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Synthesis, Photolysis, and Pyrolysis of 10-Substituted *exo*-3,4,5-Triazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes. Preparation of 8-Substituted *exo*- and *endo*-3-Aryl-3-azatricyclo[3.2.1.$0^{2,4}$]octanes

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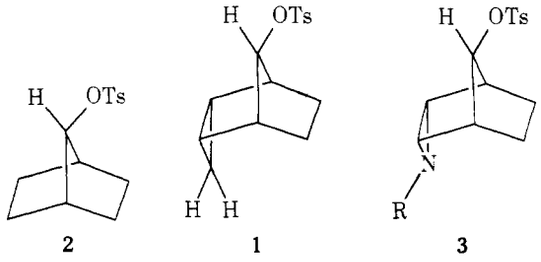
Received February 2, 1978

A systematic study of the addition of aryl azides to 7-substituted bicyclo[2.2.1]hept-2-enes to yield 10-substituted 5-aryl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes has been carried out. The influence of substituents in the 10 position on the pyrolysis and photolysis of these triazatricyclodecenes has been studied. A variety of 8-substituted 3-aryl-3-azatricyclo[3.2.1.$0^{2,4}$]octanes have been prepared.

Perhaps one of the most quoted examples of neighboring group participation in solvolysis reactions is that of the *endo*-cyclopropyl moiety of **1**.[1] The 10^{14} rate difference[2] between **1** and **2**, which results from the vigorous neighboring



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group participation of the strained 2–4 bond of **1**, is among the largest effects recorded for participation by a carbon–carbon bond. In view of this dramatic influence of the cyclopropane portion of **1**, the question of the degree of participation which might be provided by the carbon–carbon bond of similarly situated three-membered heterocyclics became of interest. As part of a general study of participation by the carbon–carbon bond of epoxides, episulfides, and aziridines, we developed a need for a synthetic route to **3**. This paper provides the details of our preliminary investigation of the synthesis of *exo*- and *endo*-3-aryl-3-azatricyclo[3.2.1.$0^{2,4}$]octanes via the photolysis and pyrolysis of 10-substituted 5-aryl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes.

Although numerous methods exist for the synthesis of aziridines,[3] most of those which are available do not lend themselves to the preparation of 8-substituted 3-aryl-*endo*-3-azatricyclo[3.2.1.$0^{2,4}$]octanes. The single approach which appeared to be attractive involved the addition of aryl azides to bicyclo[2.2.1]heptene derivatives[4,5] followed by either photolysis[5–7] or pyrolysis[6a,6b,7b,8] of the resulting 5-aryl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes. While the photochemical loss of nitrogen from the exo triazolines gave only exo aziridines, the thermal process resulted in the formation

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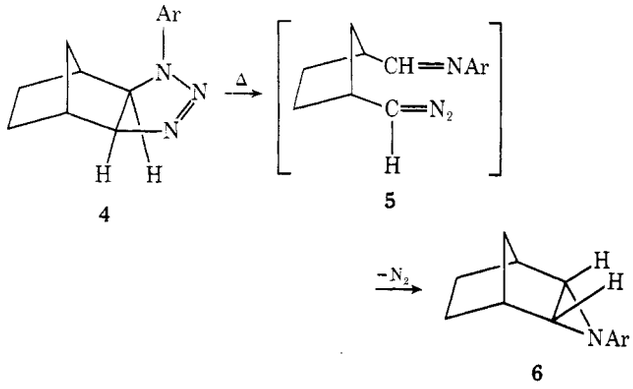
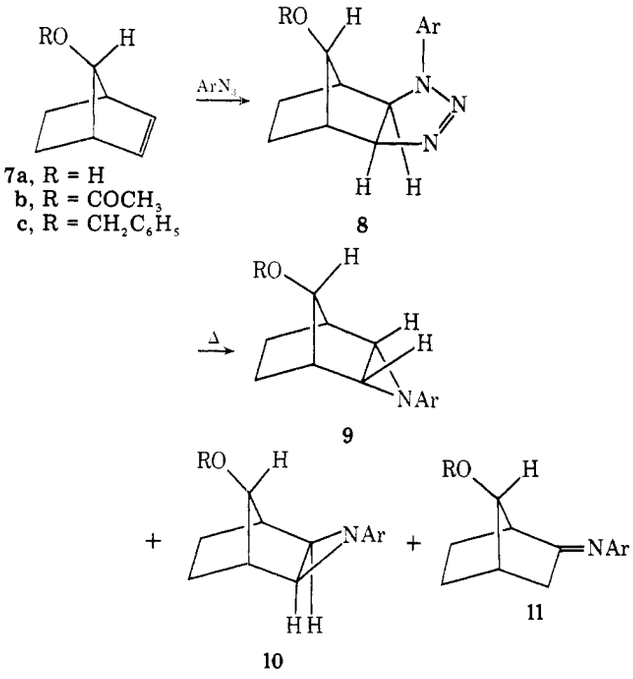
of both exo and endo aziridines. The unusual formation of endo aziridines was rationalized as occurring via thermal opening of **4** to give **5**, followed by subsequent conversion of **5** into **6** with loss of nitrogen.[7b,8h-k,8m] Although extensive

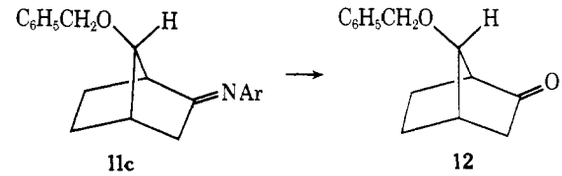


literature exists on the 3-azatricyclo[3.2.1.0^{2,4}]octanes,[5-8] relatively little is known about 8-substituted variants. This is particularly true for derivatives in which the aziridine moiety is endo. Unfortunately, of the three examples which were known,[6b,7a,9] none was suitable for our purposes. Thus, we carried out the following study.

In principle, the most straightforward approach to precursors of **3** would be the conversion of **7** into **8** and subsequent thermolysis of **8** to give mixtures of **9**, **10**, and **11**. Halton and

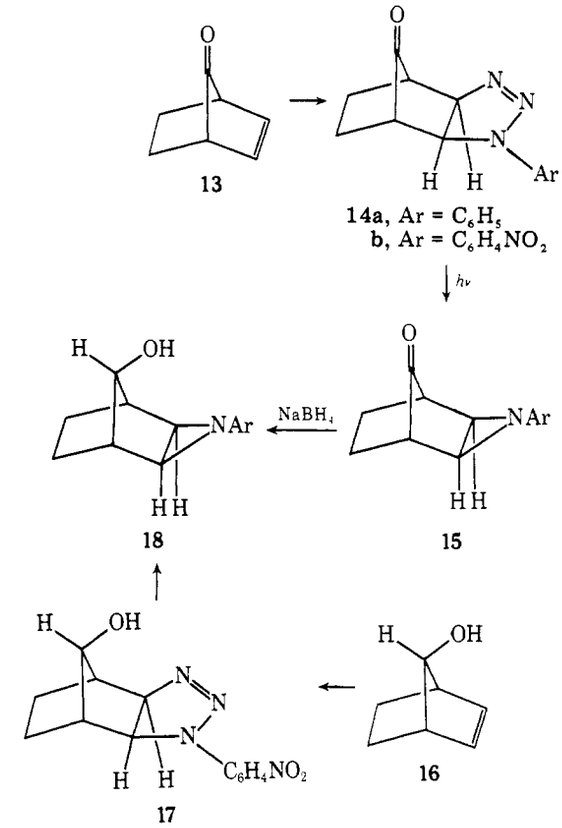


Woolhouse had previously examined the addition of phenyl azide to **7a** to give **8a** (Ar = C_6H_5) and the subsequent pyrolysis and photolysis of this triazoline.[6b] They found that while the 1,3-dipolar addition offered no problems, both pyrolysis and photolysis gave only the exo aziridine, **10a** (Ar = C_6H_5). We were able to confirm the general findings of Halton and Woolhouse on **7a**. In the initial part of our investigation, we utilized *p*-nitrophenyl azide instead of phenyl azide due to the more rapid 1,3-dipolar addition of the *p*-nitro derivative.[10] In view of the failure of **8a** (Ar = C_6H_5) to yield **9**, we decided to investigate two derivatives of **7a**. Both the acetyl derivative,[11] **7b**, and the *O*-benzylated material, **7c**, were treated with *p*-nitrophenyl azide to yield **8b** and **8c** (Ar = *p*-$O_2NC_6H_4$) in 59 and 69% yields, respectively.[12] Pyrolysis of **8b** gave only trace amounts of **10b**.[13] However, similar pyrolysis of **8c** gave 26% of **10c**[13] in addition to 24% of **12**. Presumably, **12** arose from **11c** as a result of hydrolysis under the



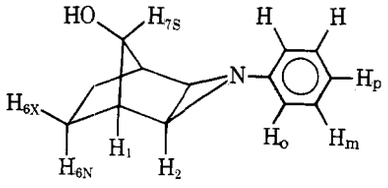
workup conditions. No indication of any endo aziridine could be detected in the thermolysis of either **8b** or **8c**. The results obtained with **8b** and **8c**, while demonstrating the existence of a subtle substituent effect, indicated that anti substituents in the 10-position of the *exo*-3,4,5-triazatricyclo[5.2.1.0^{2,6}]-dec-3-ene skeleton would be ineffective in promoting the formation of an endo-aziridine group.

In a second approach to the synthesis of the 8-substituted *endo*-3-aryl-3-azatricyclo[3.2.1.0^{2,4}]octane structure, we utilized functionality in the 10 position of the precursor which would provide a dramatically different electronic environment. Starting with the readily available bicyclo[2.2.1]hept-2-en-7-one (**13**),[14] we found that phenyl azide and *p*-nitrophenyl azide gave the 1,3-dipolar adducts **14a** and **14b** in 50

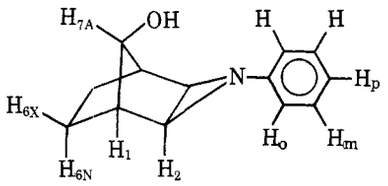


and 41% yield, respectively. Photolysis of **14a** gave 64% of **15a**, while irradiation of **14b** gave only small amounts of **15b** in addition to large amounts of extensively decomposed material.[15] Extensive studies of the pyrolysis of **14a** and **14b**, both neat and in solution, indicated that these thermal fragmentations gave only traces of the corresponding exo aziridines accompanied by extensive decomposition.[16,17] Since the presence of the carbonyl function did not promote the formation of the endo aziridine, and since it made the system more prone to decomposition, the role of a syn-hydroxyl function was explored in the hope that the steric influences of this group would promote the formation of the desired tricyclic skeleton. On the basis of earlier studies,[5] it might have been anticipated that the syn-hydroxyl group of bicyclo[2.2.1]hept-2-en-*syn*-7-ol (**16**)[18] would sterically inhibit

Table I. Least-Squares Slopes of Chemical Shifts vs. Molar Ratio of Eu(fod)$_3$ to Alcohol for 10a and 18a



10a



18a

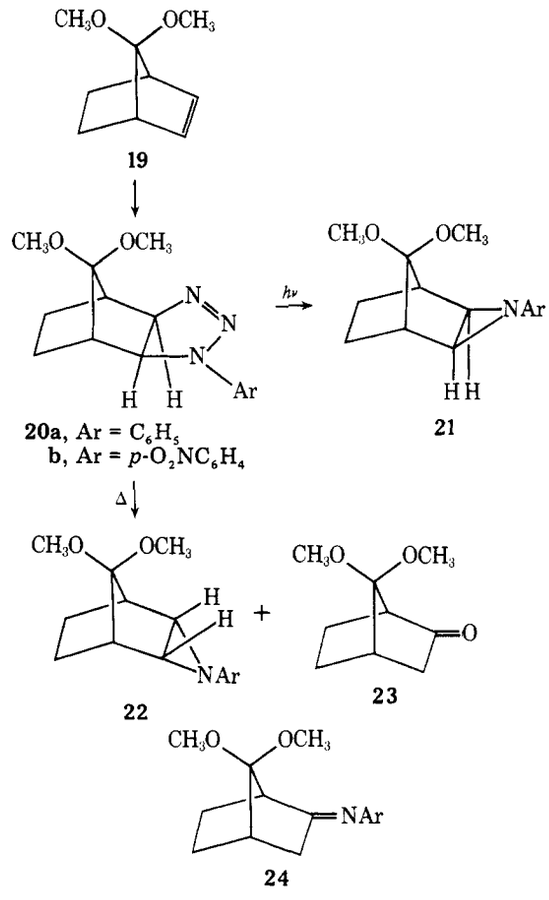
Proton	least-squares slope 10a	18a
H_1	11.35	8.98
H_2	4.21	4.65
H_{6N}	7.10	2.95
H_{6X}	12.88	3.06
H_{7S}	24.5	
H_{7A}		18.12
H_o	0.79[a]	2.97
H_m	0.79[a]	0.90[b]
H_p	0.79[a]	0.90[b]

[a] No distinction occurred between the ortho, meta, and para protons in terms of the induced chemical shift. [b] The meta and para protons were comparably shifted.

addition of the azide. However, **16** reacted readily with *p*-nitrophenyl azide to give a 30% yield of exo triazoline (**17**). Pyrolysis of **17** gave a 30% yield of **18b.** No endo aziridine could be detected.

The aziridines derived from **13** and **16** were readily interrelated. Reduction of **15a** and **15b** with sodium borohydride led to **18a** and **18b** in 71 and 82% yields, respectively. In order to firmly establish the stereochemical relationship between **10a** and **18a** a lanthanide shift study was carried out. Table I gives the least-squares slopes from a plot of chemical shift vs. the molar ratio of shift reagent to the alcohol. The data would indicate that the shift reagent complexed more tightly with **10a** than the **18a.** Presumably, this is due in part to the greater steric congestion in the vicinity of the hydroxyl group of **18a.**

The lack of formation of endo aziridines from bicyclo[2.2.1]heptene derivatives, which possessed immediate hydroxyl group precursors in the 7 position, prompted us to evaluate the use of ketals of **13.** Both phenyl azide and *p*-nitrophenyl azide added to 7,7-dimethoxybicyclo[2.2.1]heptene (**19**)[19] to give **20a** and **20b** in 58 and 65% yields, respectively. In apparent confirmation of our earlier findings on the addition of azides to **16, 19** gave only exo triazolines, as established by NMR spectroscopic studies. Photochemical loss of nitrogen from **20a** gave a 76% yield of **21a.** In contrast to the exclusive formation of exo aziridine in the irradiation of **20a,** pyrolysis of **20b** gave 22% of **22b,**[20] 53% of **23,** and considerable *p*-nitroaniline. No exo aziridine was detected. Thermolysis of **20a** gave only small amounts of **22a.** Again, none of the exo-aziridine **21a** could be found. Thus, the presence of the syn-methoxyl function appeared to be a strong endo-directing influence. The formation of **23** and *p*-nitroaniline from **20b** presumably resulted from the hydrolysis of **24** during the workup of the reaction.



19

20a, Ar = C_6H_5
b, Ar = *p*-$O_2NC_6H_4$

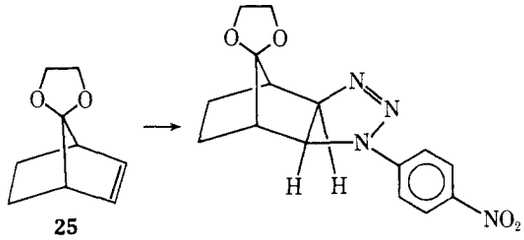
21

22

23

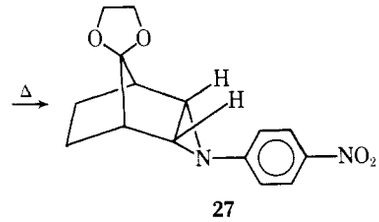
24

In a manner similar to that described above, bicyclo[2.2.1]-hept-2-ene-7-spiro-2′,5′-dioxolane (**25**)[21] gave 79% of **26** on treatment with a slight excess of *p*-nitrophenyl azide. Thermolysis of **26** at 190–200 °C gave a 21% yield of **27.** No exo



25

26



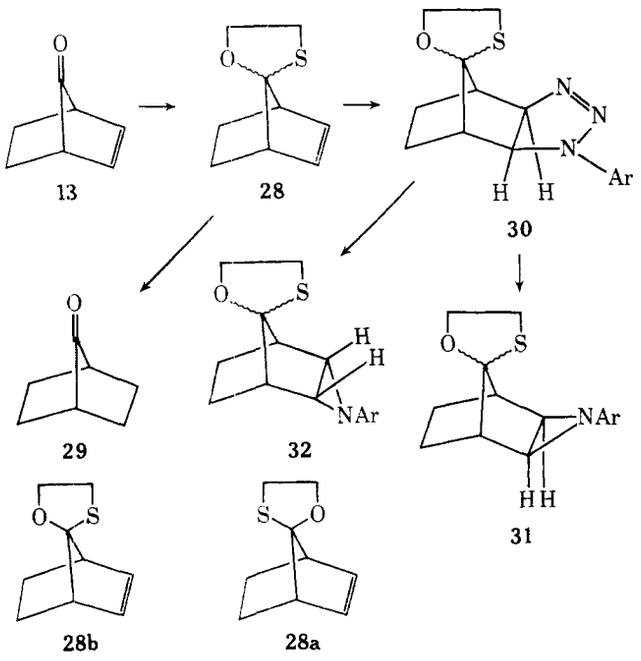
27

aziridine was detected. It is intriguing that the ketal function, even when tied into a dioxolane ring, exerts a strong endo directing influence. Attempts to hydrolyze the ketal functions of **22** and **27** were not successful. Under even very mild conditions, complex mixtures of products were obtained in which the aziridine moiety was no longer intact.

In view of the extreme acid sensitivity of **22** and **27,** it was felt that nonacidic conditions would be necessary for the preparation of our desired system. Thus, the 1,3-oxathiolane group appeared to be an attractive protecting moiety for a carbonyl function, which eventually could be converted to a hydroxyl function. 1,3-Oxathiolanes are readily formed from ketones.[22] Although such oxathiolanes are reasonably stable,

they have been restored to the corresponding ketone either through the use of Raney nickel in acetone (or benzene)[23] or by the recently developed use of chloramine-T.[24]

Treatment of **13** with 2-mercaptoethanol gave **28** as a 3:1 mixture of isomers in 50% yield. Treatment of the 3:1 mixture of **28a** and **28b** with bis(benzonitrile)palladium dichloride

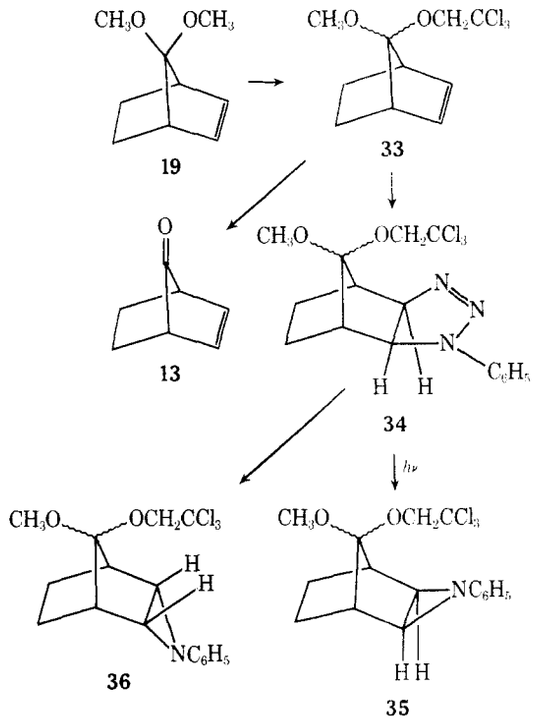


resulted in the immediate precipitation of an orange-red solid. Analysis of the remaining solution by vapor phase chromatography showed only the major isomer. Because of its low-lying d orbitals, sulfur is a much better ligand than is oxygen. Hence, it was assumed that the minor isomer, which formed the complex, had the sulfur syn to the double bond as shown in **28b** which should make **28b** a reasonable bidentate ligand. The major isomer would then possess structure **28a.** Because of the losses which would have occurred in separating the isomers, the mixture of **28a** and **28b** was used for subsequent steps. When **28** was treated with W-2 Raney nickel, a facile conversion of the oxathiolane to the ketone resulted. Unfortunately, this was accompanied by extensive reduction of the double bond to give **29** as the major product. In contrast, chloramine-T readily converted **28** back to **13.** Thus, it appeared that derivatives of **28** should serve as reasonable precursors of the desired system, **3.**

Azide addition to **28** was relatively slow and gave low yields of triazolines; *p*-nitrophenyl azide and phenyl azide added in 21 and 19% yields, respectively, even after days at 50–60 °C. NMR analysis indicated that both adducts had the stereochemistry shown in **30.** Irradiation of **30** (Ar = C_6H_5) gave an 80% yield of **31.** Pyrolysis of **30** (Ar = $C_6H_4NO_2$) gave a 20% yield of **32.** Whereas the NMR of **31** showed the aziridinyl hydrogens as a singlet at δ 2.4, the aziridinyl hydrogens of **32** appeared as a triplet at δ 3.1 (J = 1.8 Hz). These spectral data and analogy to the examples presented above established the stereochemistry as shown. Various attempts at converting **32** to the corresponding ketone were unsuccessful. This was surprising in view of the ease with which **28** had been converted into **13** and **29.**

The data presented thus far strongly support the contention that bulky substituents in the syn position at C-10 of the *exo*-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-enes promote the formation of endo aziridines on thermolysis. Obviously, the failure of **32** to yield the desired ketone was disconcerting. Therefore one additional approach was used in an attempt to reach our ultimate goal. This utilized the approach of Isador and Carlson,[25] which consists of protecting the carbonyl function as a mono-2,2,2-trichloroethyl ketal, followed by deketalization with activated zinc in tetrahydrofuran.

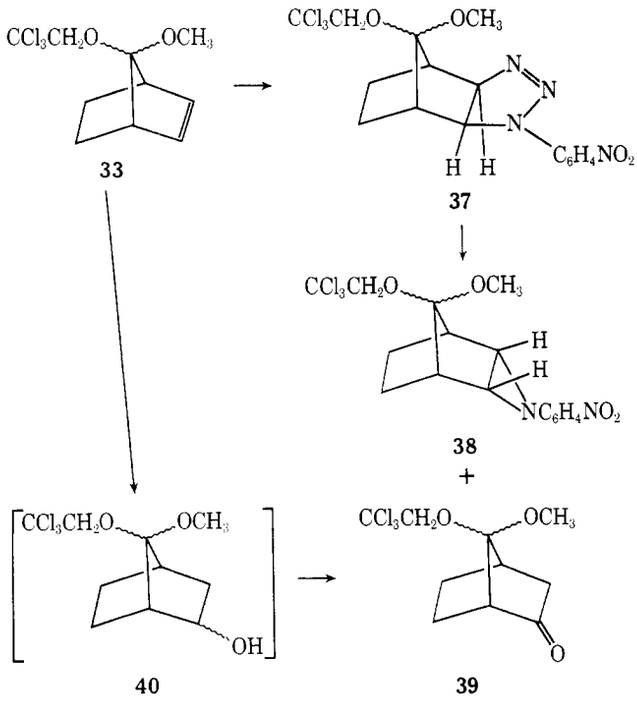
Treatment of **19** with 1.5 equiv of 2,2,2-trichloroethanol and a catalytic amount of *p*-toluenesulfonic acid gave an 82% yield of **33.** NMR spectral analysis indicated that **33** was a 1:1



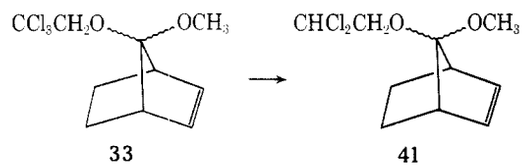
mixture of the two possible stereoisomers. In view of the difficulties encountered in the attempted deketalization of **32,** a thorough investigation of the deketalization of **33** was carried out. It was found that activated zinc dust,[26] precipitated zinc dust,[27] and zinc–copper couple[28] each quantitatively converted **33** back to **13.** These various forms of zinc required 8, 1.5, and 26 h, respectively, in order to afford a quantitative conversion.

Treatment of **33** with phenyl azide for 2 weeks at 50–60 °C gave a 71% yield of **34.** Photolysis of **34** gave **35** in 59% yield. Thermolysis of **34** gave 36% of **36.** Whereas the NMR spectrum of **35** showed the aziridinyl hydrogen as a singlet at δ 2.52, the NMR spectrum of **36** had the aziridinyl proton as a triplet (J = 2 Hz) at δ 2.80.[29] The addition of *p*-nitrophenyl azide to **33** gave 79% of the mixed ketal isomers of **37.** Thermolysis of **37** gave 19% of **38** and 63% of **39.** Presumably, **39** was formed from the corresponding *p*-nitroaniline-derived imine. The structure of **39** was established through comparison with an authentic sample prepared by the hydroboration–oxidation of **33** to give **40,** followed by direct oxidation of crude **40** to **39** with chromium trioxide–pyridine in methylene chloride (Collins reagent).

Numerous attempts at deketalization of **36** and **38** proved unsuccessful, in spite of the ease with which **33** had been converted to **13.** Activated zinc,[26] precipitated zinc,[27] and precipitated magnesium[27] all failed to deketalize **36** and/or **38.** In every case starting material was recovered unchanged. The failure of these deketalization reactions was not able to be easily rationalized. On the possibility that the metal might be complexing with the aziridine nitrogen, large excesses of metal were used. However, this was also ineffective. In an extreme test, refluxing of **38** in tetrahydrofuran with an excess of highly active precipitated zinc[27] failed to promote deketalization. In order to determine whether this resistance to deketalization was due to an abnormally high reduction potential for **36,** the half-wave potentials of **33** and **36** were



measured polarographically in 0.01 N tetra-*n*-butylammonium perchlorate in anhydrous dimethyl formamide at a dropping mercury electrode. The olefin **33** gave a value of −1.73 V, while the aziridine gave a slightly lower value of −1.53 V. Clearly, **36** should have deketalized more readily than **33**. Experimentally, this was obviously not the case! Preparative electrochemical reduction of **33** gave only **41**. This was



presumably due to a one-electron transfer to give a radical intermediate which abstracted hydrogen from the solvent. The dichloro derivative, **41**, was extremely resistant to further reduction. It had a half-wave potential of greater than −2.6 V under the conditions specified above.

In summary, we have developed useful routes to 8-substituted *exo*- and *endo*-3-aryl-3-azatricyclo[3.2.1.$0^{2,4}$]octanes. We are continuing to seek ways for the conversion of these interesting compounds into **3**.

Experimental Section[30]

7-*anti*-Hydroxybicyclo[2.2.1]hept-2-ene (7a). This alcohol was prepared stereospecifically in 9% overall yield (three steps) from bicyclo[2.2.1]hepta-2,5-diene by literature[31] methods, mp 110–113 °C [lit.[31] mp 117–118 °C]. Reduction of ketone **13** also afforded **7a** in 89% crude yield; low-temperature recrystallization from hexane afforded pure **7a**.

Phenyl Azide. A literature route[32] was used to prepare phenyl azide in 51% distilled yield, bp 44–47 °C (4 mm) [lit.[32] bp 49–50 °C (5 mm)].

5-Phenyl-10-*anti*-hydroxy-3,4,5-*exo*-triazatricyclo-[5.2.1.$0^{2,6}$]-dec-3-ene (8a). Using the literature method,[6b] **8a** was prepared in 59% yield. Three recrystallizations from benzene–chloroform gave **8a** as white crystals, mp 160.0–160.5 °C [lit.[6b] mp 187–188 °C]; spectra were identical with those published by Halton and Woolhouse[6b] [see preparation of **10a** (Ar = C_6H_5) for further comment on melting point differences].

Photolysis of 8a. Preparation of 3-Phenyl-8-*anti*-hydroxy-3-*exo*-azatricyclo[3.2.1.$0^{2,4}$]octane (10a, Ar = C_6H_5). Photolysis[6b] of crude **8a** gave **10a** (Ar = C_6H_5) in 47% yield after recrystallization. After two further recrystallizations, **10a** was obtained as fine, colorless needles, mp 121–122 °C [lit.[6b] mp 146–147 °C]. The 25–27 °C differences in melting point between the samples of **8a** and **10a** (Ar = C_6H_5) prepared here and those prepared previously must be due to inaccuracies in the melting point determinations of Halton and Woolhouse,[6b] since the compounds were both spectrally identical with the published data.

7-*anti*-Benzyloxybicyclo[2.2.1]hept-2-ene (7c).[33] A mixture of 2.7 g (24.5 mmol) of **7a** and 3.53 g (73.5 mmol) of 50% sodium hydride in mineral oil in 20 mL of anhydrous dimethyl formamide was allowed to stir for 3 h. Benzyl bromide (8.1 g, 49 mmol) was added carefully. After 1 h, 10 mL of additional dimethyl formamide was added to facilitate solution. Ether and methanol were then added and the mixture was extracted with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated. Distillation gave 4.55 g (93%) of **7c** as a colorless oil, bp 85 °C (0.15 mm).

7-*anti*-Acetoxybicyclo[2.2.1]hept-2-ene (7b).[34] Esterification of **7a** with acetic anhydride in pyridine afforded **7b** in 68% yield: bp 83 °C (20 mm); NMR ($CDCl_3$) δ 6.0 (2 H, t, J = 2 Hz), 4.6 (1 H, br s), 2.7 (2 H, m), 2.0 (3 H, s), 1.7 (2 H, m), 1.0 (2 H, m).

***p*-Nitrophenyl Azide.** In analogy to the procedure used for the preparation of *o*-nitrophenyl azide,[36] *p*-nitrophenyl azide was prepared from *p*-nitroaniline and sodium nitrite in 87% yield (after recrystallization), mp 69–70 °C [lit.[36] mp 70 °C].

5-(4-Nitrophenyl)-10-*anti*-benzyloxy-3,4,5-*exo*-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-ene (8c). A solution of 4.47 g (22 mmol) of **7c** and 3.85 g (23.5 mmol) of *p*-nitrophenyl azide in the minimum amount of carbon tetrachloride was allowed to stand in the dark for several days. Filtration then afforded 5.60 g (69%) of **8c** (Ar = $C_6H_4NO_2$) as a yellow solid. Recrystallization from chloroform–hexane gave an analytical sample: mp 180–182 °C dec; NMR (Me_2SO-d_6) δ 8.30 (2 H, d, J = 9 Hz), 7.48 (2 H, d, J = 9 Hz), 7.28 (5 H, s), 4.84 (1 H, d, J = 10 Hz), 4.40 (2 H, s), 4.03 (1 H, d, J = 10 Hz), 2.75 (2 H, m), 1.2–2.2 (4 H, m).

Anal. Calcd for $C_{20}H_{20}N_4O_3$: C, 65.92; H, 5.53; N, 15.37. Found: C, 65.83; H, 5.61; N, 15.41.

5-(4-Nitrophenyl)-10-*anti*-acetoxy-3,4,5-*exo*-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-ene (8b). A solution of 1.0 g (6.6 mmol) of **7b** and 1.13 g (6.9 mmol) of *p*-nitrophenyl azide in the minimum amount of carbon tetrachloride was allowed to stir in the dark. After 2 days, 0.46 g (22%) of **8b** was removed by filtration; after 2 weeks, the total yield was 0.77 g (59%). An analytical sample was obtained after two recrystallizations from cyclohexane–benzene: mp 185–186 °C dec; NMR (Me_2SO-d_6) δ 8.25 (2 H, d, J = 10 Hz), 7.50 (2 H, d, J = 10 Hz), 4.87 (1 H, d, J = 11 Hz), 4.23 (1 H, m), 4.08 (2 H, d, J = 11 Hz), 2.2–2.8 (2 H, m), 1.95 (3 H, s), 1.2–2.4 (4 H, m).

Anal. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 57.00; H, 5.06; N, 17.73.

Thermolysis of 8c. Preparation of 3-(4-Nitrophenyl)-8-*anti*-benzyloxy-3-*exo*-azatricyclo[3.2.1.$0^{2,4}$]octane (10c) and 7-*anti*-Benzyloxybicyclo[2.2.1]heptan-2-one (12). Triazoline **8c** (4.77 g, 13 mmol) was heated (neat) at 190 °C in a round-bottomed flask until nitrogen evolution was complete. The cooled residue was chromatographed on 200 g of neutral alumina with benzene–chloroform. Eluting first was a mixture of **10c** and **12**. Recrystallization from benzene–hexane gave 1.14 g (26%) of **10c** (Ar = $C_6H_4NO_2$) as yellow crystals. An analytical sample was obtained after two further recrystallizations: mp 148–149 °C; NMR ($CDCl_3$) δ 8.12 (2 H, d, J = 9 Hz), 7.37 (5 H, s), 6.97 (2 H, d, J = 9 Hz), 4.50 (2 H, s), 3.95 (1 H, m), 2.70 (2 H, m), 2.58 (2 H, s), 1.1–2.2 (4 H, m).

Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.50; H, 6.08; N, 8.17.

The oily residue from the above recrystallization (0.67 g, 24%) gave **12** as a yellow oil on distillation, bp 135–140 °C (0.75 mm). An analytical sample of **12** was prepared by preparative VPC (6 ft × 0.25 in. 10% SE-30 on 45/60 Chromosorb W column at 175 °C): NMR ($CDCl_3$) δ 7.37 (5 H, s), 4.56 (2 H, s), 3.94 (1 H, m), 2.67 (2 H, m), 1.3–2.4 (6 H, m).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.74; H, 7.46. Found: C, 77.61; H, 7.51.

p-Nitroaniline was also isolated.

Thermolysis of 8b. Preparation of 3-(4-Nitrophenyl)-8-*anti*-acetoxy-3-*exo*-azatricyclo[3.2.1.$0^{2,4}$]octane (10b). Triazoline **8b** (3.66 g, 11.6 mmol) was heated (neat) at 190–200 °C in a round-bottomed flask until nitrogen evolution had begun to subside. The flask was then immediately cooled in order to minimize decomposition. Chromatography of the residue on 200 g of neutral alumina with benzene–chloroform gave **10b** (Ar = $C_6H_4NO_2$) as a yellow solid in a very minor first fraction (~100 mg). Later fractions yielded *p*-nitroaniline and an oily mixture. Preparative VPC of this oil gave no identifiable compounds. Aziridine **10b** was recrystallized from hexane (with Norit) to give yellow needles. An analytical sample was obtained after two further recrystallizations: mp 120–122 °C; NMR ($CDCl_3$)

δ 8.10 (2 H, d, J = 9 Hz), 6.95 (2 H, d, J = 9 Hz), 4.9 (1 H, br s), 2.8 (2 H, br s), 2.60 (2 H, s), 2.10 (3 H, s), 0.7–2.0 (4 H, m).

Anal. Calcd[37] *m/e* for $C_{15}H_{16}N_2O_4$: 288.1110. Found: 288.1110.

Bicyclo[2.2.1]hept-2-en-7-one (13). This ketone was prepared according to the literature method[14] from hexachlorocyclopentadiene in 31% overall yield (four steps), bp 95–99 °C (115 mm) [lit.[14] bp 96–100 °C (115 mm)]. Distillation of **13** was simplified if prior workup included washing with 10% sodium bicarbonate solution.

5-(4-Nitrophenyl)-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-en-10-one (14b). A mixture of 8.4 g (78 mmol) of **13** and 13.3 g (82 mmol) of *p*-nitrophenyl azide in 20 mL of methylene chloride was refluxed in the dark for 30 min. Cooling and filtration followed by recrystallization from acetone gave 8.7 g (41%) of **14b** as a yellow solid. Further recrystallizations gave an analytical sample: mp 178–179 °C dec; an NMR spectrum was not obtained due to low solubility of **14b**, but assignment of the *exo*-triazoline ring can be made by analogy with **14a** (below).

Anal. Calcd for $C_{13}H_{12}N_4O_3$: C, 57.35; H, 4.44; N, 20.55. Found: C, 57.27; H, 4.45; N, 20.61.

5-Phenyl-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-en-10-one (14a). A solution of 1.0 g (9.3 mmol) of **13** and 1.1 g (9.3 mmol) of phenyl azide was stirred in the dark at 50–60 °C for 2 days. The solution was then cooled and filtered. Recrystallization of the resulting solid from hexane–chloroform gave 1.04 g (50%) of **14a.** A dark brown residue (0.75 g) remained. An analytical sample was obtained through further recrystallization as a colorless solid: mp 159–160 °C dec; NMR ($CDCl_3$) δ 6.8–7.6 (5 H, m), 5.0 (1 H, d, J = 12 Hz), 4.2 (1 H, d, J = 12 Hz), 2.4–2.7 (2 H, m), 1.5–2.4 (4 H, m).

Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.71; H, 5.77; N, 18.48. Found: C, 68.71; H, 5.91; N, 18.26.

Photolysis of 14b. Preparation of 3-(4-Nitrophenyl)-3-*exo*-azatricyclo[3.2.1.0^{2,4}]octan-8-one (15b). A solution of 1.0 g (3.7 mmol) of triazoline **14b** in 350 mL of reagent grade acetone was irradiated for 2 h with a 450 W Hanovia lamp (Pyrex filter). Removal of the solvent by rotary evaporation gave an oily brown solid. Chromatography of this residue on 200 g of neutral alumina with chloroform gave 300 mg (18%) of **15b.** Recrystallization from hexane–chloroform gave an analytical sample: mp 144–145 °C; NMR ($CDCl_3$) δ 8.0 (2 H, d, J = 10 Hz), 6.9 (2 H, d, J = 10 Hz), 2.9 (2 H, s), 2.6 (2 H, s), 1.8 (4 H, s).

Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.76; H, 4.96; N, 11.49.

Photolysis of 14a. Preparation of 3-Phenyl-3-*exo*-azatricyclo[3.2.1.0^{2,4}]octane-8-one (15a). A solution of 3.5 g (15 mmol) of triazoline **14a** in 300 mL of reagent grade acetone was irradiated for 5 h with a 450 W Hanovia lamp (Pyrex filter). The solvent was removed by rotary evaporation to give a brown solid. Chromatography on 70 g of neutral alumina with benzene–chloroform gave 1.95 g (64%) of **15a** as a colorless solid. Two recrystallizations from hexane gave an analytical sample: mp 114.5–115.5 °C; NMR ($CDCl_3$) δ 6.9–7.4 (5 H, m), 2.82 (2 H, s), 2.57 (2 H, s), 1.80 (4 H, s).

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.67; H, 6.76; N, 6.75.

7-*syn*-Hydroxybicyclo[2.2.1]hept-2-ene (16). This alcohol was prepared stereospecifically in 28% overall yield (two steps) from bicyclo[2.2.1]hept-2-ene by the literature method.[18] The crude alcohol (83% pure by VPC[18]) was used in further synthetic work.

5-(4-Nitrophenyl)-10-*syn*-hydroxy-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene (17). Crude **16** (3 g, 3 mmol) and 5 g (3 mmol) of *p*-nitrophenyl azide were dissolved in 75 mL of carbon tetrachloride and allowed to stand in the dark at room temperature for several days. Filtration afforded 2.0 g (30%) of **17** as a bright yellow solid. An analytical sample was obtained after recrystallization from ethyl acetate: mp 167–168 °C dec; IR (potassium bromide) 3500, 2940, 1595, 1505, 1490, 1390, 1320, 1180, 1130, 1110, 1085, 990, 930, 905, 850, 750 cm^{-1}; although an NMR spectrum was not obtained due to the extremely low solubility of **17**, structural assignment as exo is based on analogy with other triazolines of this study.

Anal. Calcd for $C_{13}H_{14}N_4O_3$: C, 56.93; H, 5.14; N, 20.43. Found: C, 56.85; H, 5.20; N, 20.33.

Thermolysis of 17. Preparation of 3-(4-Nitrophenyl)-8-*syn*-hydroxy-3-*exo*-azatricyclo[3.2.1.0^{2,4}]octane (18b). Triazoline **17** (150 mg, 0.55 mmol) was heated in a test tube immersed in an oil bath at 200 °C until nitrogen evolution had ceased. The cooled residue was subjected to preparative TLC on alumina with benzene–chloroform to give 40 mg (30%) of **18** as a yellow solid, identified by spectral comparison with material produced by an alternate route (see sodium borohydride reduction of **15b**).

Reduction of 15b. Preparation of 3-(4-Nitrophenyl)-8-*syn*-hydroxy-3-*exo*-azatricyclo[3.2.1.0^{2,4}]octane (18b, Ar = $C_6H_4NO_2$). To a stirring solution of 102.7 mg (2.70 mmol) of sodium borohydride in 3 mL of absolute ethanol at 0 °C under nitrogen was added a suspension of 159.4 mg (0.65 mmol) of ketone **15b** in 30 mL of absolute ethanol. The ice bath was then removed and the solution was stirred for 5 h at room temperature. Removal of solvent by rotary evaporation gave a brownish-green solid. The solid was dissolved in 30 mL of water and 30 mL of ether. The layers were separated and the aqueous layer was extracted with 15 mL of ether. The combined organic layers were extracted with 15 mL of brine and dried over $MgSO_4$. Filtration and evaporation gave 131.1 mg (82%) of **18b** as bright yellow crystals. Recrystallization from benzene–hexane gave an analytical sample: mp 149–151 °C; NMR ($CDCl_3$) δ 8.1 (2 H, d, J = 10 Hz), 7.1 (2 H, d, J = 10 Hz), 4.8 (1 H, d, J = 12 Hz), 3.7 (1 H, d, J = 12 Hz), 2.9 (2 H, s), 2.6 (2 H, s), 0.6–1.9 (4 H, m). Addition of deuterium oxide to the NMR sample caused the δ 4.8 peak to disappear and the δ 3.7 peak to collapse to a singlet.

Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73. Found: C, 63.46; H, 5.64.

Reduction of 15a. Preparation of 3-Phenyl-8-*syn*-hydroxy-3-*exo*-azatricyclo[3.2.1.0^{2,4}]octane (18a). To a stirring suspension of 1.21 g (31.9 mmol) of sodium borohydride in 10 mL of absolute ethanol at 0 °C under nitrogen was added in one portion a suspension of 1.53 g (7.7 mmol) of ketone **15a** in 140 mL of absolute ethanol. The ice bath was then removed and the solution was stirred for 4 h at room temperature. The solvent was then removed by rotary evaporation to yield a white solid. The solid was dissolved in 100 mL of ether and 100 mL of water. The layers were separated and the aqueous layer was extracted twice with 50-mL portions of ether. The combined ether layers were extracted with brine (50 mL) and dried over $MgSO_4$. Filtration and evaporation gave a slightly yellow solid. Recrystallization from hexane (Norit added) gave 1.10 g (71%) of **18a** as a white solid. Three further recrystallizations gave an analytical sample: mp 85–86 °C; NMR ($CDCl_3$) δ 6.9–7.5 (5 H, m), 5.7 (1 H, br s), 3.7 (1 H, br s), 2.77 (2 H, s), 2.60 (2 H, s), 1.1–1.9 (4 H, m).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.70; H, 7.44; N, 6.98.

Procedure Used in Lanthanide Shift Reagent (LSR) Determination of Structure. A 0.6 M solution of purified substrate was made up by dissolving the necessary amount of the substrate in 0.25 mL of deuteriochloroform (containing 1% tetramethylsilane) in an NMR tube. An [LSR]/[substrate] ratio of 0.4 was obtained by adding 62.2 mg (0.06 mmol) of europium tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) (Eu(fod)$_3$). The spectrum was then recorded. Aliquots of a stock solution 0.6 M in the substrate (same solvent) were then added and the spectrum was rerun. In this way, the [LSR]/[substrate] ratio was varied from 0.4 to 0.13 while [substrate] remained constant at 0.6 M. For each set of protons in the substrate, a plot of the chemical shift vs. the [LRS]/[substrate] ratio was analyzed by the least-squares method[38] to yield the values listed in the text of this paper.

7,7-Dimethoxybicyclo[2.2.1]hept-2-ene (19). Preparation of **19** was carried out in 36% overall yield (three steps) from hexachlorocyclopentadiene according to the literature procedure,[19] bp 72–76 °C (24 mm) [lit.[19] bp 58–68 °C (17 mm)].

5-(4-Nitrophenyl)-10,10-dimethoxy-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene (20b). A mixture of 12.0 g (78 mmol) of **19** and 13.4 g (81 mmol) of *p*-nitrophenyl azide in the minimum amount of carbon tetrachloride was allowed to stand in the dark for 10 days. Filtration and recrystallization from acetone gave 15.4 g (65%) of **20b.** Further recrystallizations gave an analytical sample: mp 158–160 °C dec; NMR ($CDCl_3$) δ 8.5 (2 H, d, J = 10 Hz), 7.4 (2 H, d, J = 10 Hz), 4.9 (1 H, d, J = 10 Hz), 3.9 (1 H, d, J = 10 Hz), 3.2 (3 H, s), 3.0 (3 H, s), 2.8 (2 H, m), 1.5–2.2 (2 H, m).

Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.71; N, 17.60. Found: C, 56.58; H, 5.68; N, 17.63.

5-Phenyl-10,10-dimethoxy-3,4,5-*exo*-triazatricyclo-[5.2.1.0^{2,6}]dec-3-ene (20a). A mixture of 1.0 g (6.49 mmol) of **19** and 0.77 g (6.5 mmol) of phenyl azide in carbon tetrachloride was heated on a steam bath for 2 h. Upon cooling, crystallization occurred. Filtration and recrystallization from hexane–chloroform gave 1.02 g (58%) of **20a.** Further recrystallizations gave an analytical sample: mp 153–155 °C dec; NMR ($CDCl_3$) 7.3 (5 H, m), 4.6 (1 H, d, J = 10 Hz), 3.8 (1 H, d, J = 10 Hz), 3.2 (3 H, s), 3.0 (3 H, s), 2.8 (1 H, m), 2.6 (1 H, m), 1.0–2.2 (4 H, m).

Anal. Calcd for $C_{15}H_{19}N_3O_2$: C, 65.91; H, 7.01; N, 15.37. Found: C, 65.88; H, 7.01; N, 15.42.

Photolysis of 20a. Preparation of 3-Phenyl-8,8-dimethoxy-3-*exo*-azatricyclo[3.2.1.0^{2,4}]octane (21a). A solution of 700 mg (2.6 mmol) of **20a** in 250 mL of reagent grade acetone was irradiated with a 450 W Hanovia lamp (Pyrex filter) for 2.5 h. Removal of solvent by

rotary evaporation gave a reddish-brown solid. After recrystallization from hexane (with Norit), 0.48 g (76%) of **21a** was obtained as colorless needles. Further recrystallizations gave an analytical sample: mp 91–92 °C; NMR ($CDCl_3$) δ 6.7–7.3 (5 H, m), 3.5 (6 H, 2s), 2.5 (m), and 2.4 (s) (4 H together), 1.1–2.0 (4 H, m).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.50; H, 7.76; N, 5.65.

Thermolysis of 20b. Preparation of 3-(4-Nitrophenyl)-10,10-dimethoxy-3-*endo*-azatricyclo[3.2.1.0^{2,4}]octane (22b) and 7,7-Dimethoxybicyclo[2.2.1]heptan-2-one (23). A small, round-bottomed flask containing 5.1 g (16 mmol) of **20b** was placed in an oil bath at 180–190 °C. As the solid melted, nitrogen was rapidly given off. Immediately following cessation of gas evolution, the flask was cooled and the residue was chromatographed on 200 g of neutral alumina with benzene–chloroform, followed by ethyl acetate. Three fractions were obtained: (1) 1.0 g (22%) of **22b** as a yellow solid; (2) 1.44 g (53%) of **23** (identified by spectral comparisons with authentic material[39]), and (3) 1.37 g of a relatively insoluble solid, consisting primarily of *p*-nitroaniline. Recrystallization of **22b** from hexane gave an analytical sample: mp 148–150 °C; NMR ($CDCl_3$) δ 8.1 (2 H, d, J = 10 Hz), 6.9 (2 H, d, J = 10 Hz), 3.30 and 3.25 (6 H, 2s), 2.9 (2 H, t, J = 2 Hz), 2.4 (2 H, m), 1.6 (4 H, m).

Anal. Calcd for $C_{15}H_{18}N_2O_4$: C, 62.06; H, 6.25; N, 9.65. Found: C, 61.95; H, 6.34; N, 9.66.

Thermolysis of **20b** was also carried out by heating a solution of **20b** in decalin at 180 °C. After removal of decalin by vacuum distillation [60 °C (7 mm)], preparative TLC gave a product distribution similar to that described above.

Bicyclo[2.2.1]hept-2-ene-7-spiro-2′,5′-dioxolane (25). Spiroketal **25** was prepared in 68% yield from **13** according to the method of Gassman and Macmillan,[21] bp 110 °C (25 mm) [lit.[21] bp 122–125 °C (76 mm)].

5-(4-Nitrophenyl)-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene-10-spiro-2′,5′-dioxolane (26). A mixture of 2.2 g (13 mmol) of **25** and 2.16 g (13.2 mmol) of *p*-nitrophenyl azide in 10 mL of carbon tetrachloride was stirred at 50–60 °C in the dark for 1 day. Upon cooling, filtration afforded 3.23 g (79%) of **26** as a yellow solid. Recrystallization from benzene gave an analytical sample: mp 164–166 °C dec; NMR ($CDCl_3$) δ 8.2 (2 H, d, J = 10 Hz), 7.2 (2 H, d, J = 10 Hz), 4.8 (1 H, d, J = 10 Hz), 3.6–4.0 (5 H, overlapping d and 2s), 1.2–2.6 (6 H, m).

Anal. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 57.16; H, 5.16; N, 17.69.

Thermolysis of 26. Preparation of 3-(4-Nitrophenyl)-3-*endo*-azatricyclo[3.2.1.0^{2,4}]octane-8-spiro-2′,5′-dioxolane (27). A 1.7-g (5.4 mmol) portion of **26** in a small, round-bottomed flask was heated at 190–200 °C until nitrogen evolution had ceased. The flask was then cooled and the residue was chromatographed on 40 g of neutral alumina with benzene–chloroform to yield 330 mg (21%) of **27** as a yellow solid. Recrystallizations from hexane–chloroform gave an analytical sample: mp 163.5–165.5 °C; NMR ($CDCl_3$) δ 8.0 (2 H, d, J = 9 Hz), 6.8 (2 H, d, J = 9 Hz), 3.9 (4 H, s), 2.9 (2 H, t, J = 2 Hz), 2.1 (2 H, m), 1.5 (4 H, m).

Anal. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.87; H, 5.80; N, 9.43.

Bicyclo[2.2.1]hept-2-ene-7-spiro- 2′,5′- oxathiolane (28). Following the literature procedure,[22] 7.8 g (74 mmol) of the ketone **13**, 8.6 g (111 mmol) of 2-mercaptoethanol, 15 g of freshly fused zinc chloride, and 15.8 g of anhydrous sodium sulfate yielded 6.0 g (50%) of **28**, bp 60–62 °C (0.3 mm). The 3:1 mixture of epimers was separated by preparative VPC (6 ft × 0.25 in. 10% DC 200 on 60/80 Chromosorb W column at 100 °C). For the major isomer, the following spectral data were recorded: NMR ($CDCl_3$) δ 6.2 (2 H, t, J = 2 Hz), 4.13 (2 H, t, J = 5 Hz), 2.92 (2 H, t, J = 5 Hz), 2.8 (2 H, m), 2.0 (2 H, m), 1.1 (2 H, m). For the minor isomer, the δ 4.13 and 2.92 peaks were shifted to δ 4.00 and 3.00.

Anal. Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19. Found: C, 64.04; H, 7.32.

Addition of 300 mg of **28** to 680 mg of bis(benzonitrile)palladium dichloride in 200 mL of benzene gave an immediate precipitation of a red-orange solid. Filtration and concentration of the remaining solution gave a residue which showed only the major isomer on GLC analysis (column described above). The major isomer was thus identified as **28a**. An attempt was made to recover **28b** by refluxing the precipitate in 70 mL of anhydrous ether with 200 mg of potassium cyanide for several days. Cooling of the solution followed by filtration and concentration failed to yield **28b**.

5-(4-Nitrophenyl)-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene-10-spiro-2′,5′-oxathiolane (30, Ar = $C_6H_4NO_2$). A mixture of 2.0 g (11.9 mmol) of **28** and 1.95 g (11.9 mmol) of *p*-nitrophenyl azide in carbon tetrachloride was heated at 50–60 °C in the dark for 15 days. Cooling and filtration gave 0.83 g (21%) of **30**.[40] Recrystallizations from hexane–chloroform gave an analytical sample: mp 166–168 °C dec; NMR ($CDCl_3$) δ 8.12 (2 H, d, J = 10 Hz), 7.2 (2 H, d, J = 10 Hz), 4.8 (1 H, d, J = 10 Hz), 3.9 (3 H, m), 2.8 (3 H, m), 2.5 (1 H, m), 1.1–2.3 (4 H, m).

Anal. Calcd for $C_{15}H_{16}N_4O_3S$: C, 54.21; H, 4.85; N, 16.86. Found: C, 54.42; H, 5.06; N, 16.67.

5-Phenyl-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene-10-spiro-2′,5′-oxathiolane (30, Ar = C_6H_5). A mixture of 2.0 g (11.9 mmol) of **28** and 1.42 g (11.9 mmol) of phenyl azide was stirred at 50–60 °C in the dark for 3 days. Trituration of the cooled solution with hexane gave 410 mg (19%) of **30**.[40] Recrystallizations from hexane–chloroform gave an analytical sample: mp 119–121 °C; NMR ($CDCl_3$) δ 7.3 (5 H, m), 4.7 (1 H, d, J = 11 Hz), 3.9 (3 H, d and t), 2.8–3.0 (4 H, m), 1.3–2.4 (4 H, m).

Anal. Calcd for $C_{15}H_{17}N_3OS$: C, 62.69; H, 5.96; N, 14.62. Found: C, 62.85; H, 6.00; N, 14.55.

Photolysis of 30 (Ar = C_6H_5). Preparation of 3-Phenyl-3-*exo*-azatricyclo[3.2.1.0^{2,4}]octene-8-spiro-2′,5′-oxathiolane (31, Ar = C_6H_5). A solution of 750 mg (2.6 mmol) of **30** in 300 mL of reagent grade acetone was irradiated with a 450 W Hanovia lamp (Pyrex filter) for 0.75 h. After removal of solvent by rotary evaporation, the residue was chromatographed on 40 g of neutral alumina with benzene–chloroform to give 540 mg (80%) of **31**.[40] Recrystallizations from hexane gave an analytical sample: mp 138–139 °C; NMR ($CDCl_3$) δ 6.7–7.4 (5 H, m), 3.9 (2 H, t, J = 6 Hz), 2.7 (2 H, t, J = 6 Hz), 2.4 (4 H, s in m), 1.2–2.1 (4 H, m).

Anal. Calcd for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40. Found: C, 69.29; H, 6.61; N, 5.40.

Thermolysis of 30 (Ar = $C_6H_4NO_2$). Preparation of 3-(4-Nitrophenyl)-3-*endo*-azatricyclo[3.2.1.0^{2,4}]octane-8-spiro-2′,5′-oxathiolane (32, Ar = $C_6H_4NO_2$). Careful heating of 4.1 g (12.3 mmol) of **30** (in small portions) at 190 °C followed by immediate cooling gave a dark residue. Chromatography on 215 g of neutral alumina with benzene–chloroform gave as the first fraction 1.31 g of a mixture of **32** and the isomeric imine.[41] Trituration of this mixture with hexane gave 750 mg (20%) of **32** (Ar = $C_6H_4NO_2$) as pale yellow crystals. Recrystallizations from hexane gave an analytical sample: mp 205–206 °C; NMR ($CDCl_3$) δ 8.0 (2 H, d, J = 10 Hz), 6.9 (2 H, d, J = 10 Hz), 4.1 (2 H, t, J = 6 Hz), 3.1 (4 H, m), 2.4 (2 H, m), 1.6 (4 H, s). The multiplet at δ 3.1 was resolved into two triplets (J = 6 and 1.8 Hz) by the addition of $Eu(fod)_3$ and by analysis on a 270 MHz NMR.

Anal. Calcd for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.20. Found: C, 59.04; H, 5.27; N, 9.11.

Reaction of 28 with Raney Nickel. Treatment of 500 mg of **28** with 2.25 teaspoonfuls of Raney nickel in acetone was carried out by standard procedures. After the solvents were removed by distillation (to avoid volatile loss of the expected product, **13**), GLC analysis (on a 6 ft × 0.25 in. 10% DC 200 on 60/80 Chromosorb W column at 110 °C) showed only traces of **13**; the major product was **29**.[42]

Treatment of 400 mg of **28** with 6 g of W-2 Raney nickel in 100 mL of benzene at reflux for 19 h followed by cooling, filtration, and careful rotary evaporation at room temperature gave 320 mg of a yellow oil, identified by GLC analysis as **29**.

Reaction of 28 with Chloramine-T. Reaction of 200 mg (1.2 mmol) of **28** with 330 mg (1.2 mmol) of chloramine-T gave only **13** (the expected product) by GLC analysis on a 15% OV-101 on Chromosorb G column at 45 °C (comparison with authentic **13**).

Attempted Deketalization of 32 (Ar = $C_6H_4NO_2$). Reaction of **32** with W-2 Raney nickel in acetone followed by chromatography on alumina with benzene–chloroform gave a brown solid identified as the product of nitro group reduction to the amine: the $-OCH_2CH_2S-$ group was still evident in the NMR spectrum, while the aryl region had collapsed to a narrowly separated AB quartet. Further reaction of this brown solid with W-2 Raney nickel in refluxing benzene for 18 h led to complete material loss.

A 130-mg portion of **32** (Ar = $C_6H_4NO_2$) in 6 mL of dimethyl formamide (to enhance solubility) was reacted with 363 mg of chloramine-T in 5 mL of 85% methanol–water. The reaction mixture was first stirred at room temperature and then briefly warmed to 70 °C. After cooling, the reaction mixture was worked up as described above for the deketalization of **28**. Preparative TLC on alumina with benzene gave less than 20 mg of a solid. Due to the low yield, characterization was not completed.

7-(2,2,2-Trichloroethoxy)-7-methoxybicyclo[2.2.1]hept-2-ene (33). Ketal **19** (35.0 g, 0.23 mol), 50.9 g (0.34 mol) of 2,2,2-trichloroethanol (distilled), and 1.0 g of *p*-toluenesulfonic acid were heated in benzene in a flask equipped with a Dean–Stark trap. After ~250

mL of benzene had been removed (2 h), the hydroxyl absorption of the azeotroped benzene reached a minimum (by IR analysis). The solution was then cooled and solid sodium carbonate was added. The solution was stirred for 0.5 h at room temperature and then filtered, concentrated via rotary evaporation, and fractionally distilled to yield 50.5 g (82%) of **33** as a pale yellow oil, bp 88–92 °C (0.1 mm). Ketal **33** appeared as a single peak on several GLC columns. An analytical sample was prepared by preparative VPC on a 6 ft × 0.25 in. 5% FFAP on potassium hydroxide washed Chromosorb P column at 145 °C: NMR ($CDCl_3$) δ 6.2 (2 H, m), 4.1 and 4.0 (2 H, 2s), 3.3 and 3.4 (3 H, 2s), 2.9 (2 H, m), 1.6–2.3 (2 H, m), 0.8–1.6 (2 H, m). NMR integration of the pairs of singlets at δ 4.1–4.0 as well as δ 3.3 and 3.4 indicated a syn/anti ratio of nearly 1:1.

Anal. Calcd for $C_{10}H_{13}Cl_3O_2$: C, 44.23; H, 4.79. Found: C, 44.56; H, 4.93.

Metal-Promoted Deketalizations of 33. (a) A 1.0-g portion of **33** was refluxed in 20 mL of tetrahydrofuran with 2.0 g of acid-activated[26] zinc dust. Monitoring of the reaction by TLC showed that complete disappearance of **33** required 8 h. At this point, the reaction mixture was cooled and 20 mL of ether was added. The resulting solution was then filtered, washed with two 20-mL portions of 1% hydrochloric acid, two 20-mL portions of 5% sodium bicarbonate, and 10 mL of brine, and then dried over anhydrous magnesium sulfate. Filtration and removal of solvent by distillation at atmospheric pressure gave a residue containing the expected bicyclo[2.2.1]hept-2-en-7-one (**13**) (identified by GLC and NMR comparisons with authentic material).

(b) Into a 25-mL, side-armed flask equipped with a rubber septum and reflux condenser was placed 480 mg (2.1 mmol) of zinc bromide [dried for 18 h at 150 °C (0.25 mm)]. The flask was then flushed with nitrogen and 2 mL of tetrahydrofuran (distilled from lithium aluminum hydride) was added. Potassium (160 mg) was then added to the stirred solution. The solution eventually became black as the temperature was raised to reflux and maintained for 4 h.[27] A solution of 500 mg (1.84 mmol) of **33** in 2 mL of tetrahydrofuran was injected into the flask at this point via syringe. The progress of the reaction was followed by GLC; formation of **13** was essentially complete after 1.5 h.

(c) Reaction of 1.0 g (3.7 mmol) of **33** with 2.0 g of zinc–copper couple[28] in refluxing tetrahydrofuran was followed by GLC analysis. The rate of the reaction was less than with zinc but appeared to be complete after 26 h. Workup analogous to that described for the acid-activated zinc gave **13** (identified by GLC and NMR comparisons with authentic material).

(d) Into a 50-mL, side-armed flask equipped with a rubber septum and reflux condenser was placed 1 g of sodium in small pieces and 10 mL of tetrahydrofuran (distilled from lithium aluminum hydride). The flask was flushed with nitrogen and cooled to ca. −25 °C. A solution of 1.0 g of **33** was added slowly. The solution was maintained at −25 °C for 1 h and then allowed to warm to room temperature. After several hours, the solution was filtered and worked up as described above. NMR analysis showed only **33.** This procedure was repeated with a brief period of reflux: extensive solvent breakdown occurred and no product could be isolated.

(e) The procedure used for the reaction of acid-activated zinc with **33** was followed using highly active magnesium powder.[27] Thus, 500 mg of **33** and 1 g of magnesium powder after reflux for 18 h in tetrahydrofuran gave 610 mg of a dark oil. NMR analysis indicated the presence of **33** (and the absence of **13**).

(f) Treatment of 400 mg of **33** with 800 mg of copper powder in refluxing tetrahydrofuran resulted in no formation of **13** as indicated by GLC analysis.

5-Phenyl-10-(2,2,2-trichloroethoxy)-10-methoxy-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene (34). A mixture of 15 g (55 mmol) of **33** and 7.9 g (66 mmol) of phenyl azide in carbon tetrachloride was heated at 50–60 °C in the dark for 2 weeks. The solution was then diluted with hexane and stored in the freezer for several days. Filtration afforded 15.3 g (71%) of crude **34**.[40] Recrystallizations from hexane gave relatively pure **34**: mp 140–141 °C dec; NMR ($CDCl_3$) δ 7.25 (5 H, br s), 4.65 (1 H, d, J = 11 Hz), 3.8 (3 H, s and d), 3.1 (3 H, s), 2.9 (1 H, m), 2.6 (1 H, m), 1.4–2.1 (4 H, m). Despite two attempts, acceptable elemental analyses were not obtained. However, the *p*-nitrophenyl azide adduct did analyze satisfactorily (vide post).

Photolysis of 34. Preparation of 3-Phenyl-8-(2,2,2-trichloroethoxy)-8-methoxy-3-*exo*-azatricyclo[3.2.1.0^{2,4}]octane (35). A solution of 1.7 g (4.3 mmol) of **34** in 350 mL of reagent grade acetone was irradiated with a 450 W Hanovia lamp (Pyrex filter) for several hours. Removal of solvent via rotary evaporation followed by purification of the crude **35** by passage through a 6 in. column of alumina with hexane and recrystallization from hexane gave 0.94 g (59%) of **35** as colorless crystals. Further recrystallizations from hexane gave an analytical sample: mp 93–95 °C; NMR ($CDCl_3$) δ 6.8–7.4 (5 H, m), 4.16 (2 H, s), 3.37 (3 H, s), 2.6 (2 H, m), 2.52 (2 H, s), 2.0 (2 H, m), 1.3 (2 H, m).

Anal. Calcd for $C_{16}H_{18}Cl_3NO_2$: C, 52.99; H, 5.00; N, 3.86. Found: C, 53.07; H, 5.07; N, 4.09.

Thermolysis of 34. Preparation of 3-Phenyl-8-(2,2,2-trichloroethoxy)-8-methoxy-3-*endo*-azatricyclo[3.2.1.0^{2,4}]octane (36). A 1.6-g (4.1 mmol) portion of **34** was added to a stirred flask of decalin at 190 °C. Nitrogen evolution lasted ca. 0.5 h. After 45 min, the solution was cooled and the decalin was removed by vacuum distillation [45 °C (1 mm)]. Chromatography of the residue on 75 g of neutral alumina with benzene–hexane gave 0.53 g (36%) of **36** as a colorless solid after recrystallization from hexane. Further recrystallizations from hexane gave an analytical sample: mp 100.0–100.5 °C; NMR ($CDCl_3$) δ 6.7–7.4 (5 H, m), 4.02 (2 H, s), 3.38 (3 H, s), 2.80 (2 H, t, J = 2 Hz), 2.5 (2 H, m), 1.68 (4 H, br s).

Anal. Calcd for $C_{16}H_{18}Cl_3NO_2$: C, 52.99; H, 5.00; N, 3.86. Found: C, 53.12; H, 5.04; N, 3.92.

5-(4-Nitrophenyl)-10-(2,2,2-trichloroethoxy)-10-methoxy-3,4,5-*exo*-triazatricyclo[5.2.1.0^{2,6}]dec-3-ene (37). A mixture of 25 g (92 mmol) of **33** and 15.1 g (92 mmol) of *p*-nitrophenyl azide in the minimum amount of carbon tetrachloride was allowed to stand in the dark for 11 days. Filtration gave 15.85 g (40%) of **37.** The filtrate was then allowed to stand for 3 months in the dark to afford 15.76 g of additional **37** (total yield 31.6 g, 79%).[40] Recrystallization from chloroform–hexane gave an analytical sample: mp 195–196 °C dec; NMR (Me_2SO-d_6) δ 8.3 (2 H, d, J = 9 Hz), 7.5 (2 H, d, J = 9 Hz), 4.9 (1 H, d, J = 11 Hz), 4.1 (1 H, d, J = 11 Hz), 3.9 (2 H, s), 3.4 (3 H, s), 2.9 (1 H, m), 2.7 (1 H, m), 1.2–2.0 (4 H, m).

Anal. Calcd for $C_{16}H_{17}Cl_3N_4O_4$: C, 44.11; H, 3.93; N, 12.86. Found: C, 43.88; H, 3.97; N, 12.90.

Thermolysis of 37. Preparation of 3-(4-Nitrophenyl)-8-(2,2,2-trichloroethoxy)-8-methoxy-3-*endo*-azatricyclo-[3.2.1.0^{2,4}]octane (38) and 7-(2,2,2-Trichloroethoxy)-7-methoxybicyclo[2.2.1]heptan-2-one (39). Thermolysis of 5.76 g (13 mmol) of **37** (neat) in several portions at 195–200 °C followed by cooling and chromatography of the combined residues on 400 g of neutral alumina with benzene–chloroform gave four major fractions: (1) 1.02 g (19%) of the endo aziridine, **38,** as a yellow solid; (2) 0.65 g of a mixture of **38** and **39** (predominately the latter); (3) 1.9 g (63%) of **39;** and (4) 1.63 g of insoluble material containing *p*-nitroaniline.

An analytical sample of **38** was obtained after recrystallization from hexane: mp 174–175 °C; NMR ($CDCl_3$) δ 8.1 (2 H, d, J = 10 Hz), 6.9 (2 H, d, J = 10 Hz), 4.1 (2 H, s), 3.4 (3 H, s), 3.0 (2 H, t, J = 2 Hz), 2.5 (2 H, m), 1.6 (4 H, m).

Anal. Calcd for $C_{16}H_{17}Cl_3N_2O_4$: C, 47.14; H, 4.20; N, 6.87. Found: C, 47.31; H, 4.28; N, 6.84.

Vacuum transfer of the crude **39** gave a thick oil which solidified upon cooling. An analytical sample was prepared by recrystallization from hexane: mp 69.5–70.5 °C; NMR ($CDCl_3$) δ 4.1 (2 H, AB quartet), 3.4 (3 H, s), 2.7 (2 H, m), 1.4–2.7 (6 H, m).

Anal. Calcd for $C_{10}H_{13}Cl_3O_3$: C, 41.77; H, 4.56. Found: C, 41.96; H, 4.62.

Preparation of 7-(2,2,2-Trichloroethoxy)-7-methoxybicyclo[2.2.1]heptan-2-one (39) from 7-(2,2,2-Trichloroethoxy)-7-methoxybicyclo[2.2.1]hept-2-ene (33). A solution of 3.0 g (11 mmol) of **33** in 75 mL of tetrahydrofuran (distilled from lithium aluminum hydride) was brought to 0 °C under an argon atmosphere in a flask equipped with a rubber septum. An excess of 1.0 M diborane in tetrahydrofuran was added via syringe. After stirring several hours at 0 °C, 5 mL of water was added cautiously, followed by the dropwise additions of 5 mL of 3 N sodium hydroxide and 5 mL of 30% hydrogen peroxide. The resulting solution was stirred for 0.5 h at room temperature. The layers were then separated and the aqueous layer was extracted with 25 mL of ether. The combined organic phases were diluted with ether, washed with two 40-mL portions of water and 40 mL of brine, and dried over anhydrous magnesium sulfate. Filtration and evaporation gave 2.96 g (92%) of **40** as a pale yellow oil (δ 6.2 peak absent in NMR spectrum; IR shows a 3600 cm^{-1} absorption). This oil was used without further purification. A solution of this oil in 25 mL of dry methylene chloride was added all at once to a solution (that had previously been stirred for 15 min) of chromium trioxide (6.0 g, 60 mmol) and 9.5 g (120 mmol) of dry pyridine (distilled from barium oxide) in 75 mL of methylene chloride. After 15 min of additional stirring, the solution was decanted from the dark residue. The residue was rinsed with 100 mL of ether and the combined organic solutions were allowed to evaporate and then concentrated under vacuum to remove pyridine. The residue was taken up in ether, filtered, washed

with dilute sodium hydroxide and brine solutions, and dried over $MgSO_4$. Filtration and evaporation gave 1.33 g (46%) of **39**, identical spectrally with the material described above.

Attempted Deketalization of 36 and 38. (a) A 550-mg (1.4 mmol) portion of **38** was treated with 1.1 g of acid-activated zinc dust[26] in 10 mL of refluxing tetrahydrofuran. The reaction was periodically monitored by removal of a small amount via syringe, filtration through glass wool and Celite, followed by IR examination for the presence of the carbonyl absorption. After 24 h, no carbonyl was observed. An additional 1.0 g of zinc and 10 mL of solvent were then added and reflux was continued for 3 days with no carbonyl absorption detected. The solution was then cooled, filtered, and evaporated to give 510 mg of a solid identical spectrally with **38**.

(b) This procedure was repeated using dimethyl formamide at 100 °C as the solvent. After several days, TLC analysis showed that **38** was absent. The suspension was cooled, filtered, and diluted with water and ether. The layers were separated and the ether layer was extracted several times with water and once with brine and dried over anhydrous magnesium sulfate. Filtration and evaporation gave an oil whose NMR spectrum showed none of the peaks expected for the desired ketone. This material was not characterized further.

(c) Treatment of 120 mg of crude **38** with 1 g of magnesium powder in 10 mL of dimethyl formamide at 100 °C for 3 days, followed by workup as in the acid-activated zinc attempt, gave only unchanged **38**.

(d) Using the procedure described for activated zinc deketalization of **33**, 500 mg (1.23 mmol) of **38** and precipitated zinc [from 320 mg (1.41 mmol) of zinc bromide and 110 mg of potassium][28] were stirred in refluxing tetrahydrofuran for 18 days. The mixture was then cooled and chromatographed on 25 g of neutral alumina with benzene–chloroform to give a yellow oil, identified as **38** by spectral comparison with authentic material.

(e) To a side-armed flask equipped with reflux condenser and rubber septum was added 134 mg (1.41 mmol) of $MgSO_4$, 106 mg (0.64 mmol) of potassium iodide, and 4 mL of tetrahydrofuran (distilled from lithium aluminum hydride). The flask was maintained under argon during the reaction. Approximately 100 mg of potassium was added in small pieces.[28] The temperature was raised to reflux and maintained for 2.5 h. A solution of 250 mg (0.64 mmol) of **36** in 5 mL of tetrahydrofuran was added next via syringe. After 18 h of reflux, the solution was cooled. Water and ether were added and workup was completed as in the activated zinc procedure to give an oil (230 mg) containing only unchanged **36**. This procedure was repeated with **38**, which also gave unchanged starting material.

Polarographic Procedure. Half-wave potentials were obtained by polarography with a PAR Model 174 polarographic analyzer. A dual compartment cell with separation of the cells via a coarse glass frit was used. A dropping mercury electrode served as the cathode in the main compartment. Also placed in this compartment was a platinum wire auxiliary electrode. A saturated calomel reference electrode was connected to the second compartment via a salt bridge. Dimethylformamide of sufficient purity (transparent to ca. −2.8 V) was obtained by treatment of reagent grade dimethylformamide with several batches of 3 Å molecular sieves followed by distillation. The electrolytes were stored in a desiccator. All compounds used in these determinations were of analytical purity. To obtain the $E_{1/2}$ value, each cell was filled with the solvent–electrolyte solution and then degassed with nitrogen for at least 15 min. A polarogram was then run on the blank solvent to establish the background current. After addition of several milligrams of the desired compound, the polarogram was rerun. The surfactant Triton X-100 was used in some cases to remove maxima. The $E_{1/2}$ values were taken either from the inflection point of the polarographic wave(s) or from the maximum of the differential pulse peak(s).

Procedure for Controlled Potential Reductions. Reductions were carried out at controlled potential (±0.03 V) with a Tacussel Type ASA 50-2 potentiostat connected to a cell in series with a coulometer for monitoring current flow. A cell similar to that used for polarographic work was employed in which the main compartment required ca. 60 mL of solution. The electrodes were a mercury pool as cathode and a platinum gauze anode. A saturated calomel reference electrode was connected to the cell via a salt bridge. The main compartment also contained a magnetic stirring bar and was cooled to 0–25 °C with an ice bath. Reagent grade dimethylformamide, distilled tetramethylurea, or distilled dimethyl sulfoxide were used as solvents. Lithium perchlorate or tetra-*n*-butylammonium perchlorate were used as electrolytes (0.1 N). For each run, a solution of the appropriate compound in ca. 60 mL of the electrolyte solution was cooled, degassed at least 15 min, and then maintained under nitrogen during reduction. When passage of the desired amount of current was observed, the solution in the main compartment was poured into 100 mL of water and 100 mL of ether. The layers were separated and the aqueous layer was extracted with three 100-mL portions of ether. The combined ether layers were treated with three 100-mL portions of water and 100 mL of brine and finally dried over anhydrous magnesium sulfate. Filtration and concentration via rotary evaporation yielded a residue which was analyzed by NMR and GLC.

Electrochemical Reduction of 33. Preparation of 7-(2,2-Dichloroethoxy)-7-methoxybicyclo[2.2.1]hept-2-ene (41). (a) Reduction of 1.0 g (3.7 mmol) of **33** at −1.85 V (600 C; 710 C = 2 equiv) in dimethylformamide–tetra-*n*-butylammonium perchlorate afforded an oil which contained no **13** by NMR and GLC analysis. Vacuum transfer gave 580 mg (67%) of **41**. An analytical sample was obtained by preparative VPC on a 6 ft × 0.25 in. 5% FFAP on potassium hydroxide washed Chromosorb P column at 130 °C: NMR ($CDCl_3$) δ 6.10 (2 H, m), 5.78 and 5.70 (1 H, 2t, J = 6 Hz), 3.82 and 3.72 (2 H, d, J = 6 Hz), 3.27 and 3.21 (3 H, 2s), 2.79 (2 H, m), 1.7–2.1 (2 H, m), 1.0 (2 H, m). The pairs of peaks (δ 5.7, 3.7–3.8, and 3.2) indicated the presence of unseparated syn and anti isomers.

Anal. Calcd for $C_{10}H_{14}Cl_2O_2$: C, 50.65; H, 5.95. Found: C, 50.63; H, 5.93.

(b) Reduction of 650 mg (2.4 mmol) of **33** at −1.85 V (411 C; 460 C ≈ 2 equiv) in dimethylformamide with lithium perchlorate as the electrolyte gave a residue containing only **41** (as determined by NMR analysis).

(c) Reduction of 500 mg (1.8 mmol) of **33** at −1.65 V (250 C; 360 C = 2 equiv) gave a residue containing only **41** (as determined by NMR analysis).

Acknowledgment. We are indebted to the National Cancer Institute of the Public Health Service and to the National Science Foundation for grants which supported this investigation.

Supplementary Material Available: Detailed infrared data of selected compounds (3 pages). Ordering information is given on any current masthead page.

Registry No.—**7a**, 694-70-2; **7b**, 13426-55-6; **7c**, 66323-71-5; **8a** (Ar-Ph), 66428-44-2; **8b** (Ar = $C_6H_4NO_2$), 66323-72-6; **8c** (Ar = $C_6H_4NO_2$), 66323-73-7; **10a** (Ar = Ph), 42103-77-5; **10b** (Ar = $C_6H_4NO_2$), 66323-74-8; **10c** (Ar = $C_6H_4NO_2$), 66323-75-9; **12**, 66323-76-0; **13**, 694-71-3; **14a**, 66323-77-1; **14b**, 66323-78-2; **15a**, 66323-79-3; **15b**, 66323-80-6; **16**, 13118-70-2; **17**, 66323-81-7; **18a**, 66428-45-3; **18b**, 66323-82-8; **19**, 875-04-7; **20a**, 66323-83-9; **20b**, 66323-84-0; **21a**, 66323-85-1; **22b**, 66323-86-2; **23**, 10265-39-1; **25**, 1491-12-9; **26**, 66323-54-4; **27**, 66323-55-5; **28a**, 66323-56-6; **28b**, 66428-37-3; **29**, 10218-02-7; *syn*-**30** (Ar = $C_6H_4NO_2$), 66323-57-7; *anti*-**30** (Ar = $C_6H_4NO_2$), 66428-38-4; *syn*-**30** (Ar = Ph), 66323-58-8; *anti*-**30** (Ar = Ph), 66428-39-5; *syn*-**31** (Ar = Ph), 66323-59-9; *anti*-**31** (Ar = Ph), 66428-40-8; *syn*-**32** (Ar = $C_6H_4NO_2$), 66323-60-2; *anti*-**32** (Ar = $C_6H_4NO_2$), 66428-41-9; *syn*-**33**, 66323-61-3; *anti*-**33**, 66323-62-4; *syn*-**34**, 66323-63-5; *anti*-**34**, 66428-42-0; **35**, 66323-64-6; *syn*-**37**, 66323-65-7; *anti*-**37**, 66428-43-1; **38**, 66323-66-8; **39**, 66323-67-9; **40**, 66323-68-0; *syn*-**41**, 66323-69-1; *anti*-**41**, 66323-70-4; phenyl azide, 622-37-7; *p*-nitrophenyl azide, 1516-60-5; 2,2,2-trichloroethanol, 115-20-8.

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Electrosynthesis of Hetero–Hetero Atom Bonds. 2. An Efficient Preparation of (2-Benzothiazolyl)- and Thiocarbamoylsulfenamides by Electrolytic Cross-Coupling Reaction of 2-Mercaptobenzothiazole, Bis(2-benzothiazolyl) Disulfide, and/or Bis(dialkylthiocarbamoyl) Disulfides with Various Amines

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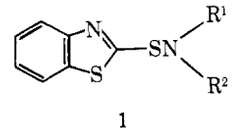
Received March 13, 1978

Two series of sulfenamides bearing 2-benzothiazolyl and thiocarbamoyl moieties were synthesized smoothly by electrolytic cross-coupling of either 2-mercaptobenzothiazole (**3**), bis(2-benzothiazolyl) disulfide (**4**) or bis(dialkylthiocarbamoyl) disulfides (**5**) with various amines in *N*,*N*-dimethylformamide. Electrolysis was carried out under constant voltages of 2–3 V (0.95–1.20 V vs. SCE) in an undivided cell, fitted with two platinum and/or two stainless steel Sus 27 electrodes. Direct electrosynthesis of thiocarbamoylsulfenamides (**2**) from dialkylamines and carbon disulfide was also accomplished in 81–96% yields.

During the last couple of decades, a number of synthetic methods for preparing (2-benzothiazolyl)- and thiocarbamoylsulfenamides (**1** and **2**) as important industrial chemicals[1] have been developed. The S–N bond-making reactions comprise the reaction of sulfenyl chlorides with amines,[2] coupling



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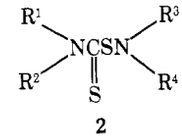

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