

tion products were worked up as before, then hydrogenated (ethyl acetate, Adams catalyst), and analyzed by glc (100-ft Carbowax 20M column, 200° for derivatives of $n = 7, 8, 10$ and 220° for $n = 11-13$). Major peaks were identified by comparison with authentic samples where these were available and by integrating the corresponding nmr spectra. The data in Table VI were reproducible to the extent that the average ratio of compact *vs.* extended attack was about $(6 \pm 1):1$. The sensitivity of the detector to 2-(2'-furyl)cycloalkanones was felt to be low and consequently the amounts of this product could have been underestimated.

The ir and nmr data of the hydrogenated tricyclics are collected in Table I and Table XI, respectively.

Acknowledgments. We thank Dr. J. E. Anderson for discussions and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of our work. A Thomas Witherden Batt scholarship during the final stages of this work is also gratefully acknowledged.

Mechanistic and Synthetic Applications of Silver(I)-Promoted Alkoxy Group Ionization Processes. An Evaluation of Cyclopropylcarbinyl and Benzhydryl Ethers^{1,2}

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Abstract: The reaction of a number of *endo*-2-methoxytricyclo[4.1.0.0^{3,7}]heptanes with silver perchlorate in benzene at 40° leads to quantitative isomerization to *anti*-7-methoxynorbornenes by a process involving initial $\text{Ag}^+ \cdots \text{OR}(\text{CH}_3)$ coordination, methoxyl group ionization, and recapture of the alkoxide after cyclopropylcarbinyl \rightarrow homoallyl rearrangement. Several norcaranyl ethers were examined under comparable conditions; depending upon structure, rearrangement, simple "demethanolation," or loss of methanol with ring opening was observed. Autocatalytic acid production was noted in one system but not another. The reactivity of dicyclopropylcarbinyl methyl ether was also assessed. The reaction of benzhydryl ethers with silver salts in aqueous methanol serves as a convenient and mild method for liberating a hydroxyl group in the presence of other sensitive functions. The potential applications of these transformations are discussed.

Over the years, innumerable investigations of solvolysis reactions have provided much detailed information about the structure and behavior of carbonium ions, as well as the fundamental role played by solvents in the generation and destruction of such ions.⁴ Generalized reaction schemes involving a spectrum of intermediates ranging from free carbocations to intimate ion pairs have been developed to accommodate the reactivity of these charged sp^2 -hybridized systems.^{4,5} It was apparent when we initiated the present investigation that much of the previous work had been conducted in solvents endowed either with appreciable nucleophilicity, high dielectric constant, protic characteristics, or a combination of these features.

An alternative powerful way to study carbonium ions is to promote their formation under conditions of essentially neutral pH in solvents of negligible nucleophilicity. Complications due to proton sensitivity,

solvation, and various related factors would thereby be minimized. More specifically, solvent perturbation of the ionization process *per se* would be greatly reduced and the absence of a solvation shell could also affect the movement of atoms more remote from the reaction site. Such would represent a deep-seated modification of the usual environment of bond heterolysis processes and could in principle provide important information about carbocation-forming reactions.

In this connection, we now show that the customarily highly endothermic ionization of neutral ethers, *viz.* $\text{ROCHR}'\text{R}''$, is substantially facilitated by prior coordination of the oxygen atom to Ag^+ in anhydrous benzene solution.^{6,7} There has been found the expected dependence of ease of methoxyl ionization on structural features and, for this reason, attention has been given primarily at this time to cyclopropylcarbinyl and benzhydryl systems. Because many molecular types fall into the first of these general structural classes,

(1) Part XXIII of the series dealing with Ag^+ -catalyzed rearrangements. For the previous paper, see L. A. Paquette and G. Zon, *J. Amer. Chem. Soc.*, **96**, 224 (1974).

(2) A preliminary account of a portion of this work has appeared: L. A. Paquette and G. Zon, *J. Amer. Chem. Soc.*, **94**, 5096 (1972).

(3) National Institutes of Health Postdoctoral Fellow, 1972-1973.

(4) (a) For leading references, see D. Bethell and V. Gold, "Carbonium Ions: An Introduction," Academic Press, London, 1967; (b) G. A. Olah and P. v. R. Schleyer, "Carbonium Ions," Vol. I-III, Wiley-Interscience, New York, N. Y., 1969-1972.

(5) (a) V. J. Shiner, Jr., M. W. Rapp, and H. R. Pinnick, Jr., *J. Amer. Chem. Soc.*, **92**, 232 (1970); (b) R. A. Snee and J. V. Carter, *ibid.*, **94**, 6990 (1972), and earlier papers in this series.

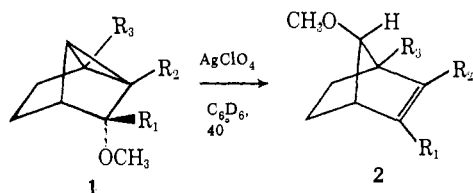
(6) (a) The subject of coordination complexes of silver ions with heteroatoms has been reviewed: C. D. M. Beverwijk, G. J. M. vander Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev., Sect. A*, **5**, 267 (1970). (b) See also T. Fueno, O. Kajimoto, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Jap.*, **41**, 785 (1968); (c) D. Gray, R. A. Wies, and W. D. Closson, *Tetrahedron Lett.*, 5639 (1968); (d) B. Franzus, W. C. Baird, E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967); (e) C. F. Wilcox, Jr., and W. Gaal, *J. Amer. Chem. Soc.*, **93**, 2453 (1971).

(7) (a) Rhodium-catalyzed rearrangements of epoxides and oxetanes are known: R. Grigg and G. Shelton, *Chem. Commun.*, 1247 (1971); (b) R. Grigg, R. Hayes, and A. Sweeney, *ibid.*, 1248 (1971); (c) G. Adames, C. Bibby, and R. Grigg, *ibid.*, 491 (1972).

we have examined several representative groups of cyclopropylcarbonyl ethers, many of which have proven to be more synthetically accessible and stable than the corresponding sulfonate esters.

Results

endo-2-Methoxytricyclo[4.1.0.0^{3,7}]heptanes. Because of the exceptionally high solvolytic reactivity^{8b} of endo-2-substituted tricyclo[4.1.0.0^{3,7}]heptanes⁸ and the ready availability of a variety of *endo*-2-methoxy derivatives,⁹ such compounds were chosen for initial investigation. Treatment of the several tricyclic ethers **1** with 1–3 mol % of silver perchlorate in anhydrous benzene at 40° resulted in clean conversion to the *anti*-7-methoxynorbornenes **2**. When the progress of these reactions



- a, R₁ = R₂ = R₃ = H
- b, R₁ = D; R₂ = R₃ = H
- c, R₂ = D; R₁ = R₃ = H
- d, R₁ = R₃ = H; R₂ = CH₃
- e, R₁ = R₂ = H; R₃ = CH₃
- f, R₁ = D; R₂ = H; R₃ = CH₃
- g, R₁ = H; R₂ = D; R₃ = CH₃

was monitored qualitatively using a Varian A-60A spectrometer, rearrangement was seen to be appreciable (≥50%) after 1–2 hr. No transitory intermediates could be detected. To ensure complete reaction, the nmr tubes were maintained at 40° for 12 hr in the absence of light. Under these conditions, pmr analysis indicated the isomerizations to be quantitative. Attempts to obtain precise rate constants were thwarted by difficulties arising from complexation of Ag⁺ to the 7-methoxynorbornene product as it was formed,⁶ thereby progressively reducing the “effective concentration” of the catalyst.^{10a}

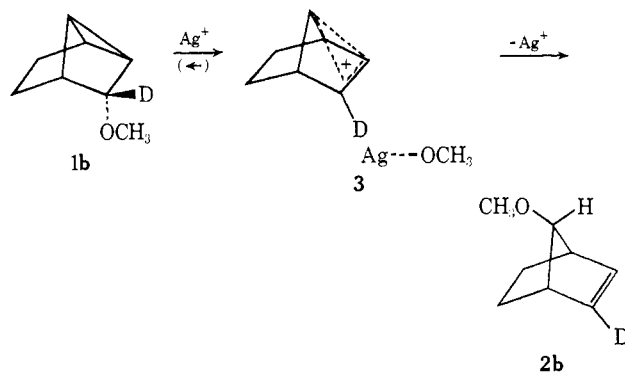
Despite this unfortunate restriction on the quantitative aspects of this study, the stereospecificity of product formation and ultimate positioning of the deu-

(8) (a) H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.*, **85**, 2324 (1963); (b) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963); (c) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965); (d) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **88**, 864 (1966); (e) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966); (f) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966); (g) J. J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Commun.*, 1202 (1967); (h) J. J. Tufariello and R. J. Lorence, *J. Amer. Chem. Soc.*, **91**, 1546 (1969); (i) J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969); (j) J. J. Tufariello and D. W. Rowe, *J. Org. Chem.*, **36**, 2057 (1971).

(9) L. A. Paquette, G. Zon, and R. T. Taylor, *J. Org. Chem.*, in press.
 (10) (a) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **94**, 7761 (1972). (b) Our experience has been that this reactivity difference is entirely general. An investigation was never made of perchloric acid-promoted rearrangements for several reasons: (a) traces of perchloric acid that may adhere to anhydrous silver perchlorate can be removed without difficulty simply by maintaining a constant vacuum (0.01 or better) over the solid for several days at room temperature; this precaution was taken in this work and perchloric acid contamination is not an issue; (b) as noted in the introduction, our objective was to work in an anhydrous solvent system; the difficulties and dangers inherent in the preparation and utilization of *anhydrous* perchloric acid need not be detailed but are clearly undesirable; and (c) little difference was anticipated between perchloric acid on the one hand and *p*-toluenesulfonic or trifluoroacetic acids on the other.

terium labels in **2b**, **2c**, **2f**, and **2g** attest to operation of the mechanism outlined for **1b** in Scheme I. The

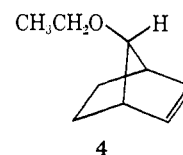
Scheme I



driving force underlying the generation of **3** is presumably associated with relief of ground-state strain in achieving the transition state for C–O ionization and the inherent stability of the cation.⁸ Prior coordination of Ag⁺ to the methoxyl oxygen is also a major factor in promoting the exceedingly facile ether ionization. Previous workers have shown that **1a** experiences the same rearrangement under conditions of acid catalysis.^{8d,e,g} We have found, however, that the catalytic influence of proton donors is significantly less effective than that of Ag⁺. As an example, when **1d** was treated with 6 mol % of *p*-toluenesulfonic acid in benzene at 40°, isomerization to **2d** did occur, but at a rate some 50 times slower than that observed with silver perchlorate under otherwise identical conditions. Also, exposure of **1b** to 1 mol % of trifluoroacetic acid in benzene at 40° produced no detectable (pmr analysis) amount of **2b** after 28 hr.^{10b} Attempts to induce isomerization of **1a** with other transition metal catalysts such as bis(benzonitrile)palladium chloride and rhodium dicarbonyl chloride dimer were likewise without success.

Silver methoxide, the coproduct attending formation of cations such as **3**, is an intriguing substance, the properties of which have only recently been scrutinized.¹¹ Under conditions of its independent generation, this salt apparently undergoes rather rapid conversion to Ag⁰. In the present circumstance where only small steady-state concentrations of the alkoxide are produced *in solution*, it clearly is capable of existing sufficiently long to serve as the source of methoxide ion responsible for the ultimate trapping of **3**.

In order to confirm the intervention of **3** and to determine whether this cation could be intercepted by other nucleophiles, the Ag⁺-catalyzed rearrangement of **1a** (1 mmol) in ethanol (20 mmol)–benzene (90:10) was examined. The products of this reaction were found to be *anti*-7-ethoxynorbornene (**4**) and **2a** (20:1 ratio).



Appropriate control experiments served to demonstrate that **2a** and its *syn* counterpart are entirely stable to

(11) R. S. Macomber, 16th Annual Report of the Petroleum Research Fund, 1972, p 88.

Table I. Silver Perchlorate Catalyzed Rearrangements of **1** in Benzene at 40°

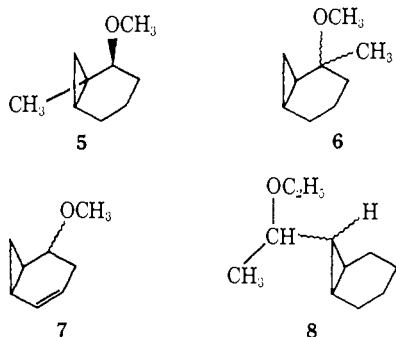
Compd	[1], mol/l.	[AgClO ₄], mol/l.	Mol % AgClO ₄ ^a	Product ^b		
				Structure	Pmr, δ _{TMS} ^{c,d,e}	Analytical data
1a	2.02	0.02	1.0	2a	5.90 (t, <i>J</i> = 2 Hz, 2, olefinic), 3.03 (s, 4, H ₇ and -OCH ₃), 2.60 (heptet, <i>J</i> = 2 Hz, 2, bridgehead), 2.08-1.70 (m, 2, exo), 1.10-0.80 (ca. AB q, 2, endo)	<i>d</i>
1b	1.33	0.03	2.4	2b	5.90 (br d, <i>J</i> = 2.5 Hz, 1, olefinic), 3.03 (s, 4, H ₇ and -OCH ₃), 2.58 (br pentuplet, <i>J</i> = 1.5 Hz, 2, bridgehead), 2.12-1.59 (m, 2, exo), 1.10-0.79 (ca. AB q, 2, endo)	For C ₈ H ₁₁ DO calcd <i>m/e</i> 125.0951, found 125.0949
1c	1.33	0.03	2.4	2c	5.88 (d, <i>J</i> = 2 Hz, 2, olefinic), 3.02 (s, 4, H ₇ and -OCH ₃), 2.57 (heptet, <i>J</i> = 2 Hz, 1, bridgehead), 2.05-1.71 (m, 2, exo), 1.09-0.79 (ca. AB q, 2, endo)	For C ₈ H ₁₁ DO calcd <i>m/e</i> 125.0951, found 125.0952
1d	1.85	0.02	1.0	2d	5.59-5.39 (m, 1, olefinic), 3.12 (br s, 1, H ₇), 3.05 (s, 3, -OCH ₃), 2.73-2.50 (m, 1, bridgehead), 2.30-2.10 (m, 1, bridgehead), 2.10-1.73 (m, 2, exo), 1.60 (d, <i>J</i> = 1.5 Hz, 3, -CH ₃), 1.27-0.74 (m, 2, endo)	Calcd for C ₉ H ₁₄ O: C, 78.21; H, 10.21. Found: C, 77.99; H, 10.22
1e	1.20	0.03	2.6	2e	6.06-5.73 (m, 2, olefinic), 3.06 (s, 3, -OCH ₃), 2.78 (br s, H ₇), 2.71-2.50 (m, 1, bridgehead), 2.03-1.59 (m, 2, exo), 1.22 (s, 3, -CH ₃), 1.21-0.76 (m, 2, endo)	Calcd for C ₉ H ₁₄ O: C, 78.21; H, 10.21. Found: C, 78.42; H, 10.20
1f	0.99	0.02	2.1	2f	5.90 (br s, 1, olefinic), 3.06 (s, 3, -OCH ₃), 2.78 (br s, 1, H ₇), 2.71-2.50 (m, 1, bridgehead), 2.03-1.59 (m, 2, exo), 1.22 (s, 3, -CH ₃), and 1.21-0.76 (m, 2, endo)	For C ₉ H ₁₃ DO calcd <i>m/e</i> 139.1107, found 139.1109
1g	1.79	0.06	3.1	2g	5.89 (br, d, <i>J</i> = 3 Hz, 1, olefinic), 3.06 (s, 3, -OCH ₃), 2.75 (br s, 1, H ₇), 2.68 (m, 1, bridgehead), 2.17-1.42 (m, 2, exo), 1.22 (s, 3, -CH ₃), and 1.23-0.73 (m, 2, endo)	For C ₉ H ₁₃ DO calcd <i>m/e</i> 139.1107, found 139.1109

^a ([AgClO₄]/[**1**]) × 100 = mol % AgClO₄. ^b Approximately quantitative yield in each case (pmr analysis). ^c Actually, a sharp s (-OCH₃) superimposed on br s (H₇). ^d Known compound (see ref 8).

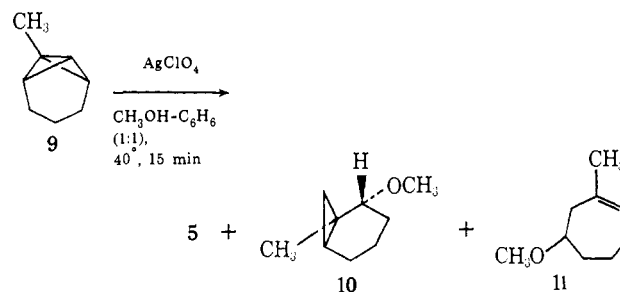
such conditions. Furthermore, the possible involvement of *endo*-2-ethoxytricyclo[4.1.0.0^{3,7}]heptane was not in evidence (vpc studies).

Structural assignment to the *anti*-7-methoxynorbornenes follows from the identity of **2a** with the known compound⁸ and the unequivocal pmr spectral characteristics of this ether which feature widely separated signals for the olefinic, bridgehead, bridge, and methylene protons (Table I). The precise relationship of the deuterium and methyl substituents in **2f** and **2g** is difficult to assess unequivocally. However, the molecules do differ sufficiently in detail to allow for their individual recognition and to discount mutual contamination during their formation. Owing to the absence of structural rearrangements other than the cyclopropylcarbiny → homoallyl bond reorganization, the structures of these two ethers then follow directly from that of their tricyclic precursors.

Norcaranyl Derivatives. The norcaranyl ring allows for the superpositioning of several cyclopropylcarbiny cation systems. In an effort to realize maximum alteration in structural detail within this series, ethers **5-8**



were chosen for investigation. Preparation of **5** was effected by reaction of 1-methyltricyclo[4.1.0.0^{2,7}]heptane (**9**) with silver perchlorate in methanol-benzene (1:1), conditions previously shown¹² to result in autocatalytic acid production with bicyclobutane ring opening and attendant protic solvent incorporation.¹³ When allowed to react at 40° for 15 min under these conditions, **9** underwent essentially complete conversion to a mixture of three methoxy compounds. The isomeric substances were separated by preparative vpc and characterized as **5** (72%), **10** (11%), and **11** (17%)

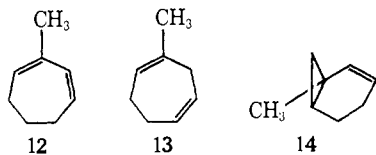


by suitable spectral comparison.¹³ Heating of a solution of isomerically pure **5** with silver perchlorate and benzene at 100° for 11 hr led to formation of a mixture of products in which **11** was the major constituent (82%). Three minor components (**10**, **4**, and **4**%) were also detected by vpc and, based upon their relatively short retention times (*t_r*), they have been tenta-

(12) L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Amer. Chem. Soc.*, **94**, 9222 (1972).

(13) Similar ring-opening behavior has been reported for several examples where rhodium dicarbonyl chloride dimer in methanol was utilized: P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **94**, 7748 (1972).

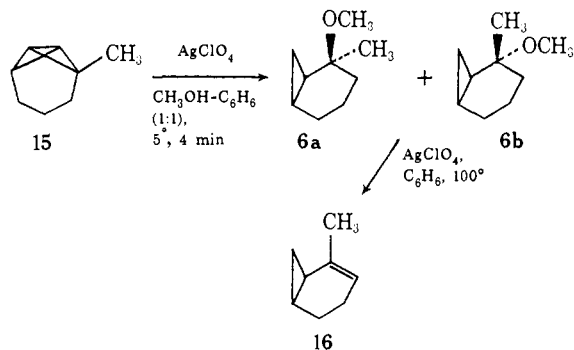
tively identified as "demethanolation" products. No ($\leq 1\%$) 2-methyl-1,3-cycloheptadiene (**12**)¹⁰ was formed, but the possibility that these hydrocarbons are **13** and **14** is not precluded. This point was not examined further.



A plot of $[5]$ vs. time, determined for the above reaction conditions but with *o*-xylene as an internal standard, clearly revealed the autocatalytic nature of the overall rate of disappearance of **5** with an induction period of approximately 3 hr. No detectable buildup of isomer **10** was evidenced by vpc. Based upon a comparison of the relative vpc peak areas of starting material, products, and internal standard, a gradual material loss was detected which reached a value of 52% after 11 hr. The reasons for this decomposition are not known at this time. Appropriate control experiments demonstrated that major product **11** is stable toward Ag^+ -induced loss of methanol and/or decomposition at 100° for 11 hr and that this system does not generate an acidic catalyst leading to such reactions. Another control study also established that **11** remains unaltered when introduced into the reaction mixture obtained after approximately 86% conversion of **5**.

Careful vpc analysis of aliquots obtained when a mixture of **5** and **10** (89:11) was treated as above suggested that the anti isomer **10** is somewhat more sluggish to rearrangement compared to **5**. However, the concomitant decomposition precludes definitive conclusions to be made regarding this interesting point.

The closely related isomeric pair **6a/6b** was likewise readily obtained by AgClO_4 -promoted methanolysis of 2-methyltricyclo[4.1.0.0^{2,7}]heptane (**15**). Syn and anti stereochemical assignments to **6a** (78%) and **6b** (22%) are reliably based on the predominant retention of configuration observed for electrophilic additions to such ring systems.¹⁴ Owing to the tertiary nature of the incipient ionization site in these epimers, the **6a/6b** mixture underwent reaction with AgClO_4 -benzene (100°) at a rate qualitatively faster than **5** and **10**. Intriguingly, however, 2-methyl-2-norcaradiene (**16**) was



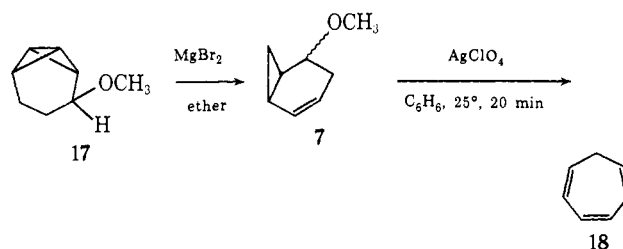
the predominant (93%) product in this instance. Two similarly fast-eluting minor products were also de-

(14) K. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970); W. R. Moore, K. G. Taylor, P. Miller, S. S. Hall, and Z. L. F. Gaibel, *Tetrahedron Lett.*, 2365 (1970); L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **93**, 4503 (1971); W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

tected (vpc) in relative yields of 4 and 3%, but limited quantities precluded their characterization.

Because preparative vpc separation of **6a/6b** proved impractical, kinetic investigations were performed on the purified mixture. In contrast to the reaction profile exhibited by **5**, plots of $\ln([6]_t/[6]_0)$ vs. time gave reasonable straight lines which passed through the 0-0 intercept.^{15a} Complications arising from autocatalysis were clearly lacking. The value of the overall catalytic rate constant, $1.4 \pm 0.4 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$, thus reflects the capability of $\text{Ag}(\text{I})$ to induce relatively facile C-O bond heterolysis.

Norcaranyl ether **7**, obtained by magnesium bromide promoted rearrangement of **17**, provides yet another example of the diverse reactivity of these systems. Exposure of a benzene solution of **7** to a trace amount (*ca.* 1 mol %) of silver perchlorate at 25° led to rapid reaction (20 min) with formation chiefly of cycloheptatriene (**18**) together with several minor products of



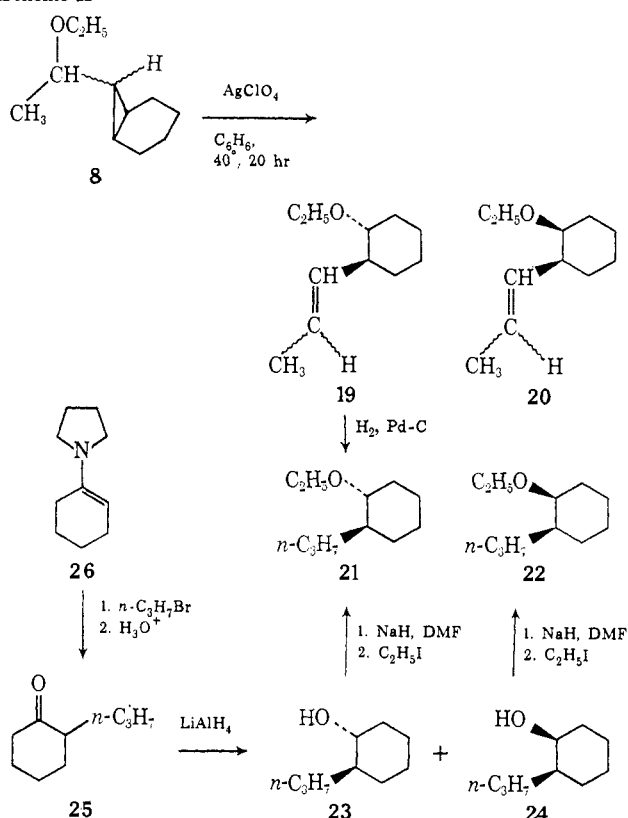
longer retention times, none of which was present in quantities such that analytical and spectroscopic data could be obtained.

A final structural variation of a rather different type is embodied in the ethoxy derivative **8** which was first isolated and identified by Moore and coworkers^{15b} as a solvent insertion product formed upon generation of 7-norcaranylidene in diethyl ether. Complete rearrangement of **8** was effected by heating at 40° for 20 hr with AgClO_4 in benzene. In this particular instance, a deep purple colored reaction mixture was produced which was essentially completely decolorized upon quenching with aqueous sodium chloride solution. Although the pmr spectrum of the major (90%) product isolated by preparative vpc was consistent with the generalized structures represented by **19** and **20**, it gave no clear-cut evidence regarding stereoisomeric homogeneity. Subsequent catalytic hydrogenation of this material yielded **21** without detectable amounts of **22**. Thus, part structures in which the ethoxy and propylidene groups are cis fused to the cyclohexane framework are excluded from further consideration. Vpc analysis of **19** under a wide variety of conditions, including the utilization of silver nitrate coated columns, failed to show other than a symmetrical peak. We note that the stereochemical assignments to **21** and **22** are founded upon the expectation that lithium aluminum hydride

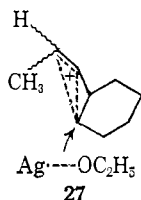
(15) (a) For the mixture of **6a** and **6b** to obey good second-order kinetics, the two ethers are required to have almost equal reactivities. Although a referee has found this surprising, we wish to make the point that such comparable proclivity for ionization in the epimeric pair is fully as expected. Standard solvolytic studies of *exo*- and *endo*-bicyclo[3.1.0]- and bicyclo[4.1.0]alkyl ester systems have provided convincing evidence that comparable cyclopropyl participation accompanies ionization in both epimers, that the pair of isomers react at very similar rates, and furthermore that a single conformationally stable minimum energy cyclopropylcarbinyl cation likely results. For a recent leading reference, consult L. A. Paquette, O. Cox, M. Oku, R. P. Henzel, and J. A. Schwartz, *Tetrahedron Lett.*, 3295 (1973); (b) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

reduction of ketone **25** proceeded with adherence to steric approach and product development control.¹⁶ On this basis, the formation of predominant amounts of **23** (71%) and lesser quantities of **24** (29%) is taken to mean that **23** is the more stable trans isomer (Scheme II). The fact that **19** arises exclusively is consistent

Scheme II

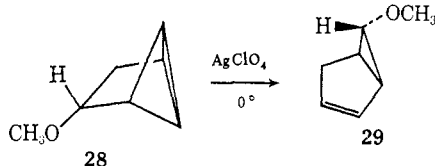


with intervention of cation **27** and its exclusive capture



by ethoxide attack at the rearside of C_1 .⁴ The stereospecificity serves as a disclaimer for transient formation of an "open cation" where some C–O bonding from the cis direction would be anticipated.

Other Cyclopropylcarbinyl Systems. Since the inception of our study, Scheidt and Kirmse¹⁷ have obtained evidence that the methoxy-substituted tricyclohexane **28** rearranges rapidly to give **29** (87%) when

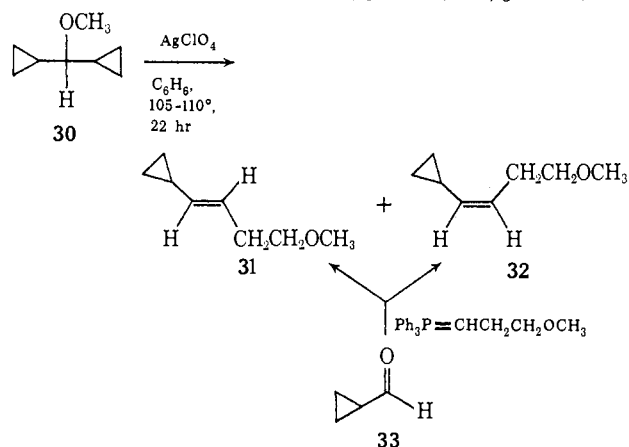


treated with silver perchlorate at 0° . Clearly, an

(16) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Amer. Chem. Soc.*, **78**, 2579 (1956); H. C. Brown and V. Varma, *ibid.*, **88**, 2871 (1966); E. C. Ashby, J. R. Boone, and J. P. Oliver, *ibid.*, **95**, 5427 (1973).

(17) F. Scheidt and W. Kirmse, *J. Chem. Soc., Chem. Commun.*, 716 (1972).

Ag^+ -catalyzed cyclopropylcarbinyl–allylcarbinyl cation interconversion has occurred rather than customary Ag^+ -promoted isomerization of the bicyclo[1.1.0]butane moiety.^{1, 10, 18} That relief of steric strain has a marked effect on such transformations is again revealed by the behavior of dicyclopropylcarbinyl methyl ether (**30**). Silver perchlorate-catalyzed rearrangement of **30** was carried out in benzene solution at $105\text{--}110^\circ$; after 22 hr, only 65% conversion was realized. The product mixture contained 86% of **31**, 10% of **32**, and



4% of an unknown substance of unusually high volatility.

The gross structures of the vinylcyclopropanes follow from their independent synthesis by suitable Wittig reaction on cyclopropanecarboxaldehyde (**33**). Individual stereochemical assignments follow convincingly from the vicinal olefinic coupling constants obtained from appropriate double-irradiation pmr experiments which revealed values of 15 and 10 Hz, respectively, for **31** and **32**. Further corroborative evidence for these conclusions was obtained from infrared $>\text{C}=\text{C}<$ stretching and $=\text{CH}$ bending absorptions (see Experimental Section).

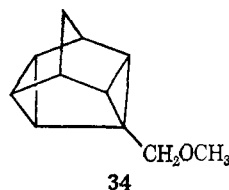
Kinetic data for reaction of **30** with AgClO_4 –benzene denoted again the autocatalytic nature of the overall rate of product formation. Additionally, the rate profile appeared to be accelerated by an increase in silver perchlorate concentration but irresponsive to variation in ether substrate concentration. This last feature stands in stark contrast to the previously studied bicyclobutane–methanol– AgClO_4 triad.¹² However, duplicate precision runs indicated that exact reproducibility of these kinetic profiles is difficult to attain. Consequently, definitive mechanistic inferences are not presently warranted.

Since ongoing acid production was considered to be a likely source of the above catalytic phenomena, "pH" measurements of aqueous washings were made on reaction mixtures after approximately 43 and 100% conversion of **30** and values of 5.65 and 5.25, respectively, were recorded. Control experiments demonstrated that subjection of the AgClO_4 –benzene solution alone to the reaction conditions does not eventuate in increased acidity ("pH" 6.90).

Some attention was also given to the novel cyclopropylcarbinyl ether **34**.¹⁹ This substance proved to be

(18) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, **94**, 7771 (1972); L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **94**, 7780 (1972), and earlier papers in this series.

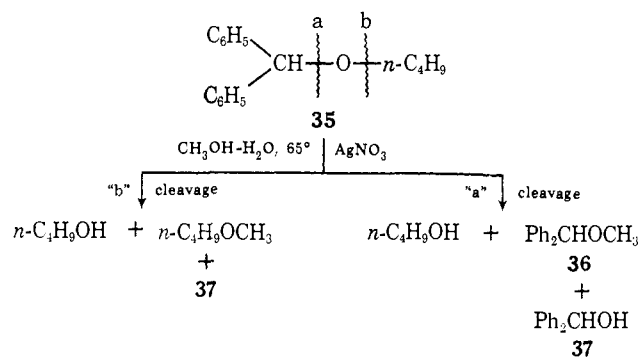
(19) L. A. Paquette and J. S. Ward, *Tetrahedron Lett.*, 4909 (1972).



totally inert toward AgClO_4 -benzene below 100° . At temperatures in the range of 115 – 125° , gradual decomposition set in. In experiments where **34** was heated with AgClO_4 -benzene-ethanol such that partial decomposition occurred and recovery was made of the starting material, no evidence was obtained for ethoxy incorporation. Consequently, it would appear that **34** experiences significant difficulty in ionization of its methoxyl group.

Benzhydryl Ethers. In an attempt to expand the synthetic applications of Ag(I) -promoted ether solvolyses, we have examined the reactivity characteristics of the prototypical benzhydryl *n*-butyl ether system **35**. Relative carbonium ion stabilities would require in most cases (and certainly in **35**) that heterolysis of the benzhydryl-oxygen bond (bond a) be kinetically favored. This course of events could give rise to an exceedingly mild method for removal of the benzhydryl blocking group, one that would require merely the presence of Ag^+ and some protic medium.

Treatment of **35** with a 50-fold molar excess of silver nitrate in refluxing (65°) methanol-water (9:1) for 6 days resulted in 80% conversion of the ether to **36**; less than 1% benzhydrol (**37**) was detected.

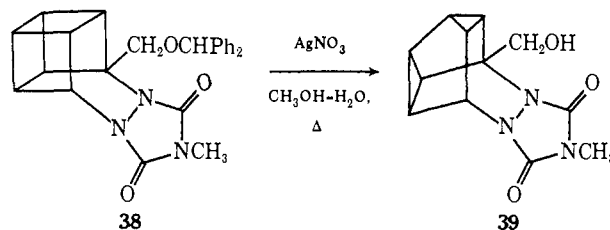


A brief kinetic study of the reactivity of **35** gave evidence of autocatalysis. In an attempt to modify the incursion of acid, the reaction of **35** with AgClO_4 in refluxing methanol-benzene (1:1) was investigated; however, the reaction in this medium proved too sluggish for practical kinetic analysis (or synthetic applications). After 5 days, only 1% conversion to **36** was detected by vpc techniques.

A particularly noteworthy example of the utility of this technique for the selective removal of benzhydryl blocking groups in the presence of other sensitive substituents is seen in the conversion of the cubyl ether **38** to alcohol **39**.²⁰ Here, not only has the diazabicyclic rearrangement²¹ transpired but the hydroxymethyl side chain has been simultaneously deblocked and made available for further functionalization without incursion of hydrolytic ring opening of the heterocyclic ring.

(20) This reaction was performed by G. H. Birnberg.

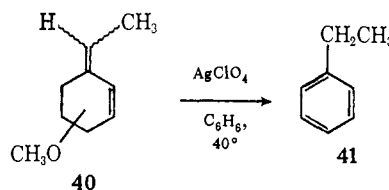
(21) L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970); L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *ibid.*, **94**, 4739 (1972).



Discussion

The findings here presented point to an alternative method by which carbonium ions may be generated. The technique could prove particularly useful in those many instances where ethers are synthetically more accessible than the derived alcohols and perhaps where some control of carbonium ion behavior (neutral pH, hydrocarbon solvent, etc.) is desirable. There also exists, of course, the possibility of selectively removing *O*-benzhydryl substituents for the purpose of deblocking hydroxyl groups.

Based upon our results, it can safely be assumed that methoxy group ionization will probably occur if the resulting carbonium ion is at least 10^4 times more kinetically accessible than the cyclohexyl cation.²² Since many molecular types do fall into this category, the implications are potentially far-reaching. Predictions whether simple rearrangement or "demethanolation" will result must necessarily be founded upon the structural features of the molecule and particular attention must seemingly be given to questions such as degree of substitution, developing conjugated π frameworks, and the like. In this connection, the conversions of **7** to cycloheptatriene (**18**) and of **40** to ethylbenzene (**41**)²³ are not surprising, but the differing behavior of **5**



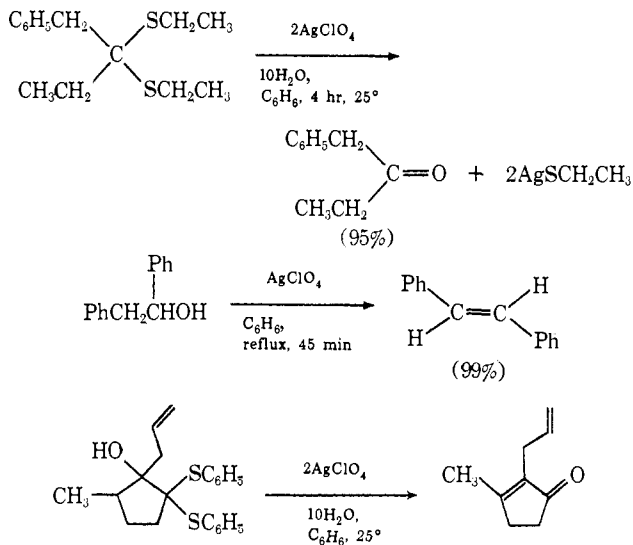
and **6** was not entirely expected. However, the dichotomy in behavior of these norcaranyl ethers may arise to some unknown degree because of the autocatalytic acid production observed with **5** alone. Although this seems to be a rather frequently observed phenomenon under such conditions, little is known about the mechanics of the process.

In several recent interesting applications of silver perchlorate chemistry, Mukaiyama and his workers have successfully demonstrated the applicability of this reagent for mild thioketal hydrolysis, dehydration, and combinations of these reactions.²⁴ Several representative reactions are illustrated. At the present time, however, it is not known whether these transformations are truly dependent upon Ag^+ or if autocatalytic acid production is responsible. Whatever the case, the interesting fact remains that unusually mild conditions are required.

(22) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955).

(23) G. Zon and L. A. Paquette, *J. Amer. Chem. Soc.*, **96**, 215 (1974).

(24) (a) T. Mukaiyama, S. Kobayashi, K. Kamio, and H. Takel, *Chem. Lett.*, 237 (1972); (b) T. Mukaiyama, M. Kuwahara, T. Izawa, and M. Uaki, *ibid.*, 287 (1972).



Experimental Section

Preparative and analytical vpc work was performed on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and pmr 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 CEC-MS9 instrument at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Rearrangement of *endo*-2-Methoxytricyclo[4.1.0.0^{2,7}]heptanes with AgClO_4 in Benzene. General Procedure. A solution of pure (preparative vpc) **1**⁹ (ca. 1–2 M) and silver perchlorate (1–3 mol %) in C_6D_6 (containing small quantities of C_6H_6 from the anhydrous silver perchlorate solution) was prepared in a dry nmr tube and the progress of reaction was monitored at ca. 40° using a Varian A-60A spectrometer. Extensive ($\geq 50\%$) rearrangement was witnessed after 2 hr in each case, but no evidence was gained for the incursion of long-lived transitory intermediates. Customarily, the rearrangements were taken to completion by heating the tubes in a water bath maintained at 40° for a total reaction period of 12 hr (in the absence of light). After shaking well with saturated aqueous sodium chloride solution (1.5–2.0 ml) and pentane (1 ml) extraction, the exclusive product was isolated by preparative vpc in yields ranging from 50 to 70% (2 ft \times 0.25 in. Al column packed with 12% OV-11 on 80–100 mesh Chromosorb W at 65°). Comparison of pmr traces for the *in situ* and isolated products indicated that no further rearrangement had occurred during the combined work-up and isolation procedures.

AgClO_4 -Catalyzed Rearrangement of **1a in Benzene–Ethanol.** A solution of **1a**⁹ (10 μl , 0.08 mmol) in absolute ethanol (94 μl , 1.6 mmol) was prepared in a stoppered small glass tube. One-half of this stock solution was removed and diluted with dry benzene (6.3 μl , control sample), and the remainder was treated with an anhydrous solution of AgClO_4 in benzene (6.3 μl of 0.1877 M). Both samples were heated at 40.0° for 20 min and then quenched with brine and extracted with pentane as previously described. Vpc analysis of the Ag^+ reaction mixture revealed the presence of (order of elution) **2a** (6%), **4** (92%), and starting material (**1a**, 2%). The measured ratio of **4**:**2a** (0.054 by isolated yields; 0.065 by vpc peak areas) was very close to that predicted for a statistical product distribution (0.050); however, it should be noted that a relatively small amount of **2a** may have been present in the starting material due to unavoidable (under a variety of preparative vpc conditions) traces of rearrangement during isolation of **1a**. Vpc analysis of the control sample revealed that no detectable amount of **4** was present. Additional control experiments demonstrated that neither **2a** nor *syn*-7-methoxynorbornene is converted to **4** under the above reaction conditions.

For **4**: $\delta_{\text{TMS}}^{\text{C}_6\text{D}_6}$ 5.90 (t, $J = 2$ Hz, 2, olefinic), 3.26 (q, $J = 7.0$ Hz, 2, $-\text{OCH}_2\text{CH}_3$), 3.27–3.16 (br s, 1, H₇), 2.59 (apparent sextet, $J = 2$ Hz, 2, bridgeheads), 2.05–1.74 (m, 2, exo), 1.03 (t, $J = 7.0$ Hz, 3, $-\text{OCH}_2\text{CH}_3$), and 1.12–0.82 (m, 2, endo). *Anal.* Calcd for $\text{C}_9\text{H}_{14}\text{O}$: C, 78.21; H, 10.21. Found: C, 77.89; H, 10.22.

Ring Opening of 1-Methyltricyclo[4.1.0.0^{2,7}]heptane (9**) with**

AgClO_4 in Methanol–Benzene. A solution of anhydrous AgClO_4 –benzene (1.0 ml of 0.18 M) was shaken with absolute methanol (1.0 ml) and after 1 min **9**^{10,25} (100 μl , ca. 1 mmol) was added. After standing at ambient temperature for 15 min, during which time a relatively small amount of black precipitate formed, the reaction mixture was quenched by shaking with brine (2 ml) and was extracted with pentane (1 ml), and the combined organic layers were washed with 5% aqueous potassium hydroxide solution (2 ml). Preparative vpc on column A²⁶ (90° , 60 ml of He/min) allowed isolation of (elution order) **5** (72%), **10** (11%), and **11** (17%), which were identified by comparison of their pmr spectra with those reported.¹³

Reaction of 2-Methyltricyclo[4.1.0.0^{2,7}]heptane (15**) with AgClO_4 in Methanol–Benzene. Preparation of **6a** and **6b**.** A magnetically stirred solution of anhydrous AgClO_4 –benzene (1.0 ml of 0.18 M) and absolute methanol (1.0 ml) was cooled with an ice–water bath for 10 min before addition of **15**¹⁰ (164 mg, 1.52 mmol) over a period of 30 sec. The reaction was quenched after 4 min by shaking with brine (2 ml) and the organic layer was extracted with pentane (1 ml). Washing of the combined organic layers with saturated sodium bicarbonate solution and drying was followed by preparative vpc collection (69%) of the two extensively overlapped components using column B²⁶ (80° , 60 ml of He/min). Reinjection of this analytically pure fragrant colorless oil on column C²⁶ (68° , 15 ml of He/min) indicated it to be a 78:22 mixture of **6a** (12.7 min)–**6b** (15.3 min). For **6a**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.28 (s, 3, $-\text{OCH}_3$) and 1.87–0.18 with maximum (s, $-\text{CH}_3$) at 1.33 (m, 13); the methoxyl and methyl groups in **6b** gave rise to singlet absorptions at 3.25 and 1.22, respectively. *Anal.*²⁷ Calcd for $\text{C}_9\text{H}_{16}\text{O}$: C, 77.09; H, 11.50. Found: C, 77.16; H, 11.45.

2-Methyl-2-norcarene (16**).** A glass ampoule containing a solution of **6a/6b** (78:22, 14 mg, 0.1 mmol) in anhydrous AgClO_4 –benzene (0.350 ml of 0.051 M) was heated in the absence of light at 100.6° for 1.3 hr. The cooled reaction mixture was shaken with brine (2 ml) and extracted with pentane (1 ml), and the combined extracts were washed with saturated sodium bicarbonate solution (2 ml). Preparative vpc using column B²⁶ (55° , 60 ml of He/min) led to collection (5.7 mg, 53%) of the major (93%) component, which was identified as **16** from its characteristic²⁸ pmr spectrum: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.30–5.08 (m, 1, olefinic), 2.50–0.88 with maximum (s with fine splitting, $-\text{CH}_3$) at 1.82 (m, 9), and 0.88–0.48 (m, 2, H₇). For C_9H_{12} calcd *m/e*, 108.0939; found, 108.0941.²⁹ Two slower eluting unknowns were detected (vpc) but not characterized.

Gas Chromatographic Kinetic Analyses for AgClO_4 -Promoted Reactions. General Procedure. All runs were performed in the absence of light at $100.6 \pm 0.2^\circ$ using a constant temperature circulating oil bath. Purified (preparative vpc) substrates and *o*-xylene (99.9%) internal standard were injected at room temperature into anhydrous solutions of AgClO_4 –benzene which were contained in a dry glass vial that was fitted with a rubber septum. Differences in initial substrate and AgClO_4 concentrations were governed by substrate availability and lability toward AgClO_4 , respectively. Aliquots (50–300 μl) were removed by syringe and quickly transferred to and carefully sealed in dry glass ampoules which were flushed with nitrogen and equipped with a rubber septum cap. Kinetic ampoules were rapidly cooled by submersion in an ice–water bath; work-up included dilution with an equal volume of pentane, shaking with brine (1.5 ml), and storage at 0° . Vpc analyses of the supernatant organic layers were completed within less than 6 hr to minimize errors (due to product volatility) and were carried out with a Hewlett-Packard Model 5750 gas chromatograph in the flame-ionization mode, except in cases noted. Peak areas were determined by the “cut-and-weigh” technique and were not corrected for differential flame-ionization sensitivities due to the relatively small amount of samples available.

(25) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963).

(26) The following Al columns were employed in the course of this research: column A, 12 ft \times 0.25 in. 5% Carbowax 20M on 60–80 mesh Chromosorb G; B, 2 ft \times 0.25 in. 12% OV-11 on 80–100 mesh Chromosorb W; C, 10 ft \times 0.125 in. 5% Carbowax 20M on 60–80 mesh Chromosorb G; D, 12 ft \times 0.25 in. 12% OV-11 on 80–100 mesh Chromosorb W; E, 12 ft \times 0.25 in. 8% Carbowax 20M on 60–80 mesh Chromosorb G; F, 6 ft \times 0.25 in. 23% AgNO_3 –glycerol (30:70) on 60–80 mesh firebrick; G, 24 ft \times 0.125 in. 1% SE-30 Hewlett-Packard “high-efficiency” column; H, 6 ft \times 0.25 in. 5% SE-30 on 60–80 Chromosorb G.

(27) We thank Dr. S. E. Wilson for the preparation of this sample.

(28) L. A. Paquette and S. E. Wilson, *J. Org. Chem.*, **37**, 3849 (1972).

(29) We thank R. T. Taylor for the purification of this sample.

A. 2-Methoxy-1-methylbicyclo[4.1.0]heptanes (5 and 10). Vpc analysis of six aliquots obtained over a period of approximately 11 hr (ca. 83% conversion) from the reaction of pure **5** (0.081 *M*) in AgClO₄-benzene (0.150 *M*) with *o*-xylene internal standard (0.031 *M*) was carried out using column C²⁶ (75°, 15 ml of He/min) for **5**, **10**, and **11** and column G²⁶ (70°, 15 ml of He/min) for demethanolation products. The following product composition and order of elution for all components was noted (both columns): unknown products A-C (10, 4, and 4%, respectively), *o*-xylene, **5**, **10**, and major product **11** (82%); no (<~1%) **12** (*t*_r slightly longer than A) was detected. The ratio given by (area of all products + area of **5**)/area of *o*-xylene gradually decreased from an initial value of 1.90 to a final value of 0.99 indicating a net material loss of 52% due to decomposition. An appropriate control experiment demonstrated that **11** is stable toward reaction with AgClO₄ under the above reaction conditions. An additional control experiment in which **11** was added to the above reaction mixture (after ca. 86% conversion) led to no significant change in the **11**:*o*-xylene ratio after resealing and heating for 9 hr. A kinetic run at 72 ± 1° using a solution of **5/10** (89:11, 0.066 *M*) and *o*-xylene internal standard in AgClO₄-benzene (0.149 *M*) indicated relative ratios of unreacted **5/10** equal to 88:12 (3% **11**) and 81:19 (32% **11**) after 48 and 148 hr, respectively, with corresponding overall material loss of 15 and 36%.

B. 2-Methoxy-2-methylbicyclo[4.1.0]heptanes (6a/6b). Vpc analysis of aliquots (5-6 per run) obtained over periods of 1400-2000 sec (ca. 60% conversion) utilized column C²⁶ (68°, 15 ml of He/min); the fastest eluting major product **16** (93%) was closely followed by unknowns A (4%) and B (3%), and then *o*-xylene.

Three kinetic runs were performed with a 78:22 mixture of **6a/6b**, using *o*-xylene (0.067 *M*) as internal standard and reagent concentrations listed below. Over the extent of reaction monitored (ca. 60%), the ratio given by (area of all products + area of **6a** and **6b**)/area of *o*-xylene remained constant within experimental error, as did the relative ratio of all products; however, the relative ratio of **6a**:**6b** varied smoothly during the course of reactions to give the final values listed below. Plots of ln [(**6a** + **6b**)]/(**6a** + **6b**) vs. time exhibited good linearity and slopes were calculated from manually fitted straight lines. Values for overall catalytic rate constants (*k*_{overall}) are given in Table II.

Table II. Summary of Kinetic Data for **6a/6b**

Run	[6a + 6b] _i , <i>M</i>	[AgClO ₄] _i , <i>M</i>	Slope, sec ⁻¹	<i>k</i> _{overall} , <i>M</i> ⁻¹ sec ⁻¹	Final ratio 6a : 6b
1	0.173	0.029	5.26 × 10 ⁻⁴	1.81 × 10 ⁻²	67.7:32.3
2	0.346	0.029	4.13 × 10 ⁻⁴	1.43 × 10 ⁻²	64.5:35.5
3	0.173	0.058	6.22 × 10 ⁻⁴	1.07 × 10 ⁻²	66.7:33.3

5-Methoxy-2-norcarene (7). A. Vpc analysis using column D²⁶ (100°, 75 ml of He/min) of a 4-month-old mixture of **17** and *endo*-2-methoxytricyclo[4.1.0.0^{3,7}]heptane (**1a**)⁹ (initial ratio of **17**:**1a** = 23:77), which had been stored at 0°, revealed the apparently quantitative conversion of **17** to a new slower eluting substance (**7**; ratio **7**:**1a** = 23:77) that was isolated by preparative vpc (same conditions) and identified on the basis of its characteristic pmr spectrum: δ_{TMS}^{CeD₆} 6.54-6.07 (m, 1, olefinic), 5.80-5.45 (m, 1, olefinic), 3.65-3.37 (m, 1, >CHO-), 3.07 (s, 3, -OCH₃), 2.13-1.68 (m, 2, H₃), and 1.50-0.25 (m, 4, cyclopropyl). *Anal.* Calcd for C₈H₁₂O: C, 77.37; H, 9.74. Found: C, 77.13; H, 9.89.

B. Magnesium Bromide Catalysis.²⁹ A 40-mg sample of **17** was added to 1.8 ml of 0.1 *M* ethereal magnesium bromide solution and the reaction was allowed to proceed at 25° for 3 hr. After the addition of water and pentane, the organic phase was dried, filtered, and concentrated. Vpc analysis of this material (column B, 70°, 80 ml of He/min) revealed essentially complete isomerization to **7**. Collection of the single product afforded 16.8 mg of colorless liquid with a pmr spectrum identical with that of the above material.

Reaction of 7 with AgClO₄-Benzene. A pmr sample of **7** (20 mg, 0.16 mmol) in benzene-*d*₆ was treated at room temperature with a solution of AgClO₄-benzene (10 μl of 0.18 *M*; ca. 1 mol % catalyst) causing immediate yellow coloration and formation of a small amount of white precipitate. After 20 min at this temperature, pmr analysis indicated essentially complete disappearance of **7** and formation of 1,3,5-cycloheptatriene (**18**), as judged from its characteristic absorptions. Work-up as above followed by vpc analysis

using column D²⁶ (100°, 75 ml of He/min) confirmed the presence of **18** and revealed that several minor products of longer retention times had also been produced.

Reaction of 8 with AgClO₄ in Benzene. A solution of **8**¹⁵ (0.50 g, 2.5 mmol) and anhydrous AgClO₄ (1.8 mmol) in benzene (10 ml) was heated at 40° for 20 hr. The deep purple colored reaction mixture was separated from a small amount of grey precipitate and shaken with brine (100 ml). The aqueous layer was washed with pentane (10 ml) and the combined and dried tan colored organic layers were concentrated at reduced pressure. Flash-vacuum distillation using a pot temperature of 140° (1 mm) and a receiver cooled to -79° gave an oil from which the major (~90%) component **19** was isolated (56 mg, 11%) by preparative vpc using column E²⁶ (165°, 60 ml of He/min). This material was identified as **19** from its pmr spectrum and hydrogenation to **21** (*vide infra*): δ_{TMS}^{CeDCl₃} 5.50-5.28 (m, 2, olefinic), 3.71-3.17 (m, 2, -OCH₂CH₃), 3.17-2.58 (m, 1, >CHO-), and 2.20-0.75 (m) with superposition of br d (*J* ≈ 5 Hz, >CCH₃) and t (*J* ≈ 7.0 Hz, -OCH₂CH₃) at 1.64 and 1.13, respectively (15 total). For C₁₁H₂₀O, calcd *m/e*, 168.1514; found, 168.1516.

Hydrogenation of 19. A solution of **19** (36 mg, 0.21 mmol) in absolute ethanol (2.0 ml) was added to a magnetically stirred suspension of 10% Pd-C (15 mg) in absolute ethanol (3 ml), which was presaturated with hydrogen under a pressure of 1 atm, and the mixture was stirred at room temperature for 1.5 hr. The filtered solution was treated with water (5 ml) and extracted with pentane (2 × 2 ml). Preparative vpc of the dried organic washings using column E²⁶ (120°, 60 ml of He/min) afforded (50%) the major (ca. 90%) component, which was identified as **21** from a comparison of its vpc retention time and pmr/ir spectra with authentic material (*vide infra*). No (<~1%) **22** was detected by vpc.

2-*n*-Propylcyclohexanone (23).³⁰ A solution of 1-pyrrolidino-cyclohexene (**26**) (21 g, 0.138 mol), benzene (50 ml), and 1-bromopropane (50 ml, 0.55 mol) was refluxed for 17 hr. Additional 1-bromopropane (50 ml) was added, and after further reflux (16 hr) the cooled reaction mixture was treated with water (30 ml) and boiled for 1 hr. Upon cooling to room temperature, the reaction mixture was shaken with sulfuric acid solution (30 ml) and the aqueous layer was extracted with ether (50 ml). The combined organic layers were washed with saturated sodium bicarbonate solution (100 ml) and water (100 ml), dried, and concentrated under reduced pressure. Short-path vacuum distillation gave 2.25 g (11%) of **25** as a colorless oil, bp 95-105° (20-22 mm) [lit.³¹ bp 94-95° (25 mm)].

cis- and *trans*-2-*n*-Propylcyclohexanols (**23** and **24**). An ether (10 ml) solution of **25** (2.25 g, 16 mmol) was added over a period of 15 min to a magnetically stirred suspension of lithium aluminum hydride (0.6 g, 16 mmol) and reflux was maintained for 0.5 hr following complete addition. Hydrolysis by sequential addition of water (0.6 g), 10% aqueous sodium hydroxide solution (0.6 g), and more water (1.8 g) preceded suction filtration of a white precipitate, which was thoroughly washed with ether (4 × 70 ml). The combined filtrates were washed with water (50 ml) and brine (50 ml) before drying and concentration on a rotary evaporator. The residual crude product (2.11 g, 93%) was shown by ir to be free of **25** and by vpc to consist of a 71:29 mixture of **23** and **24** by subsequent conversion to **21** and **22**, respectively, without further purification.

cis- and *trans*-1-Ethoxy-2-*n*-propylcyclohexanes (**21** and **22**). A mechanically stirred suspension of sodium hydride (1.14 g, 48 mmol) in anhydrous dimethylformamide (20 ml) was treated with a solution of crude **23/24** (2.11 g, 15 mmol) in 10 ml of the same solvent over a period of 45 min and the mixture was heated at 50° for 3.5 hr. The slurry was diluted with dimethylformamide (20 ml) and cooled to 5°, and ethyl iodide (12.5 g, 80 mmol) was slowly added (*caution*: foaming!) during 0.5 hr. After stirring at room temperature overnight, the reaction mixture was poured into ice water (600 g) and extracted with pentane (5 × 100 ml). The combined pentane layers were thoroughly washed with water (2 × 100 ml) and brine (100 ml) before drying and concentration at reduced pressure. Short-path distillation gave an oil (1.3 g, 52%), bp 100° (20 mm), which was found by vpc analysis using column E²⁶ (120°, 60 ml of He/min) to be a two-component mixture. The faster eluting minor (**22**, 29%) and slower eluting major (**21**, 71%)

(30) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(31) J. R. Dice, L. E. Loveless, Jr., and H. L. Cates, Jr., *J. Amer. Chem. Soc.*, **71**, 3546 (1949).

stereoisomeric products were each isolated by preparative vpc (same conditions) and were found to exhibit very similar ir spectra and mass spectral fragmentation patterns. For $C_{11}H_{20}O$ calcd m/e , 170.1671; found, 170.1673.

For **21**: ν_{\max}^{neat} 2930, 2860, 1448, 1372, 1354, and 1104 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.85–3.05 (m, 2, $-\text{OCH}_2\text{CH}_3$), 3.05–2.45 (m, 1, $>\text{CHO}-$), and 2.20–0.50 with superimposed t ($J = 7.0$ Hz, $-\text{CH}_2\text{CH}_3$) at 1.13 (m, 19).

For **22**: ν_{\max}^{neat} 2930, 2860, 1448, 1372, 1330, 1118, 1102, and 1084 cm^{-1} . *Anal.* Calcd for $C_{11}H_{20}O$: C, 77.58; H, 13.02. Found: C, 77.45; H, 13.01.

Reaction of Dicyclopropylcarbinyl Methyl Ether (30) with AgClO_4 in Benzene. A. Preparative Scale. A benzene (0.8 ml) solution of **30**²² (300 mg, 2.4 mmol) and anhydrous AgClO_4 (0.054 mmol) was heated at 105–110° for 22 hr in a sealed glass ampoule with exclusion of light. The cooled reaction mixture was processed as described above and vpc analysis using column E²⁶ (120°, 60 ml of He/min) indicated 69% conversion of **30** to a faster eluting minor (4%) and a slower eluting major (96%) component, which was identified as an analytically pure 90:10 mixture of **31**:**32** by collection, reinjection on column F (65°, 120 ml of He/min), and comparison of t_r values with those of authentic material (*vide infra*). This conclusion was verified by appropriate pmr/ir spectral comparisons. *Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.89; H, 10.87.

The minor product **32** was not isolated in sufficient quantity for complete characterization; however, a dilute solution pmr spectrum featured absorptions at $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.20–4.92 (m, olefinic), 3.38 (s, $-\text{OCH}_3$), 2.60–2.20 (m), and 1.00–0.20 (m, cyclopropyl). Mass spectral analysis indicated that the highest mass peak was at m/e 85.

B. Kinetic Analyses. Vpc analysis of aliquots removed over a period up to 24 hr for four kinetic runs was performed using column E²⁶ (115°, 60 ml of He/min; thermal conductivity). The order of component elution was: minor unknown A, **30**, and **31/32** (one peak). In contrast to preparative scale runs, the relative amount of unknown product A was somewhat higher in the small-scale kinetic runs, and the relative amounts of A and **31/32** were noted to vary within the ranges of 9.9–13.7 and 90.1–86.3%, respectively. Total volume per ampoule was 0.300 ml. The progress of reaction was accompanied by increased darkening of the solution and precipitate formation, with at least five new additional fast eluting minor components being detected after 70–100% conversion.

cis- and trans-1-Cyclopropyl-2-(2-methoxyethyl)ethylenes (31 and 32). A magnetically stirred suspension of 3-methoxypropyltriphenylphosphonium chloride³⁶ (1.65 g, 4.4 mmol) in ether (50 ml) was treated with a solution of *n*-butyllithium (4.4 mmol) in hexane (2 ml) and after gas evolution ceased the light orange colored mixture was refluxed for 0.5 hr before addition of a solution of cyclopropanecarboxaldehyde³⁷ (310 mg, 4.4 mmol, bp 100–110°) [lit.³⁷ bp 97–100° (740 mm)] in ether (2 ml). After 18 hr of reflux, the mixture was cooled, treated with pentane (20 ml) and water (50 ml), dried (organic layer), and freed of solvent by careful distillation. Flask-vacuum distillation of the residue using a pot temperature of 100° (1 mm) and a receiver cooled to –79° gave material from which the major (*ca.* 95%) product component peak was isolated (133 mg, 24%) by preparative vpc using column E²⁶ (100°, 60 ml of He min). Repreparative vpc of this material using column F²⁶ (65°, 120 ml of He min) led to isolation of isomerically pure **31** (32%, faster eluting) and **32** (68%, slower eluting), which were readily identified from their characteristic pmr/ir spectra and essentially identical mass spectral fragmentation patterns.

For **31**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.73–4.73 (m, 2, olefinic, $J = 15$ Hz),³⁸ 3.36 (apparent t, $J = 7.0$ Hz, 2, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.29 (s, 3, $-\text{OCH}_3$), 2.25

(q with fine splitting, $J = 6-7$ Hz, 2, $-\text{CH}_2\text{CHO}-$), 1.58–1.05 (m, 1, $>\text{CH}-$), and 0.83–0.15 (m, 4, cyclopropyl); ν_{\max}^{neat} 3085, 2998, 2900, 2830, 2730, 1667, 1460, 1382, 1195, 1119, 1019, 960, and 812 cm^{-1} ; for $C_8H_{14}O$ calcd m/e , 126.1045; found, 126.1046.

For **32**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.51–4.58 (m, 2, olefinic, $J = 10$ Hz),³⁸ 3.42 (apparent t with fine splitting, $J = 7.0$ Hz, 2, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.32 (s, 3, $-\text{OCH}_3$), 2.44 (q with fine splitting, $J = 7$ Hz, 2, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.75–1.19 (m, 1, $>\text{CH}-$), and 0.98–0.11 (m, 4, cyclopropyl); ν_{\max}^{neat} 3082, 3010, 2870, 2827, 2730, 1650, 1452, 1382, 1194, 1118, 941, 810, and 730 cm^{-1} ; for $C_8H_{14}O$ calcd m/e , 126.1045; found, 126.1046.

Measurement of "pH" for Reaction of 30 with AgClO_4 in Benzene. A sealed predried glass ampoule that was charged with **30** (100 mg, 0.79 mmol) and a solution of anhydrous AgClO_4 (0.09 mmol) in benzene (0.50 ml) was heated at 100.6° in the absence of light for 10 hr. The cooled reaction mixture was shaken with an aqueous solution (1.00 ml) of sodium chloride (0.10 mmol) and the separated organic layer was washed with distilled water (1 ml). Using an electronic pH meter and glass electrode system, which was precalibrated at pH 7.00, the combined aqueous layers were found to exhibit a "pH" of 5.65. Vpc analysis (same conditions as above) of the organic layer indicated 43% conversion of **30** to **31/32**. Approximately 0.4 mg of a concentrated HNO_3 soluble metallic mirror was deposited on the reaction tube surface. Exact repetition of this procedure with heating for 20 hr led to complete reaction (vpc) and gave aqueous washings with "pH" 5.25. A control experiment indicated no significant proton concentration ("pH" 6.90) in the aqueous washings from a solution of AgClO_4 (0.09 mmol) in benzene (0.50 ml) which had been heated at 100.6° for 23 hr.

Benzhydryl *n*-Butyl Ether (35). Conversion of benzhydrol (**37**) to pure **35** was achieved (42%) by sequential reaction with sodium hydride–dimethylformamide and *n*-butyl bromide in the usual manner,³³ followed by column chromatography on silica gel (pentane elution). The pmr spectrum of **35** was wholly consistent with expectation. For $C_{17}H_{20}O$ calcd m/e , 240.1514; found, 240.1517.

Ag(I)-Promoted Solvolyses of Benzhydryl *n*-Butyl Ether (35). A. AgNO_3 –Methanol–Water. A magnetically stirred suspension of AgNO_3 (4.25 g, 25 mmol) in absolute methanol (20 ml) was warmed to gentle reflux under a nitrogen atmosphere and just enough water (4.0 ml) was added to effect complete solution. A solution of **35** [120 mg, 0.5 mmol in methanol (1.0 ml)] was injected through a rubber septum cap and reflux was continued in the absence of light. Aliquots (0.25 ml) were removed over a period of 140 hr and were each shaken with water (5 ml) and extracted with dichloromethane (2×1 ml). The combined organic layers were washed with brine (3 ml) and saturated sodium bicarbonate solution and dried before evaporation under a stream of nitrogen. Vpc analyses of components **35**, **36**, and **37** were performed with column G²⁶ (180°, 60 ml of He/min). Peak areas were determined by the "cut-and-weigh" technique and were not corrected for differential thermal conductivities. Less than 1% of **37** was detected over a period of 140 hr.

B. AgClO_4 –Methanol–Benzene. A solution of **35** (100 mg, 0.4 mmol) and AgClO_4 (0.36 mmol) in anhydrous benzene (2.0 ml) and dry methanol (2.0 ml) was refluxed under nitrogen in the dark and aliquots (50–100 μl) were quenched by shaking with brine (2 ml). Base washing, drying, and vpc analysis of the organic layer as described above revealed that after 112 hr the reaction (dark orange coloration) had produced only 1% of **36**.

Rearrangement–Deblocking of 38.²⁰ A solution of 135 mg of **38** (0.33 mmol) in 25 ml of methanol–water (4:1) containing 3.3 g (19.5 mmol) of silver nitrate was refluxed in the dark for 9 days. After cooling, 70 ml of water and 35 ml of chloroform were added and the mixture was well shaken. The aqueous phase was re-extracted with chloroform and the combined organic layers were washed with water (2×150 ml) and brine (70 ml), dried, and evaporated. Purification was achieved by preparative thick-layer chromatography on silica gel plates (elution with 75% ether–25% hexane). The high R_f component was benzhydryl methyl ether (**36**) while the low R_f material (36 mg, 44%) proved to be **39**: mp 135–136° (from ether); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.07 (m, 1), 4.70 and 4.10 (AB₂ pattern, $J_{AB} = 8$ Hz, 1 H and 2 H, respectively), 3.05 (s, 3, $-\text{CH}_3$), and 2.02 (m, 6, cyclopropyl). *Anal.* Calcd for $C_{12}H_{13}N_3O_2$: C, 58.29; H, 5.30; N, 17.00. Found: C, 58.27; H, 5.30.

Treatment of Benzhydrol (37) with Aqueous Methanolic Silver Nitrate. A mixture of 8.00 g (47.0 mmol) of silver nitrate and 184 mg (1.00 mmol) of benzhydrol (**37**) in 40 ml of methanol and 7.5 ml of water was refluxed for 140 hr in the dark. Work-up in the

(32) Ether **30** was prepared (48% yield) in the usual manner³³ from dicyclopropylcarbinol³⁴ and was identified by comparison of its pmr/ir spectra with those published.³⁵

(33) See, for example, G. Zon and L. A. Paquette, *J. Amer. Chem. Soc.*, submitted for publication.

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(38) Reported olefinic J values are for vicinal vinylic spin–spin coupling and were determined by appropriate multiple irradiation experiments using a Varian HA-100 nmr spectrometer. The authors wish to thank D. James for his assistance in these measurements.

usual manner afforded an oil which by vpc analysis (column H,²⁶ 180°, 60 ml of He/min) was shown (planimetry) to consist of 48.5% of **36** ($t_r = 6.6$ min) and 51.5% of unreacted **37** ($t_r = 8.5$ min).

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Azasulfonium Salts. Intermediates in a General Procedure for the Alkylation of Aromatic Amines¹

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Abstract: A new, general process has been developed for the ortho alkylation of aromatic amines. Starting with anilines or N-alkylated anilines bearing ortho, meta, or para substituents with electronic character, varying from electron-donating groups such as methyl to electron-withdrawing groups such as nitro, ortho-alkylated anilines were prepared *via* the intermediacy of an *o*-alkyl- α -thioalkoxy substituent. The general procedure involved (a) mono-N-chlorination of the aniline with a suitable halogenating agent, (b) conversion of the N-chloroaniline into an azasulfonium salt through reaction with a dialkyl sulfide, (c) treatment of the azasulfonium salt with base to yield an azasulfonium ylide, (d) Sommelet-Hauser type rearrangement of the ylide to produce a substituted dienone imine, and (e) hydrogen transfer and accompanying rearomatization of the dienone imine to give the *o*-alkyl- α -thioalkoxy substituted aniline. Raney-nickel reduction then produced the ortho-alkylated aniline. Overall yields ranged from good to excellent. The scope and limitations of the process are discussed.

Alkylation of the aromatic nucleus is an old and extensively studied topic. Most attention has been directed toward the use of the Friedel-Crafts reaction,² which is undoubtedly the best known and most widely used method for the alkylation of aromatic rings. Major limitations of the Friedel-Crafts alkylation are associated with the introduction of *n*-alkyl groups, with the formation of isomers when substituted aromatics are used as starting materials, and with the substitution of aromatics bearing strong electron-withdrawing substituents. An additional limitation is associated with the inability of aromatic amines, such as anilines, to be readily used as substrates in Friedel-Crafts alkylations. We now wish to report the details of our process for the specific ortho-alkylation of aromatic amines. The application of our simple experimental procedure provides a superior method for the synthesis of a variety of isomerically pure polysubstituted aromatic compounds. In addition, it allows for the introduction of *n*-alkyl groups such as the *n*-pentyl and *n*-hexyl moieties.

In its simplest form, our procedure involves an intramolecular migration modeled after the classical Sommelet-Hauser rearrangement.^{3,4} In principle, ylides

of the general formula **1** should rearrange to give dienone imines, **2**, which on hydrogen transfer and accompanying rearomatization should produce the aniline derivative **3** with exclusive ortho substitution. Substantiation of this hypothesis was provided by Claus and coworkers, who demonstrated that sulfilimines, **4**, will rearrange in base to yield **3**, presumably *via* the intermediacy of **1** and **2**.⁵ Unfortunately, the formation of sulfilimines is limited to anilines with an unsubstituted amino group, and the conditions used for sulfilimine formation (aniline, dimethyl sulfoxide, and phosphorous pentoxide) do not lend themselves to utilization in the presence of acid sensitive substituents. We reasoned that a more general procedure could be developed if an aniline, **5**, could be directly converted into the ylide **1** without the initial formation of a sulfilimine. Our investigation of the problem has led to the development of a procedure in which **5** is converted into **3** *via* the intermediacy of the azasulfonium salt **6**.

Initial efforts were devoted to the ortho substitution of a series of *N*-*tert*-butylanilines, **7**, which were available to us as a result of a prior study.⁶ Treatment of **7**

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