 Hz) at τ 8.38). Spectral properties of **25** were: ir (CCl_4 solution) 5.99 μ (w); nmr ($CDCl_3$) τ 4.1 (2 H, br s), 7.32 (1 H, br d), 7.9–9.3 (9 H, m containing a 3 H s at τ 8.70).

Reaction of 5 with Rhodium Dicarbonyl Chloride Dimer in Methanol. To a stirred solution of 520 mg (5.5 mmol) of **5** in 5 ml of absolute methanol cooled in ice was added 23.8 mg (0.06 mmol, 1 mol %) of rhodium dicarbonyl chloride dimer. After stirring for 5 min, no starting material could be detected by vpc analysis. The methanol was removed by distillation, and distillation of the residue afforded 521 mg (75%) of clear, colorless liquid, bp 91–92° (76 mm), which was identified as a 4:1 mixture of *exo*-2-methoxynorcarane (**34**) and *endo*-2-methoxynorcarane (**35**) by nmr and vpc comparison with authentic samples.

Reaction of 5 with Zinc Iodide in Methanol. In a similar manner, 392.9 mg (4.18 mmol) of **5**, 2 ml of absolute methanol, and 78.6 mg (0.246 mmol, 6 mol %) of zinc iodide were stirred at 25° for 4 hr to afford 350.6 mg (67%) of a *ca.* 4:1 mixture of **34** and **35**.

Reaction of 5 with (π-Allyl)palladium Chloride Dimer in Methanol. In a similar manner, 336 mg (3.57 mmol) of **5**, 2 ml of absolute methanol, and 14.8 mg (0.04 mmol, 1.1 mol %) of (π-allyl)palladium chloride dimer gave 347.2 mg (77%) of a *ca.* 4:1 mixture of **34** and **35**.

2-Norcaranone (37). In a 500-ml three-necked flask equipped with a magnetic stirrer, addition funnel, reflux condenser with a gas outlet, and a gas inlet stopcock was placed 4.4 g (60%, 0.11 mol) of a sodium hydride–mineral oil dispersion. The mineral oil was removed by three hexane washings and the last traces of hexane were removed by evacuating the system. Dry nitrogen gas was admitted and 24.2 g (0.11 mol) of trimethyl sulfoxonium iodide[22] was added and the system was maintained under a nitrogen atmosphere. From the dropping funnel, 125 ml of dry dimethyl sulfoxide (DMSO) was added with stirring and vigorous hydrogen evolution. After 15 min, a solution of 9.6 g (0.10 mol) of 2-cyclohexenone (**36**) in 20 ml of dry DMSO was slowly added to the milky white solution. After the initial exotherm, the clear red solution was stirred at 50° for 2 hr, cooled to 25°, poured onto 250 ml of cold water, and extracted with three 50-ml portions of ether. The extracts were washed twice with water and then saturated salt solution and were dried over anhydrous magnesium sulfate. After filtering the solution and removing the ether, distillation of the residue afforded 4.91 g (45%) of clear, colorless **37**, bp 93–95° (18 mm) [lit.[31] bp 85–85.5° (10 mm)].

Reduction of 37 with Lithium Aluminum Hydride. In a 250-ml three-necked flask equipped with a magnetic stirrer, addition funnel, reflux condenser, and drying tube were placed 1.0 g (26.3 mmol) of lithium aluminum hydride and 80 ml of anhydrous ether. A solution of 4.9 g (44.6 mmol) of **37** was slowly added with stirring, and the mixture was refluxed for 2 hr, cooled to 25°, decomposed by

(43) V. A. Mironov, O. S. Chizhov, Ia. M. Kimelfeld, and A. A. Akhrem, *Tetrahedron Lett.*, 499 (1969).

careful dropwise addition of 4.0 g of 10% sodium hydroxide solution, and stirred overnight. Anhydrous magnesium sulfate was added to dry the mixture and the solution was filtered. The ether was removed and distillation of the residue afforded 4.64 g (93%) of a 30:70 mixture of *exo*-2-norcaranol (**38**)[31] and *endo*-2-norcaranol (**39**),[31] respectively, bp 90–107° (19 mm). Pure samples of **38** and **39** were obtained by preparative gas chromatography at 110° on a 10 ft × 1/4 in. 10% Carbowax 20M-KOH (4:1) on 60–80 Chromosorb W column.

***exo*-2-Methoxynorcarane (34) and *endo*-2-Methoxynorcarane (35).** In a 250-ml three-necked flask equipped with addition funnel, magnetic stirrer, reflux condenser, and drying tube was placed 1.8 g (60%, 45 mmol) of a sodium hydride–mineral oil dispersion. The mineral oil was removed by three hexane washings and the last traces of hexane were then removed by evacuation of the apparatus. Dry nitrogen was then admitted and 60 ml of anhydrous ether was added, followed by a solution of 2.00 g (17.7 mmol) of a 30:70 mixture of **38** and **39** in 5 ml of ether. After stirring at 25° for 2 hr, 10.0 g (70 mmol) of methyl iodide was added and the mixture was stirred at 25° for an additional 3 days. The excess sodium hydride was decomposed by the addition of 1:1 ether–methanol. Saturated ammonium chloride solution was added to precipitate the salts, the ether was decanted, and the salts were washed twice with ether. The combined washings were washed twice with saturated salt solution and were dried over anhydrous magnesium sulfate. After filtering the solution and distilling the ether, distillation of the residue yielded 1.87 g (85%) of a mixture of **34** and **35**, bp 92–97° (66 mm) [lit.[31] bp 60° (40 mm)], whose spectral data compared favorably with the literature values.[30,31]

Reaction of 13 with Rhodium Dicarbonyl Chloride Dimer in Methanol. A stirred solution of 460 mg (4.26 mmol) of **13** in 5 ml of methanol at 0° was treated with 24 mg (0.062 mmol, 1.5 mol %) of rhodium dicarbonyl chloride dimer, which caused a vigorous exothermic reaction. After stirring for 5 min, the methanol was distilled and distillation of the residue afforded 490 mg (82%) of clear, colorless liquid, bp 90–92° (55 mm), which was identified as an 80:10:10 mixture of *exo*-2-methoxy-1-methylnorcarane (**43**), *endo*-2-methoxy-1-methylnorcarane (**44**), and 4-methoxy-2-methylcycloheptene (**45**). The components were separated by preparative vpc at 90° on a 9 ft × 1/4 in. 25% β,β′-oxydipropionitrile on 42–60 Firebrick column. The spectral properties of **45** were: ir (CCl_4 solution) 8.98, 9.10, and 9.21 μ; nmr ($CDCl_3$) τ 4.40 (1 H, t, J = 7 Hz), 6.71 (3 H, s), 7.0 (1 H, m), 7.6–9.0 (11 H, m containing a 3 H s at τ 8.29); *m/e* calcd for $C_9H_{16}O$, 140.1201; found, 140.1203.

1-Methyl-2-norcaranone (21). Using the procedure described for the preparation of **37**, 4.4 g (60%, 0.11 mol) of a sodium hydride–mineral oil dispersion, 24.2 g (0.11 mol) of trimethylsulfoxonium iodide, and 11.0 g (0.10 mol) of 2-methylcyclohexenone (**20**)[21] gave 10.40 g (76.5%) of clear, colorless **21**:[44] bp 88–90° (19 mm); ir (neat) 5.91 and 10.98 μ; nmr ($CDCl_3$) τ 7.6–9.6 (m), 8.93 (s).

1-Methyl-2-norcaranone Tosylhydrazone (22). A solution of 1.86 g (10 mmol) of *p*-toluenesulfonylhydrazine, 30 ml of methanol, 1.24 g (10 mmol) of **21**, and two drops of concentrated hydrochloric acid was refluxed for 2 hr. The methanol was removed and the resulting oil was triturated with ether. The ether was evaporated and the resulting off-white solid was recrystallized from methanol–water to give 2.33 g (80%) of **22**. Three recrystallizations gave an analytical sample: mp 148–150°; ir (KBr) 3.10, 6.26, 7.14, and 8.66 μ.

Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.62; H, 6.86; N, 9.55; S, 10.93. Found: C, 61.65; H, 6.91; N, 9.61; S, 10.94.

1-Methyl-2-norcarene (17). To a stirred solution of 2.3 g (7.9 mmol) of **22** in 100 ml of anhydrous 1:1 ether–tetrahydrofuran was added 12.5 ml of 1.62 *M* methyllithium in ether *via* a syringe. The solution changed to orange and then a yellow-orange precipitate was deposited. After stirring for 15 min, the mixture was decomposed on ice-water. The layers were separated and the aqueous layer was extracted with two 25-ml portions of 1:1 ether–pentane. The combined organic layers were washed twice with water and once with saturated salt solution, and were dried over anhydrous magnesium sulfate. The solution was filtered, the solvents were distilled, and distillation of the residue afforded 0.46 g (54%) of clear, colorless **17**: bp 75–77° (190 mm); ir (CCl_4 solution) 6.10 μ; nmr ($CDCl_3$) τ 4.10 (1 H, br d, J = 10 Hz), 4.4–4.8 (1 H, m), 7.8–9.1 (8 H, m containing a 3 H s at τ 8.84), and 9.15–9.7 (2 H, m).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.96; H, 11.15.

Reduction of 21 with Lithium Aluminum Hydride. Using the procedure described for the reduction of **37**, 6.00 g (48.4 mmol) of **21** was reduced with 1.0 g of lithium aluminum hydride to give 5.65 g (93%) of a clear, colorless 5:1 mixture of *exo*-1-methyl-2-norcaranol (**46**) and *endo*-1-methyl-2-norcaranol (**47**), bp 84–87° (15 mm). Pure samples of **46** and **47** were obtained by preparative vpc at 100° on a 10% Carbowax 20M-KOH (4:1) on 60–80 Chromosorb W. The spectral properties of **46** were: ir[33] (CCl_4) 2.91 and 9.73 μ; nmr ($CDCl_3$) τ 6.14 (1 H, t), 7.7–9.4 (11 H, m including variable O*H* and a 3 H s at τ 8.84), 9.57 (1 H, s), 9.68 (1 H, d). The spectral properties of **47** were: ir (CCl_4) 2.86, 9.02, 9.48, 9.82, 10.18, and 10.34 μ; nmr ($CDCl_3$) τ 5.99 (1 H, m), 7.8–9.4 (11 H, m including O*H* s and a 3 H s at τ 8.94), 9.5–10.0 (2 H, m).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.84; H, 11.14.

***exo*-2-Methoxy-1-methylnorcarane (43) and *endo*-2-Methoxy-1-methylnorcarane (44).** In a procedure similar to that used for the preparation of **34** and **35**, 2.25 g (17.7 mmol) of a 5:1 mixture of **46** and **47**, 1.8 g (60%, 45 mmol) of a sodium hydride–mineral oil dispersion, and 10.0 g of methyl iodide gave 1.95 g (78%) of clear, colorless liquid, bp 92–97° (64 mm), which was subjected to preparative vpc at 90° on a 9 ft × 1/4 in. 25% β,β′-oxydipropionitrile on 42–60 Firebrick to give pure **43** and **44**. The spectral properties of **43** were: ir (CCl_4) 9.11 μ; nmr ($CDCl_3$) τ 6.4–6.7 (1 H, m), 6.67 (3 H, s), 7.8–9.2 (10 H, m containing a 3 H s at τ 8.91), 9.2–9.8 (2 H, m).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.93; H, 11.37.

The spectral properties of **44** were: ir (CCl_4) 9.03 and 9.19 μ; nmr ($CDCl_3$) τ 6.5–6.7 (1 H, m), 6.67 (3 H, s), 7.8–9.5 (10 H, m containing a 3 H s at τ 8.95), 9.5–10.0 (2 H, m).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.87; H, 11.47.

Hydrogenation of 45. A solution of 220 mg (1.57 mmol) of **45** in 10 ml of absolute methanol over 50 mg of 5% palladium-on-carbon was hydrogenated on an atmospheric pressure hydrogenator to give 200 mg (90%) of a 3:2 mixture of *cis*-1-methoxy-3-methylcycloheptane (**48**) and *trans*-1-methoxy-3-methylcycloheptane (**49**), bp 89–93° (45 mm).

***cis*-1-Methoxy-3-methylcycloheptane (48).** Pure *cis*-3-methylcycloheptanol (**50**)[35] (bp 91.6–91.8° (12 mm)) (1.00 g, 7.8 mmol) was methylated in the manner previously described for the preparation of **34** and **35** and **43** and **44** to give 0.97 g (90%) of **48**: bp 90–92° (43 mm) [lit.[35] bp 77° (12 mm)]; nmr (CCl_4) τ 6.6–7.0 (1 H, m), 6.82 (3 H, s), 7.8–9.1 (11 H, m), 9.06 (3 H, d, J = 5 Hz).

***trans*-1-Methoxy-3-methylcycloheptane (49).** Pure *trans*-3-methylcycloheptanol (**51**)[35] (bp 88.2–89.6° (12 mm)) (1.10 g, 8.6 mmol) was methylated in the manner previously described for the preparation of **34** and **35** and **43** and **44** to give 1.10 g (90%) of **49**: bp 90–91° (45 mm) [lit.[35] bp 76° (12 mm)]; nmr (CCl_4) τ 6.5–6.9 (1 H, m), 6.82 (3 H, s), 7.9–9.1 (11 H, m), 9.10 (3 H, d, J = 6 Hz).

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(44) D. H. Marr and J. B. Strothers, *Can. J. Chem.*, **45**, 225 (1967).