chemical studies, while the 12-OH and 13-OH mixture provides the means for related investigations of 4-protoadamantyl derivatives.

## Experimental Section

**General.** Melting points are uncorrected. $^2$H NMR spectra were obtained at 15.4 MHz, using a Varian XL-100-15 Fourier-transform instrument with proton decoupling. Overlapping signals were quantitatively deconvoluted by means of a du Pont Model 310 curve resolver with the assumption of Lorentzian line shapes. GLC analyses were performed on a Varian Model 920 gas chromatograph, employing the following columns: (A) 20 ft × 0.25 in. 20% SE-30 on acid-washed DMCS-treated Chromosorb W; (B) 6 ft × $^1/_8$ in. Carbowax 20M on acid-washed DMCS-treated Chromosorb W.

**2(a)-Adamantanol-*4*(a)-*d* and -4(*e*)-*d* (2 and 3).** An oven-dried 250-mL three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, and nitrogen atmosphere was charged with 920 mg (3.97 mmol) of 4(a)-bromo-2(a)-adamantanol (1),[5] 46.0 g (533 mmol) of *tert*-butyl alcohol-*d*,[7] and 150 mL of anhydrous tetrahydrofuran. After addition of 2.00 g (433 mmol) of finely cut lithium wire (prewashed in hexane) at room temperature, the stirred mixture was heated under reflux for 16 h, cooled, and poured into 500 mL of ice water. Extraction with ether, drying over MgSO$_4$, and solvent removal left a brown solid, which was recrystallized from hexane at –78 °C to give 485 mg (3.2 mmol, 80%) of white powder: mp (sealed tube) 259–263 °C (lit.[11] mp 258–260 °C); mass spectrum, *m/e* 153 (M$^+$); $^1$H NMR (CDCl$_3$) δ 1.3–2.3 (m, 14 H), 3.9 (m, 1 H), as expected.[19] The $^2$H NMR spectrum consisted of two largely overlapping peaks near δ 1.89, which were fully resolved by the introduction of Pr(fod)$_3$ as recorded in Table I; the ratio of signals at δ –7.27 (2) and –4.13 (3) was 83:17.

**2-Adamantanone-*4*(a)-*d* and -4(*e*)-*d* (4 and 5).** Alcohol mixture 2 and 3 was oxidized to the corresponding ketones, 4 and 5, using Jones reagent as reported by Numan and Wynberg:[11] mp (sealed tube) 253–255 °C (lit.[11] mp 254–256 °C); mass spectrum, *m/e* 151 (M$^+$); $^1$H NMR as expected;[20] $^2$H NMR as in the text and Table I.

**Four Diastereomeric 2-Adamantanols-*4*-*d* (2, 3, 6, and 7).** Ketones 4 and 5 were reduced with LiAlH$_4$ in ether in the usual manner[21] to give the four isomeric labeled alcohols. The dispersed $^2$H NMR spectrum, Table I, consisted of four absorptions. The peak assignments for 2 (41%) and 3 (9%) were made from the spectrum of the precedent twofold alcohol mixture, while those for 6 (42%) and 7 (8%) followed from matching intensities with the signals from 2 and 3, respectively.

**4-Protoadamantanone-*exo-5*-*d* and -*endo-5*-*d* (9 and 10).** Protoadamantene[5] (8) (268 mg, 2.00 mmol) was deuterioborated and oxidized, using an excess of deuterioborane in tetrahydrofuran (Alfa) as described for the hydroboration by Boyd and Overton.[13] The resulting crude mixture of 4- and 5-protoadamantanols was dissolved in 5 mL of dry methylene chloride and added to a stirred solution of 426 mg (1.98 mmol) of pyridinium chlorochromate (Aldrich) and 536 mg (3.94 mmol) of sodium acetate in 10 mL of methylene chloride at room temperature. After 2 h the mixture was filtered through Florisil, and the solvent was removed by rotary evaporation, leaving a yellow solid crude product, which was established by GLC (column A, 150 °C) to consist of 67% 4-protoadamantanone and 33% 5-protoadamantanone. The 4-ketone (50 mg, 0.33 mmol) was isolated by preparative TLC:[13] mp (sealed tube) 212–214 °C (lit.[13] mp 210–212 °C); $^2$H NMR, Table I and text.

***exo*-4-Protoadamantanol-*exo-5*-*d* and -*endo-5*-*d* (12-OH and 13-OH).** These labeled alcohols were prepared in 70% yield by the oxymercuration–reduction of 268 mg (2.00 mmol) of protoadamantene[5] (8) with 638 mg (2.00 mmol) of Hg(OAc)$_2$ and then 500 mg (11.9 mmol) of NaBD$_4$ (Alfa), using the procedure described by Schleyer and co-workers[16] for the undeuterated

alcohol. The product was recrystallized from hexane at –78 °C: mp 202–203 °C (lit.[16] mp 203–206 °C); mass spectrum *m/e* 153 (M$^+$); $^2$H NMR, Table I and text. The NMR peak assignments were made by oxidation of a sample of the mixed alcohols to the corresponding ketones, 9 and 10, whose spectrum had been analyzed as described in the text. The oxidation of 200 mg (1.30 mmol) of 12-OH and 13-OH was effected in 91% yield by using buffered pyridinium chlorochromate as employed in the synthesis of 9 and 10 via hydroboration (see above).

***exo*-4-Protoadamantyl-*exo-5*-*d* and -*endo-5*-*d* 3,5-Dinitrobenzoate (12-ODNB and 13-ODNB).** The alcohol mixture 12-OH and 13-OH was converted to the 3,5-dinitrobenzoates in 70% yield by using the procedure described by Schleyer and co-workers[16] for preparation of the undeuterated esters: mp 141–143 °C (lit.[16] mp 142–144 °C); $^1$H NMR as expected.[16]

**Isomerization–Saponification of Dinitrobenzoates 12-ODNB and 13-ODNB to Alcohols 2 and 3.** A solution of 157 mg (0.50 mmol) of dinitrobenzoate mixture 12-ODNB and 13-ODNB in 10 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (Columbia, distilled from BaO immediately before use) containing 59 mg (0.55 mmol) of 2,6-lutidine (Aldrich) was boiled under reflux under nitrogen for 5 days. The solvent was evaporated under vacuum, 50 mL of 20% methanolic potassium hydroxide was added, and the solution was refluxed for 12 h. The bulk of the methanol was removed by rotary evaporation, and the residue was poured into 500 mL of water and extracted with ether. The ether extract was washed with water and dried (MgSO$_4$). Rotary evaporation left a white solid, indicated by GLC (column B, 150 °C) to be only 2-adamantanol. Sublimation (0.5 mm) gave 65 mg (0.43 mmol, 85%) of 2 and 3: mp (sealed tube) 257–259 °C (lit.[11] mp 257–260 °C, dideuterated); $^2$H NMR, Table I and text.

(19) Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, WI, 1974; Vol. 1, p 120.
(20) Reference 19, Vol. 2, p 134.
(21) Fieser, L. F.; Fieser, M. "Reagents For Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 584.

## Complexation of Arenediazonium Ions by Crown Ethers: A CNDO/2 Study

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In 1975, Haymore, Ibers, and Meek[1] reported the preparation of a solid one-to-one complex of benzenediazonium hexafluorophosphate with the cis-anti-cis isomer of dicyclohexano-18-crown-6. The infrared spectrum of this complex, in which the diazonio group neck of the aryldiazonium ion is inserted into the collar of the crown ether,[2] provided the first example of a benzenediazonium ion complex in which $\nu$(NN) of the cation increased upon complexation (from 2285 cm$^{-1}$, uncomplexed, to 2317 cm$^{-1}$, complexed). Subsequently, this unusual infrared spectral shift upon complexation has been confirmed for solid

(1) Haymore, B. L.; Ibers, J. A.; Meek, D. W. *Inorg. Chem.* **1975**, *14*, 541.
(2) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 2564.

complexes of several substituted benzenediazonium tetrafluoroborates with 18-crown-6[3,4] and for complexation of *p-tert*-butylbenzenediazonium tetrafluoroborate with 18-crown-6 in dichloromethane.[4]

Simplistically, the infrared spectral shifts may be rationalized by considering the resonance interactions illustrated in 1–4. Insertion of the diazonio group into the
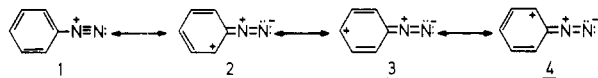


electronegative crown ether cavity should enhance the contribution of resonance form 1 (in which the positive charge is localized on $N_\alpha$) to the hybrid. This would increase the triple bond character of the $N_\alpha$-$N_\beta$ bond and produce a higher $\nu$(NN) value. Also consistent with this interpretation is the decrease in $\lambda_{max}$ of the ultraviolet absorption for *p-tert*-butylbenzenediazonium tetrafluoroborate[3] in the presence of 18-crown-6, which indicates a more localized $\pi$-electron system in the crown ether complexed diazonium ion.

However, an increased contribution from resonance form 1 to the hybrid for the complexed diazonium ion should also diminish the C-$N_\alpha$ bond strength and thereby produce a lower stability of the diazonium salt when complexed by a crown ether molecule. This prediction is diametrically opposite to the markedly enhanced thermal[3] and photochemical[5] stabilities and the decreased shock sensitivity[6] of crown ether complexed diazonium compounds when compared with the corresponding uncomplexed species.

In order to gain insight into the changes which occur when aryldiazonium ions are complexed by crown ethers, we have performed CNDO/2 calculations for the benzenediazonium ion and for a model of the benzenediazonium ion complexed with a crown ether.

For the benzenediazonium ion, bond lengths were selected from crystallographic data.[7] The benzene ring of the benzenediazonium ion was assumed to be a regular hexagon with a C-C bond length of 1.400 Å. The C-H, C-$N_\alpha$, and $N_\alpha$-$N_\beta$ bond lengths were fixed at 1.080, 1.385, and 1.097 Å, respectively.

Complexation of the benzenediazonium ion by a crown ether molecule was simulated by three dimethyl ether molecules which were symmetrically located around the $N_\alpha$-$N_\beta$ bond so that the triangle described by the three oxygen atoms was perpendicular to the $N_\alpha$-$N_\beta$ bond with $N_\alpha$ at the center of the triangle. The three dimethyl ether molecules were oriented to fit the observed $D_{3d}$ structure reported for KSCN complexed with 18-crown-6.[8] Idealized tetrahedral bonding was assumed for each dimethyl ether molecule. The C-C and C-O bond distances of 1.504 and 1.418 Å which were utilized were those reported in the KSCN·18-crown-6 complex[8] and C-H bond lengths of 1.090 Å were assumed.

Conceivable interactions between a crown ether molecule and a complexed arenediazonium ion include charge-transfer and electrostatic effects. In order to consider the possibility of the former (electron transfer from occupied
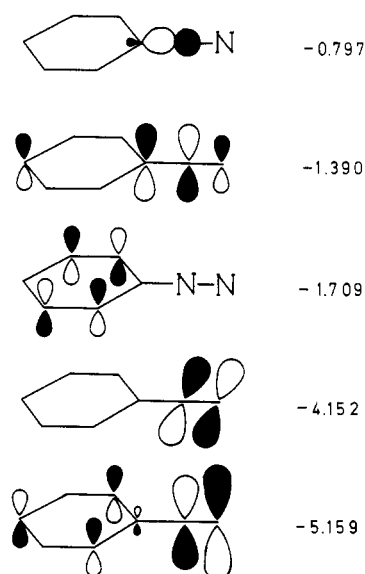
(3) Bartsch, R. A.; Chen, H.; Haddock, N. F.; Juri, P. N. *J. Am. Chem. Soc.* **1976**, *98*, 6753.

(4) Korzeniowski, S. H.; Petcavich, R. J.; Coleman, M. M.; Gokel, G. W. *Tetrahedron Lett.* **1977**, 2647.

(5) Bartsch, R. A.; Haddock, N. F.; McCann, D. W. *Tetrahedron Lett.* **1977**, 3779.

(6) Sheppard, W. A.; Gokel, G. W.; Webster, O. W.; Betterton, K.; Timberlake, J. W. *J. Org. Chem.* **1979**, *44*, 1717.

(7) For a summary, see: Sorriso, S. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley-Interscience: New York, 1978; Part I, pp 97–105.

(8) Dunitz, J. D.; Dobler, M.; Seiler, P.; Phizacherley, R. P. *Acta Crystallogr., Sect. B* **1974**, *30*, 2733.



**Figure 1.** Schematic representation and orbital energies (in eV) of the five lowest unoccupied MO's in the benzenediazonium ion. The orbital energy of the highest occupied MO is –19.629 eV.
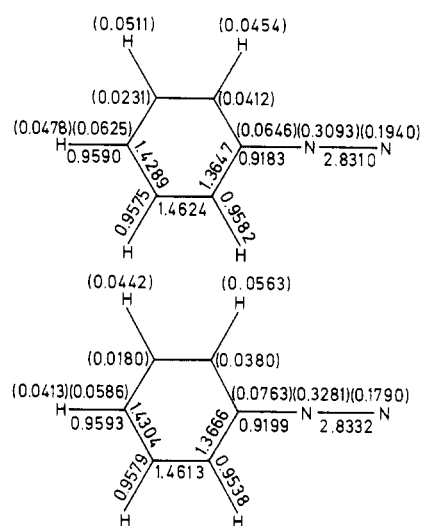


**Figure 2.** Wiberg bond indices and atomic charges (in parentheses) for the free (upper) and the complexed (lower) benzenediazonium ion.

orbitals of the crown ether to unoccupied orbitals of the diazonium ion), the forms of the unoccupied diazonium ion molecular orbitals (MO's) must be examined (Figure 1). Electron flow into MO 20 would produce a small increase in the $\pi$-bonding character of the C-$N_\alpha$ bond. Electron flow into MO 23 and MO 24 would cause enhanced $\pi$ and $\sigma$ antibonding character, respectively, in the C-$N_\alpha$ bond. From the LCAO expansion coefficients and the orbital energies, it is possible to estimate that the effect of MO 23 should be slightly larger than the effect of MO 20. The net result is that a pure charge-transfer interaction should weaken both the $\pi$ and $\sigma$ bonds between C1 and $N_\alpha$. Clearly this prediction is inconsistent with the stabilization which is observed for crown ether complexed diazonium salts.

The CNDO/2 calculations for the benzenediazonium ion and for the benzenediazonium ion plus three dimethyl ether molecules yield the Wiberg bond indices and atomic charges[9] recorded in Figure 2. In going from the uncomplexed benzenediazonium ion to the model for the com-

(9) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

plex, the positive charge on $N_\alpha$ increases in agreement with the expectation for an electrostatic interaction.

Equally important is the increase in positive charge on C1 upon complexation. This means that the arguments of classical electron theory[10] may be used to rationalize the increased stability of the complexed diazonium ions. For example, the greater thermal stability of the p-nitro-benzenediazonium ion (compared with that of the benzenediazonium ion) may be attributed to the contribution of resonance form 5 to the hybrid. The positive charge on
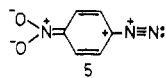


C1 retards $S_N1$ decomposition $(ArN_2^+ \rightarrow Ar^+ + N_2)$ of the diazonium ion. Similar reasoning may be employed to explain the enhancement in aryldiazonium salt stability with crown ether complexation. In agreement with the results of the CNDO/2 calculations, a downfield shift for C1 occurs in the $^{13}C$ NMR spectrum of p-tert-butyl-benzenediazonium tetrafluoroborate in dichloromethane when 18-crown-6 is added.[4]

In addition to increasing the positive charge on C1, the calculations indicate that the $C-N_\alpha$ bond becomes slightly stronger for the complexed diazonium ion species. This will also stabilize the complexed diazonium ion. The effect is not large because the model utilizes only three dimethyl ether molecules instead of a molecule of 18-crown-6.

From the results presented in Figure 2, it is also apparent that the $N_\alpha-N_\beta$ bond strength increases for the complexed benzenediazonium ion. Again, the effect is attenuated because our model employed three dimethyl ether molecules instead of one 18-crown-6 molecule. However, the increase in bond strength is consistent with the unusual increase in $\nu(NN)$ which is observed when benzenediazonium ions are complexed by crown ethers.

Thus, the results of our CNDO/2 calculations reveal that crown ethers complex aryldiazonium ions using electrostatic interactions and that both the spectral changes and modified stabilities may be rationalized.

(10) Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Holt, Rinehart, and Winston: New York, 1959; p 457.

## Synthesis of 1,2,4-Thiadiazolin-3-one 1,1-Dioxides

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Recently we reported the synthesis of carbamates of α-amino sulfonamides (3) by the Curtius rearrangement (Scheme I).[1] On additional investigation of this synthesis, we have found that under some conditions the reported

(1) Gilmore, W. Franklin; Lin, Horng-Jau *J. Org. Chem.* 1978, 43, 4535-7.
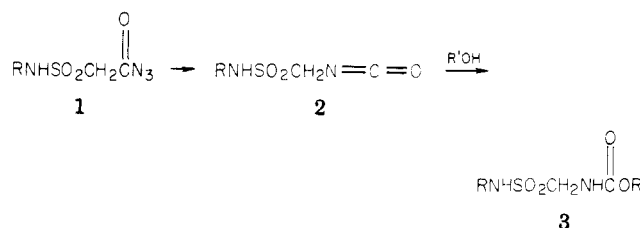
**Scheme I**



**Scheme II**
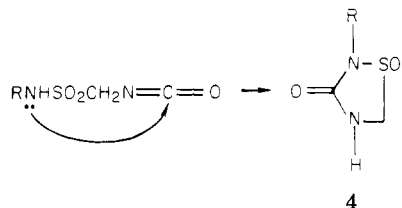


method fails to give the carbamates. We now report an alternate reaction path for the isocyanates (2).

### Results and Discussion

In our initial work with the formation of unsubstituted and monosubstituted sulfonamido acyl azides (1) by diazotization of unsubstituted and monosubstituted sulfonamido acyl hydrazides, we anticipated two side reactions. We recognized that N-nitrosation of the sulfonamido nitrogen might occur. However, by use of only a slight excess of sodium nitrite, this problem has been avoided. We also anticipated that the weakly acidic unsubstituted or monosubstituted sulfonamido group might react with the isocyanate group to form either a cyclic or an acyclic urea as shown in Scheme II.

In repeating our previously reported procedure[1] we observed that during extended drying of the ether solution of the azide (1) frequently a gas (presumably nitrogen) was evolved. When this occurred little, if any, carbamate (3) was obtained upon heating and the addition of an alcohol. Instead 4 was isolated regardless of whether an alcohol was added. The previously reported carbamates are best obtained by the modified procedure described below. In the modified procedure the ether solution of the azide is dried for a short period with cooling and the ether is evaporated in vacuo without heating. Also the appropriate alcohol is added after 2.5 min of heating the benzene solution instead of 30 min. This procedure is reproducible for a number of reactions carried out by several individuals whereas the previously reported procedure is not consistently reproducible.

The 1,2,4-thiadiazolin-3-one 1,1-dioxides (4) are best prepared by heating a benzene solution of the azide for about 1 h. Members of this heterocyclic system have been previously reported;[2,3] however, the reported procedures do not use readily available starting materials and are not easily adaptable to the preparation of compounds having no substituent in the 4-position. The 1,2,4-thiadiazolin-3-one 1,1-dioxides prepared by our procedures are shown in Table I.

### Experimental Section

All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. NMR spectra were

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(3) Arbuzov, B. A.; Zobova, N. N.; Rubinova, N. R. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1975, 1438.