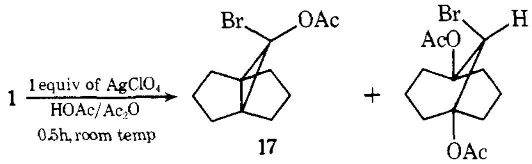
on the basis of its ir (CCl_4) carbonyl absorption at 1824 cm^{-1}, its mass spectrum (Calcd for $C_9H_{12}O$: *m/e* 136.0888. Found: *m/e* 136.0883. Calcd for C_8H_{12}: *m/e* 108.0939. Found (P − CO, rel. intensity 1.2): *m/e* 108.0938. Calcd for C_7H_8O: *m/e* 108.0575. Found (P − C_2H_4, rel. intensity 1.0): *m/e* 108.0575), and its ^{13}C NMR[12] ($CDCl_3$): δ 174.1, 32.8, 30.7, 30.4.[13,14] Compound **10** showed λ_{max} 250 (log ϵ 4.23) nm (lit.[16] 250 (log ϵ 3.95)); also calcd for $C_9H_{12}O$: *m/e* 136.0888. Found: *m/e* 136.0886.

The mode of product formation is shown in Scheme I. Thus ionization of **1** to partially opened ion **11**[17] is followed by collapse at $C_9(k_C)$ to give **4** (S = H), or at C_1 (C_5, k_B) to give **3** (S = H). Dehydrobromination of **4** gives **9.** While acid formation may funnel through **9,** we show the alternative protolysis of the cyclopropane ring of **4.** Ion **13** may be derived from **4** either directly or via **14;** production of the cis acid (**7**) is expected.[4c,18] The less favored formation of unsaturated acid **8** can involve the alternate direction of protolytic cleavage of the C_1-C_9 bond with concomitant elimination to aldehyde **15;** Tollens oxidation by Ag^+ then produces **8.**[19] Bridgehead olefin **3** suffers a fate similar to those derived from **5**[4b,d] and **6.**[4c]

While the small amount of **10** formed fits prior expectations for the mode of reaction of **11,** the absence of typical bridgehead olefin products **12** and/or **16** was worrisome. Hydrolysis in less aqueous media would be expected to enhance fragmentation to **16;**[4c] indeed Ag^+ assisted solvolysis of **1** in 99% aqueous acetone produced roughly equal amounts of **10** and **16** (^1H NMR δ 5.80 (s); ir $\nu_{C=O}$ at 1690 cm^{-1}. Calcd for $C_9H_{13}OBr$: *m/e* 216.0150. Found: *m/e* 216.0156). Additionally, the Ag^+ assisted acetolysis of **1** gave a derivative of **12** (**18**), as shown in eq 3. The spectral identification of **17** was made secure via its base catalyzed conversion to **7.** Similarly, **18** was converted to **12,** and subsequently **10.**



17
28%

18
2%

(3)

In 90% aqueous acetone, the ratio k_B/k_C, as measured by the percent bridgehead olefin products divided by the percent cyclopropyl products, is 0.024 for **1,** ≥360 for **5,** and 1.8 for **6a.** The difference between the bridgehead olefins derived from **1** and **5** is that the former is transoid in a six-membered ring, while the latter is transoid in a seven-membered ring; both are cisoid in six-membered rings. The energy required to produce the k_B/k_C change—roughly *6 kcal/mol*—is a first approximation to the energy difference between transoid seven and transoid six bridgehead olefins which *bear a halogen substituent* (the difference for alkyl or hydrogen substituted ones should be greater). Similarly, the difference between analogous cisoid seven and cisoid six bridgehead olefins (**5** vs. **6a**) is calculated to be ca. 3 kcal/mol.

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(7) Mp 43–44 °C (lit.[8] 40–43 °C). Calcd for $C_9H_{14}O_2$: *m/e* 154.0994. Found: *m/e* 154.0996. The ^{13}C NMR showed only six peaks: δ 186.0, 59.8, 49.8, 38.1, 34.0, 26.3.

(8) A. C. Cope and E. S. Graham, *J. Am. Chem. Soc.*, **73,** 4702 (1951).

(9) Compare $\nu_{C=O}$ 1822 cm^{-1} for 1,1-di-*tert*-butylcyclopropanone[10] and 1825 for *trans*-1,2-di-*tert*-butylcyclopropanone.[11]

(10) J. K. Crandall and W. H. Machleder, *J. Am. Chem. Soc.*, **90,** 7347 (1968).

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(12) The carbonyl absorption at δ 174.1 is some 40 ppm upfield from that of *trans*-di-*tert*-butylcyclopropanone,[11] which is the only other case reported. In the presence of 2.5 equiv of CrAcAc, the ^{13}C NMR peaks appeared at δ 173.6, 35.3, 33.8, and 29.9. Importantly, we recovered **9** unchanged (ir, ^1H NMR) after ^{13}C NMR analysis.

(13) Also ^1H NMR (CCl_4): δ 2.5–1.1 (m); uv (CH_2Cl_2) 325 (ϵ 27), 336 (ϵ 22) nm.

(14) As might be expected from its structure, **9** was relatively inert. It was stable to oxygen and, after stirring for 16 h at room temperature in anhydrous MeOH, was recovered unchanged. After refluxing for 8 h in MeOH, a ca. 75% yield of a very acrid smelling material was obtained. ^1H NMR absorptions at δ 5.35 and 2.8–1.1, as well as ir peaks at 1700 and 1640 cm^{-1}, were observed for the unidentified product(s). Furthermore, **9** did not hydrogenate appreciably (Pt/C, EtOH, 50 psi, 2 h), although a small peak at 1730 cm^{-1} was observed ($\nu_{C=O}$ 1726 cm^{-1} for bicyclo[3.3.1]nonan-9-one[15]).

(15) C. S. Foote, *J. Am. Chem. Soc.*, **86,** 1853 (1964).

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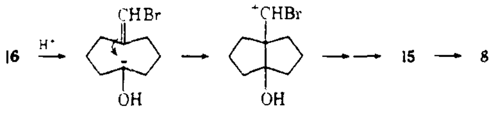
(18) An alternate mode for production of **7** and **8** is direct electrophilic attack on **1** by $HClO_4$. To test this, 1 equiv of EtBr was allowed to react with 0.9 equiv of $AgClO_4$ in 90% aqueous acetone. To the resulting 0.9 equiv of $HClO_4$ was added 1 equiv of **1**, and the mixture stirred 12 h at room temperature; 92% of **1** was recovered. Even less likely than protonolysis of **1** is Ag^+ cleavage. When the more susceptible [3.3.1]propellane was exposed to $AgClO_4$ in aqueous acetone (which contained 1 equiv of $HClO_4$) for 17 h, only 28% starting material was recovered. However, no other tractable products resulted. We thus feel confident that **1** reacts via initial C–Br bond heterolysis.

(19) The possibility that **8** arose from **16,** i.e.,



was excluded by a control experiment, as it also was for the analogous nine- and ten-membered ring compounds.

(20) Fellow of the Alfred P. Sloan Foundation, 1976–1978.

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Stabilization of Aryldiazonium Ions by Crown Ether Complexation

Sir:

Despite an early beginning, the chemistry of aromatic diazonium compounds remains in vogue as additional synthetic

Table I. First-Order Rate Constants for the Thermal Decomposition of **1** in 1,2-Dichloroethane at 50.0 °C

[18-crown-6]/[**1**][a]	λ_{max},[b] nm	$k_{obsd} \times 10^4$, s^{-1} [c]
0	285	2.28
1.00	276	1.36
4.99	269	0.429
24.8	268.5	0.117
99.7	268	0.0516

[a] [**1**] = 5.85×10^{-5} M. [b] Measured diazonium ion absorption maximum. [c] Estimated maximum error is 2% of the rate constant.

Table II. First-Order Rate Constants for the Thermal Decomposition of **1**[a] in 1,2-Dichloroethane in the Presence of Equimolar Crown Ether at 50.0 °C

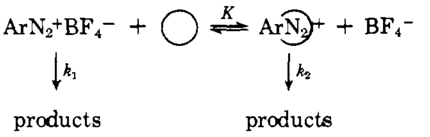
Crown ether	λ_{max}, nm	$k_{obsd} \times 10^4$, s^{-1} [c]
None	285	2.28
Dibenzo-18-crown-6	276	1.74
Dicyclohexyl-18-crown-6	280	1.42
18-Crown-6	276	1.36

[a] [**1**] = 5.85×10^{-5} M. [b] Measured diazonium ion absorption maximum. [c] Estimated uncertainty is 2% of the rate constant.

and mechanistic aspects are revealed in laboratories throughout the world.[1] Recently, Gokel and Cram[2] observed solubilization of aryldiazonium salts in chlorocarbon solvents by crown ether[3] (macrocyclic polyether) complexation. We wish to report that such complexes exhibit markedly enhanced thermal stability relative to the corresponding uncomplexed diazonium ions.

The thermal decomposition (Schiemann reaction) of *p-tert*-butylbenzenediazonium fluoroborate[4] (**1**) in 1,2-dichloroethane was selected as a suitable model system. Solubility of **1** in this solvent eliminates the potential problem of studying kinetics under heterogeneous reaction conditions. Kinetics were followed by ultraviolet spectroscopy. The diazonium salt **1** exhibited a maximum at 285 nm in 1,2-dichloroethane. In the presence of certain crown ethers, the diazonium ion chromophore shifted to somewhat shorter wavelengths. Reaction products[5] were transparent in this spectral region.

Rate constants for the first-order decomposition of **1** in 1,2-dichloroethane in the absence and presence of varying 18-crown-6[3] concentrations are recorded in Table I. As is readily evident, the presence of 18-crown-6 suppresses the thermal decomposition of **1**, with greater 18-crown-6 concentration producing larger retardation. In view of the report by Swain, Sheats, and Harbison[7] that the rate of decomposition of benzenediazonium fluoroborate is generally solvent independent, the observed rate retardations support a specific complexation of **1** by 18-crown-6.



$$\begin{array}{ccc} \mathrm{ArN_2^+BF_4^-} + \bigcirc & \overset{K}{\rightleftharpoons} & \mathrm{ArN_2}\!\bigcirc^{+} + \mathrm{BF_4^-} \\ \downarrow k_1 & & \downarrow k_2 \\ \text{products} & & \text{products} \end{array} \qquad (1)$$

From the scheme depicted in eq 1, where O represents 18-crown-6, appropriate kinetic derivation[8] reveals that a plot of $1/(k_1 - k_{obsd})$ vs. 1/[18-crown-6] should be linear with slope = $1/(k_1 - k_2)K$ and intercept at 1/[18-crown-6] = 0 of $1/(k_1 - k_2)$, if [18-crown-6] $\gg$ [$\mathrm{ArN_2^+BF_4^-}$]. Plotting the last three sets of data in Table I in this fashion produces a strictly linear graph with intercept = $1/(2.26 \times 10^{-4}\ s^{-1})$. This indicates $k_2 = 0$, or at least $k_1 \gg k_2$. Thus, the crown ether complexed diazonium ions do not detectably decompose under conditions where uncomplexed diazonium ions are converted into products. Therefore, *complexation with crown ethers represents a new method of stabilizing arenediazonium ions.* Similar stabilization by a "macrocyclic effect" has been recently reported for decompositions of metal ion complexes.[9]

In order to probe the optimal parameters (cavity size and identity of heteroatoms) for the macrocyclic complexing agent, the effects of a variety of crown ethers and related compounds upon the thermal decomposition rate of **1** in 1,2-dichloroethane were assessed. Within experimental error, the presence of 15-crown-5, *N*-tosylmonoaza-18-crown-6, hexathia-18-crown-6, or hexathia-21-crown-6[10] had no influence upon the rate of decomposition of **1**. As presented in Table II, equimolar dicyclohexyl-18-crown-6[11] and dibenzo-18-crown-6 produced rate retardations of a lesser magnitude than that observed with equimolar 18-crown-6. Thus, of the complexing agents which were examined, the readily available[12] 18-crown-6 exhibits the strongest complexation of **1**.[13,14]

A potential for solid state stabilization of arenediazonium salts, particularly shock sensitive species, by crown ether complexation is currently under investigation.

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Supplementary Material Available: kinetic derivation of scheme depicted in eq 1 (2 pages). Ordering information is given on any current masthead.

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(13) A value of $K = 1.56 \times 10^5\ \mathrm{mol^{-1}\ l.}$ is calculated from the kinetic data in Table I.
(14) 18-Crown-6 and **1** readily form a 1:1 complex with mp 107.5–108 °C (uncomplexed **1** had a mp of 96.5–97.5 °C). The value ν(NN) (Nujol mull) is observed to increase from 2277 cm^{-1} in uncomplexed **1** to 2306 cm^{-1} in the complex.[15]
(15) The formation of a complex between benzenediazonium hexafluorophosphate and dicyclohexyl-18-crown-6 and the increase in ν(NN) upon complexation have previously been reported; B. L. Haymore, J. A. Ibers, and D. W. Meek, *Inorg. Chem.*, **14**, 541 (1975).

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