rated and the aqueous layer further extracted with Et_2O. Combination of the ethereal layers was followed by drying (K_2CO_3) and solvent evaporation.

The crude mixture of **3**, **4**, and *n*-BuOH was then dissolved in ca. 5 ml of dry pyridine, to which was added ca. 1 ml of Ac_2O. The solution was heated to 75° for 1 h, followed by cooling, addition of H_2O, and extraction with Et_2O. The Et_2O extracts were then washed with 1 N HCl until the wash remained acidic. Drying of the ether layer was followed by rotoevaporation using a hot water bath (ca. 75 °C) to evaporate the *n*-BuOAc. The resulting crude oil was analyzed by NMR. The only methine peaks seen proved to be those for **3**-OAc and **4**-OAc in the ratio of 2.8:1. It was assumed that this ratio also applied to the alcohols **3** and **4**.

Separation and purification of **3**-OAc and **4**-OAc was achieved by chromatography on silica gel (of 355 mg of crude material). Both acetates were eluted with 4% Et_2O–96% hexane, with **4**-OAc coming through first. The total isolated yield of cyclopropyl acetates was 38%.

3-OAc: NMR ($CDCl_3$) δ 5.50 (narrowly split multiplet, olefinic H), 3.82 (s, cyclopropyl H), 2.13 (s, 4 allylic H), 2.1–1.2 (m, 6 aliphatic H), 1.90 (s, OAc); ir ($CDCl_3$) 3020 (m), 1740 (s), 1665 (w), 1250 cm^{-1} (s). Anal. Calcd for $C_{12}H_{16}O_2$: 192.1150. Found (70 eV): 192.1160.

4-OAc: NMR ($CDCl_3$) δ 5.50 (narrowly split multiplet, olefinic H), 3.95 (s, cyclopropyl H), 2.8–1.5 (m, 4 allylic + 6 aliphatic H), 2.07 (s, OAc); ir ($CDCl_3$) 3020 (m), 1735 (s), 1654 (w), 1245 cm^{-1} (s). Anal. Calcd for $C_{12}H_{16}O_2$: 192.1150. Found (70 eV): 192.1160.

Oxygenation of 5. In a manner exactly analogous to that described for **1**, 50 mg (0.23 mmol) of **5** was oxygenated and acetylated. To within the error limits of NMR analysis, the only detectable product was 4-OAc.

10α-Hydroxytricyclo[4.3.1.0^{1,6}]dec-3-ene (3). In 1 ml of a 5% KOH in 25% aqueous MeOH solution was dissolved 16 mg of pure **3**-OAc. The mixture was heated for 2 h at 50 °C, followed by dilution with H_2O and extraction with Et_2O. After drying (K_2CO_3), filtering, and evaporating the solvent, ca. 5 mg of solid white product was recovered. The ir ($CDCl_3$) showed peaks at 3590 (sharp, free OH), 3540 (sharp, intramolecularly hydrogen-bound OH), and 3430 cm^{-1} (broad, intermolecularly hydrogen-bound OH).

10β-Hydroxytricyclo[4.3.1.0^{1,6}]dec-3-ene(4). In the manner described above, a 50-mg sample of pure **4**-OAc was hydrolyzed (in 1 ml of the basic solution, and for only 40 min at 50 °C); 13 mg of product was recovered. The ir ($CDCl_3$) showed peaks at 3600 (sharp, free OH) and 3430 cm^{-1} (broad, intermolecularly hydrogen-bound OH).

Oxygenation of 10α-Bromotricyclo[4.3.1.0^{1,6}]decane. A variation of the procedure described above was tried, both to examine the effect on yield and mechanism (if any) of changing solvent. In a dried 100-ml Schlenk flask were placed 0.88 g (4.1 mmol) of 10α-bromotricyclo[4.3.1.0^{1,6}]decane and 6 ml of THF. To the resulting solution was added 26 ml of a 1.6 M hexane solution of *n*-BuLi (42 mmol), under N_2. After stirring for 1 h at room temperature (during which time the solution turned orange) the solution was cooled to −78 °C, and O_2 bubbled in for 1 h. The work-up of the reaction was carried out as described for the oxygenation of **1**. By pumping on the crude product at 1.5 Torr, it was possible to remove the *n*-BuOH; the resulting oil showed singlets at δ 2.98 and 3.17 (for cyclopropyl H) in a ca. 1:1 ratio.

Acetylation of the yellow oil was carried out as before (but at room temperature for 20 h). Chromatography of the products gave 0.34 g (43%) of an inseparable mixture of 10α-acetoxy- and 10β-acetoxytricyclo[4.3.1.0^{1,6}]decane in a 1:1 ratio. Analysis of a GLC-purified sample (20% DEGS on Chromosorb P column) gave the following.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.18; H, 9.35. Found: C, 74.23; H, 9.23.

Spectral data for the mixture showed NMR peaks (CCl_4) at δ 3.72 (s, cyclopropyl H), 3.63 (s, cyclopropyl H), 2.00 (s, OAc), 1.96 (s, OAc), and 2.3–0.9 (m, aliphatics); ir (CCl_4) peaks at 3020 (w), 1754 (shoulder), 1740 (s), and 1235 cm^{-1} (s).

Catalytic hydrogenation (Et_2O, Pt/C) of a 25-mg sample of a 2.8:1 mixture of **3**-OAc and **4**-OAc served to establish that the peak at δ 3.63 belonged to the 10α-acetoxy- and that at δ 3.72 to the 10β-acetoxytricyclo[4.3.1.0^{1,6}]decane.

Reaction of 10α-Lithiotricyclo[4.3.1.0^{1,6}]dec-3-ene (2) with Lithium *tert*-Butylhydroperoxide. **1** (100 mg) was converted to the corresponding organolithium (**2**) exactly as described for the oxygenation of **1**. Subsequently, an addition funnel above the Schlenk flask containing **2** was charged with 5 mmol of *n*-BuLi in 3 ml of hexane and 5 ml of Et_2O. To this were cautiously added 5 mmol (90 mg) of *t*-BuOOH (previously dried, over K_2CO_3, in pentane) in 5 ml of Et_2O (a syringe was utilized). The resulting ethereal solution of LiOO-*t*-Bu was then added dropwise to the solution of **2** (which had been cooled to −78 °C). Thus the only way **3** and/or **4** could form would be via reaction with *t*-BuOOLi. The work-up and subsequent acetylation of the product mixture was performed as described for the oxygenation of **1**. To within the error of NMR analysis, the only cyclopropyl acetate formed was **3**-OAc.

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Registry No.—**1**, 58191-00-7; **2**, 58191-01-8; **3**, 58191-02-9; **3**-OAc, 58191-03-0; **4**, 58239-38-6; **4**-OAc, 58239-39-7; **5**, 58239-40-0; 10,10-dibromotricyclo[4.3.1.0^{1,6}]dec-3-ene, 38749-47-2; 10α-bromotricyclo[4.3.1.0^{1,6}]decane, 58191-04-1; 10α-acetoxytricyclo[4.3.1.0^{1,6}]decane, 58191-05-2; 10β-acetoxytricyclo[4.3.1.0^{1,6}]decane, 58239-41-1; lithium *tert*-butylhydroperoxide, 14680-31-0.

References and Notes

(1) D. T. Longone and W. D. Wright, *Tetrahedron Lett.*, 2859 (1969).
(2) The saturated alcohols corresponding to **3** and **4** were also required. In addition to their synthesis via reduction of **3** and **4**, the saturated bromide analogue of **1** was lithiated (*n*-BuLi) in THF and oxygenated to give a ca. 1:1 mixture of the epimeric saturated alcohols. This provides independent evidence for the involvement of electron transfer in the oxygenation. Details are given in the Experimental Section.
(3) (a) A literature precedent for stereoretentive lithiation–deuteration is C. P. Lewis and M. Brookhart, *J. Am. Chem. Soc.*, **97**, 621 (1975); (b) E. Vogel, A. Vogel, H.-K. Kübbeler, and W. Sturm, *Angew. Chem., Int. Ed. Engl.*, **9**, 514 (1970), reported a possible case of nonstereoretention in a lithiation–carboxylation sequence. However, since they started with a mixture of epimers, and the overall yield was low, one cannot be sure that selective loss of one isomer was not occurring.
(4) We have established the overall stereoretention of the lithiation–deuteration and lithiation–carboxylation sequences (using *n*-BuLi). These sequences were carried out on **1**, at room temperature or below, with invariant stereochemical results. In the latter case, the stereochemistry was proven by iodolactonization of the acid. We also showed that loss ot the epimeric acid was not occurring, since when the reaction was carried out with Mg, followed by CO_2, both acids resulted. Details of these experiments will be published soon.
(5) Of course we realize that some or all of the reaction may proceed via a radical chain mechanism, wherein the inversion of the cyclopropyl center (e.g., **7** → **8**) may be more complicated. There seems to be some evidence for cage reactions in oxygenations of Grignards, but other cases definitely involve chains. A good summary of this point is given by G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, "Selective Oxidation Processes", *Adv. Chem. Ser.*, **No. 51** (1965), and by A. G. Bemis, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1966.
(6) (a) J. San Filippo, Jr., C.-I. Chern, and J. S. Valentine, *J. Org. Chem.*, **40**, 1678 (1975); (b) R. A. Johnson and E. G. Nidy, *ibid.*, **40**, 1680 (1975); (c) E. J. Corey, K. C. Nicolaou, M. Shibasaki, Y. Machida, and C. S. Shiner, *Tetrahedron Lett.*, 3183 (1975).
(7) (a) R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, *J. Am. Chem. Soc.*, **88**, 4261 (1966). (b) Some evidence for the intermediacy of radicals in the oxygenation of aryllithiums also has been presented [E. Müller and T. Töpel, *Chem. Ber.*, **72**, 273 (1939)].
(8) E. Vogel, W. Wiedemann, H. Kiefer, and W. Harrison, *Tetrahedron Lett.*, 673 (1963).
(9) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).
(10) P. Warner and S. Lu, submitted for publication.

Base-Promoted Elimination Reactions in the 2-Aza-5-norbornene System. Stereospecific Ring Opening of 2-(*p*-Toluenesulfonyl)-*exo*-3-(trichloromethyl)-2-azabicyclo[2.2.1]hept-5-ene by Lithium Alkyls[1]

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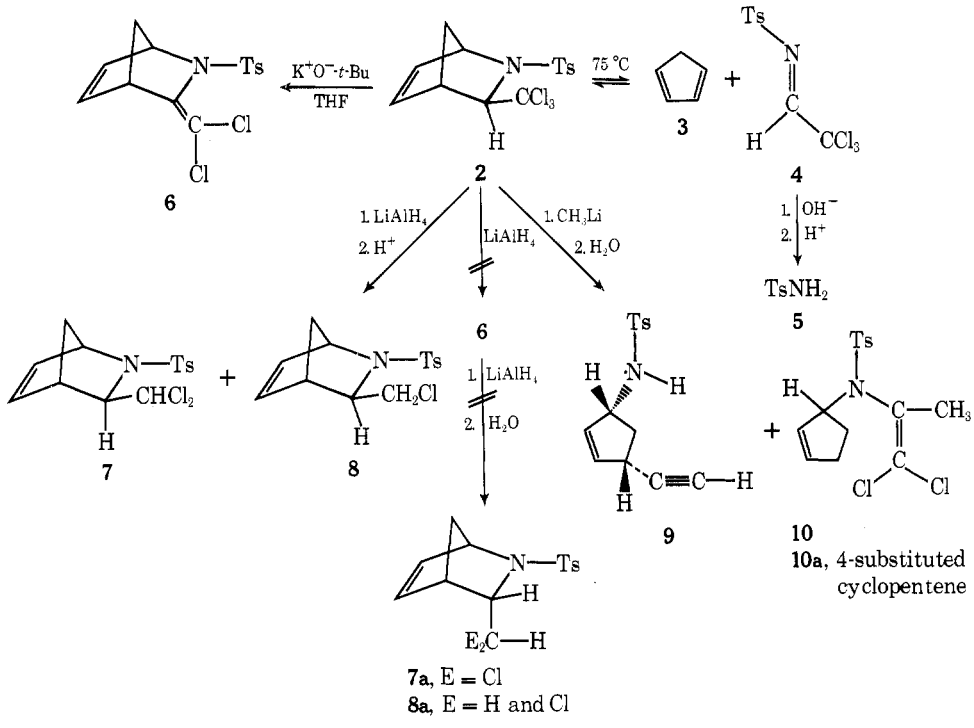
An ongoing interest in aza-aromatic and -antiaromatic character[2] has stimulated our curiosity as to the nature of

Chart I



heterocyclic analogues of homoaromatic and -antiaromatic ring systems, such as the recently synthesized 2-azabicyclo-[2.2.1]hepta-2,5-diene nucleus[3] (1). In a survey of possible routes to this system, we have examined the utility of base-promoted elimination reactions on 2-aza-5-norbornene derivatives. The action of various bases on 2-(*p*-toluenesulfonyl)-*exo*-3-(trichloromethyl)-2-azabicyclo[2.2.1]hept-5-ene[4] (2) has indeed shown some promise as a route to 1 and its derivatives. In addition, however, lithium alkyls have been found to effect a series of interesting elimination processes leading to a stereospecific ring opening of the 2-aza-5-norbornene nucleus (Chart I). The present report on this novel reaction would seem to be timely, in view of the current interest in the rearrangements of 2-halonorbornenes that are induced by lithium alkyls.[5]

Unfortunately, heating 2 with aqueous, alcoholic sodium or potassium hydroxide led to profound decomposition and the isolation of only *p*-toluenesulfonamide (5). This product seemed to have arisen from a retro-Diels–Alder reaction, for when 2 was heated at 75 °C in anhydrous pyridine-d_5, cyclopentadiene (3) was clearly discernible in the NMR spectrum at that temperature. In the presence of aqueous base, the liberated *N*-tosylimine (4) would undergo rapid hydrolysis to 5. In agreement with a recent report,[6] however, the action of potassium *tert*-butoxide in anhydrous tetrahydrofuran on 2 gave smooth dehydrohalogenation and a high yield of 3-(dichloromethylene)-2-(*p*-toluenesulfonyl)-2-azabicyclo[2.2.1]hept-5-ene (6).

Lithium aluminum hydride in anhydrous tetrahydrofuran, on the other hand, caused both mono- and didechlorination of 2. The formation of 7 and 8 could have occurred either by nucleophilic substitution of complex hydride on the trichloromethyl group, or by hydride base-promoted elimination to yield 6, followed by hydralumination of such an enamine.[7] If the latter pathway were involved, 6 would be expected to undergo exo attack and hydrolysis would then lead to *endo*-chloromethyl and *endo*-dichloromethyl derivatives (7a and 8a). However, examination of the NMR spectra of 7 and 8 shows that the C_3 proton is split only by the protons on the $ClCH_2$ and Cl_2CH groups, respectively. If the C_3 protons were exo, they would also be split by the C_4 proton.[6] Since they are not, the C_3 proton in 7 and 8 must be endo and, therefore, the hydride must have replaced the chlorine by a direct nucleophilic substitution.

By contrast, good yields of *cis*-3-*p*-toluenesulfonamido-5-ethynylcyclopentene (9) were realized by treating 2 with 4 equiv of either *n*-butyllithium in hexane or methyllithium in ethyl ether. Quenching such a reaction mixture with deuterium oxide led to 7 deuterated only on the N–H and C≡C–H sites. This finding supports the lack of proton abstraction at the C_3-H and C_5-H sites and, hence, the retention of the cis relation of the tosylamido and ethynyl groups on the cyclopentene ring. From the reaction of 2 with methyllithium, a small amount of an unstable substance was isolated whose spectral data are in good accord with the structure of 3-[(*N*-2,2-dichloro-2-propenyl)-*p*-toluenesulfonamido]cyclopentene (10) admixed with the 4-sulfonamide isomer (10a).

The formation of 9 and 10 from 2 and methyllithium can be rationalized as proceeding in the following steps (Chart II): (a) base-promoted elimination to yield 6; (b) chlorine–lithium exchange to form 11;[8] (c) ring opening by syn or anti elimination of the sulfonamide anion; (d) chlorine–lithium exchange leading to 9; and (e) as an alternative to step b, the addition of methyllithium to 6, followed rupture at the C_3–C_4 bond (12).

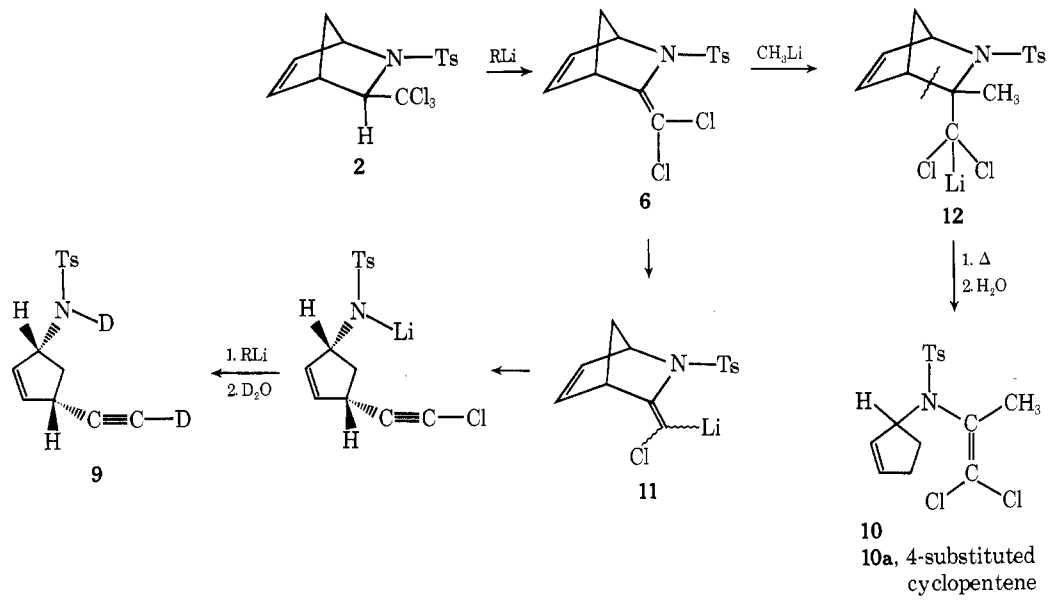
In continuing research, the suitability of the *exo*-chloromethyl-3-aza-5-norbornene derivative (8) for the synthesis of the enamine of 2-methyl-2-azabicyclo[2.2.1]hepta-2,5-diene is being explored. It should also be noted that the accessibility of cis-3,5-disubstituted cyclopentenes, such as 9, from 2 may prove to be of value in the synthesis of prostaglandins.

Experimental Section[9]

Treatment of 2-(*p*-Toluenesulfonyl)-*exo*-3-(trichloromethyl)-2-azabicyclo[2.2.1]hept-5-ene (2) with Various Bases. A. Metal Alkoxides. Heating a solution of 1.0 g (3.0 mmol) of 2 in 20 ml of ethanolic potassium hydroxide solution, which contained 5 equiv of base, yielded, after 4 h at reflux and acidification with hydrochloric acid, *p*-toluenesulfonamide (5) as the only identifiable product.

In agreement with a recent report,[6] the treatment of 2 in tetra-

Chart II



hydrofuran solution with potassium *tert*-butoxide yielded 3-(dichloromethylene)-2-(*p*-toluenesulfonyl)-2-azabicyclo[2.2.1]hept-5-ene (**6**): ir (additional to published bands) strong bands at 696, 746, 765, 838, 900, and 993 cm^{-1}.

However, a solution of 1.0 g of **2** dissolved in 50 ml of a solution of methanol and deuterium oxide (1:1) which contained 3 equiv of sodium methoxide underwent no reaction upon standing at 25 °C for 8 h. Examination of the NMR spectrum also showed that the endo C_3 hydrogen had not undergone any exchange for deuterium.

B. Lithium Aluminum Hydride. A solution of 2.7 g (7.3 mmol) of **2** dissolved in 30 ml of anhydrous tetrahydrofuran was added dropwise to 600 mg (16 mmol) of the hydride dissolved in 30 ml of the same solvent. After a 6-h reflux period the excess of the hydride was destroyed by the cautious addition of an aqueous ammonium chloride solution. The suspension was filtered and the organic layer was separated and then dried over anhydrous magnesium sulfate. Removal of the solvent from the organic extract left a pale yellow oil, which turned semisolid. A TLC analysis of the product on silica gel with a developing solvent of hexane–ethyl ether (v/v 2:1) showed ca. 10% of **2**, two major components, **7** and **8**, and four minor ones. Recrystallization from 95% ethanol gave 1.2 g of a colorless solid containing only the major components (ca. 60% yield of a 70:30 mixture of **7** and **8**). These two components could be separated by chromatography on a 2.0 × 75 cm column of silica gel with benzene used as the eluent.

The first component to be eluted was 2-(*p*-toluenesulfonyl-*exo*-3-(dichloromethyl)-2-azabicyclo[2.2.1]hept-5-ene (**7**), mp 123–124 °C, from 95% ethanol: NMR ($CDCl_3$) 1.40 (br d, J = 9 Hz, H_7 syn to C=C), 2.42 (s, CH_3, sh d, H_7 anti to C=C), 3.1 (d, J = 3.0 Hz, endo H_3), 3.42 (br m, H_4), 4.57 (m, H_1), 5.88 (d of d, H_5), 6.25 (m, H_6), 6.47 (d, J = 3.0 Hz, $HCCl_2$), and 7.5 ppm (m, C_6H_4); MS (70 eV) peaks at *m/e* 335, 333, and 331.

Anal. Calcd for $C_{14}H_{15}Cl_2NO_2S$: C, 50.58; H, 4.55; N, 4.22. Found: C, 50.58; H, 4.76; N, 4.33.

The second component was 2-(*p*-toluenesulfonyl)-*exo*-3-(chloromethyl)-2-azabicyclo[2.2.1]hept-5-ene (**8**), mp 154–155 °C, from 95% ethanol: NMR ($CDCl_3$) 1.46 (br d, J = 9 Hz, H_7 syn to C=C), 1.80 (br d, J = 9 Hz, H_7 anti to C=C), 2.42 (s, CH_3), 2.82 (d of d, J = 10.5, J' = 3.0 Hz, HCHCl anti to N-Ts), 3.30 (br m, H_4), 3.40 (t, J = 10.5 Hz, H_3), 4.27 (d of d, J = 10.5, J = 3.0 Hz, HCHCl syn to N-Ts), 4.58 (br m, H_1), 5.77 (d of d, H_5), 6.08 (m, H_6), and 7.47 ppm (m, C_6H_4); MS (70 eV) peaks at *m/e* 299, 297, and 248.

Anal. Calcd for $C_{14}H_{16}ClNO_2S$: C, 56.64; H, 5.42; N, 4.70. Found: C, 56.41; H, 5.38; N, 4.77.

C. Pyridine-d_5. The NMR spectrum of **2** in pyridine-d_5 showed the following absorptions: 1.32 (d, J = 9.0 Hz), 2.18 (s, CH_3), 2.57 (d, J = 9.0 Hz), 3.58 (m), 4.27 (s), 5.02 (m), 6.43 (m), 6.79 (d of d), 7.20 (d, J = 8.5 Hz), and 7.93 ppm (d, J = 8.5 Hz). After a 4-h heating period at 75 °C new spectral peaks appeared at 2.87 (q, J = 1.5 Hz) and 6.46 ppm (br m), the distinct doublets at 7.20 and 7.93 ppm were now blurred by the emergence of new doublets at 7.23 and 8.17 ppm, and a shoulder developed on the methyl signal. The integrated ratios of the protons at H_7, H_1, H_3, and H_4, however, maintained their proper values for **2**. The new peaks are in good agreement with those expected for the re-formation of cyclopentadiene (**3**), apparently by a retro-Diels–Alder reaction [lit. NMR data for C_5H_6 (in C_6H_6): 2.97 (q, apparent J = 1.4 Hz) and 6.53 (m)]. Eventually heating led to a precipitation of pyridine hydrochloride (peak at 8.72 ppm).

D. Alkyllithium. Under a nitrogen atmosphere a solution of 730 mg (2.0 mmol) of **2** in 50 ml of anhydrous benzene was treated at 25–30 °C with 4.0 equiv of 1.5 M *n*-butyllithium (or methyllithium in ether) in heptane. After a 3-h stirring period the solution was quenched with water, the benzene layer separated, and the aqueous layer extracted twice with ether. After the combined organic extracts were dried over anhydrous magnesium sulfate and the solvent removed, the NMR spectrum of the crude product showed one component to comprise ca. 70% of the mixture. Column chromatography on silica gel with a benzene eluent gave this pure compound **9** as colorless plates: mp 93–94° from 95% ethanol; negative test for halogen; NMR ($CDCl_3$) 1.48 (t, J = 6 Hz) and 1.70 (t, J = 6 Hz; components of a doublet of triplets, J = 13 Hz, H_4 anti to N-Ts and C≡C–H), 2.13 (d, J = 2.4 Hz, C≡C–H), 2.41 (s, CH_3), 2.54 (d of d, J = 8 and 13 Hz, H_4 syn to N-Ts and C≡C–H), 3.30 (m, H_5), 4.35 (br q, J = 9 and ~2–3 Hz, H_3), 5.15 (br d, J = 9 Hz, NH), 5.65 (m, H_1 and H_2), 7.30 (d) and 7.80 ppm (d); ir ($CHCl_3$, NaCl) 3375 (sh), 3330 (br, s, NH), 2125 (m, C≡C), 1600 (C=C), 1345 and 1150 ($N-SO_2$); MS (70 eV) prominent peaks at *m/e* 261 (P), 196, 106, and 78. These data are in accord with **9** being 3-*p*-toluenesulfonamido-5-ethynylcyclopentene.

Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.32; H, 5.78; N, 5.36. Found: C, 64.40; H, 5.76; N, 5.15.

From the reaction of **2** with methyllithium in ethyl ether solution, a small amount of a labile component (**10**, ca. 10%) was isolated by a laborious thin layer chromatographic separation on silica gel employing a hexane–ethyl ether eluent (2:1 v/v). This component, which moved faster than **2** and slower than **9**, contained chlorine and decomposed in moist air. The spectral data are in accord with the structure of this substance **10** being a mixture of 3- and 4-[(*N*-2,2-dichloro-2-propenyl-*p*-toluenesulfonamido]cyclopentene: (a) ir (CCl_4, NaCl) no bands indicative of N–H, O–H, or C≡C–H groups, but a band of moderate intensity at 1625 cm^{-1}, suggestive of the C=C–N group (absent in the spectrum of **2**); and (b) NMR (C_6D_6), total of 17 protons, 0.82–1.6 (m, 2 H, C_4 protons), 1.7–2.1 (m, 1 H, C_5 proton), 2.1 (s, CH_3 of tolyl), 2.4–2.5 (d, 3 H, isomeric CH_3 groups due to 3- and 4-positional isomers), 2.9–3.25 (m, 1 H, C_5 proton), 4.9–5.5 (m, 3 H, C_1, C_2, and C_3 H), 7.1 (d, 2 H), and 7.7 ppm (d, 2 H).

In order to search for sites of metalation in this product, the reaction between **2** and *n*-butyllithium was repeated in benzene solution, as described above, except that the reaction mixture was worked up with deuterium oxide. After the isolation of pure prod-

uct by column chromatography, it was dissolved in $CDCl_3$ and shaken repeatedly with deuterium oxide to ensure N-deuteration. The NMR spectrum of the resulting product no longer displayed any signals at 2.1 and 5.15 ppm, but the position and intensity of the other bands for **9** were unchanged. The results confirm that the acetylenic and amide protons of **9** were abstracted during the reaction with *n*-butyllithium, but that the allylic and vinylene protons were not. Consequently, no epimerization had occurred at the allylic C_3 and C_5 positions of the cyclopentene ring and, therefore, the sulfonamido and ethynyl groups in **9** are cis to each other.

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Registry No.—**2**, 42082-52-0; **6**, 53112-02-0; **7**, 58191-30-3; **8**, 58191-31-4; **9**, 58191-32-5; **10**, 58191-33-6; potassium *tert*-butoxide, 865-47-4; lithium aluminum hydride, 16853-85-3; pyridine-d_5, 7291-22-7; butyllithium, 109-72-8; methyllithium, 917-54-4.

References and Notes

(1) This contribution is part IV of the series "Rearrangements of Heterocyclic Compounds". Part III: J. J. Eisch and D. R. Comfort, *J. Org. Chem.*, **40**, 2288 (1975).
(2) (a) J. J. Eisch and F. J. Gadek, *J. Org. Chem.*, **36**, 2065, 3376 (1971); (b) J. J. Eisch and G. Gupta, *Tetrahedron Lett.*, 3273 (1973); (c) J. J. Eisch, F. J. Gadek, and G. Gupta, *J. Org. Chem.*, **38**, 431 (1973).
(3) J. C. Jagt and A. M. van Leusen, *J. Org. Chem.*, **39**, 564 (1974).
(4) (a) G. Kresze and R. Albrecht, *Chem. Ber.*, **97**, 490 (1964); (b) G. R. Krow, C. Pyun, R. Rodebaugh, and J. Marakowski, *Tetrahedron*, **30**, 2977 (1964).
(5) (a) P. G. Gassman, J. P. Andrews, Jr., and D. S. Patton, *Chem. Commun.*, 437 (1969); (b) P. G. Gassman and T. J. Atkins, *J. Am. Chem. Soc.*, **92**, 5810 (1970); (c) P. G. Gassman and J. J. Valcho, *Ibid.*, **97**, 4768 (1975).
(6) M. S. Raasch, *J. Org. Chem.*, **40**, 161 (1975).
(7) J. M. Coulter, J. W. Lewis, and P. P. Lynch, *Tetrahedron*, **24**, 4489 (1968).
(8) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **67**, 1420 (1945).
(9) Cf. ref 1 for the specification of experimental techniques.

Carbene Multiplicity in Decompositions of 2-Methyl-2-phenyldiazopropane

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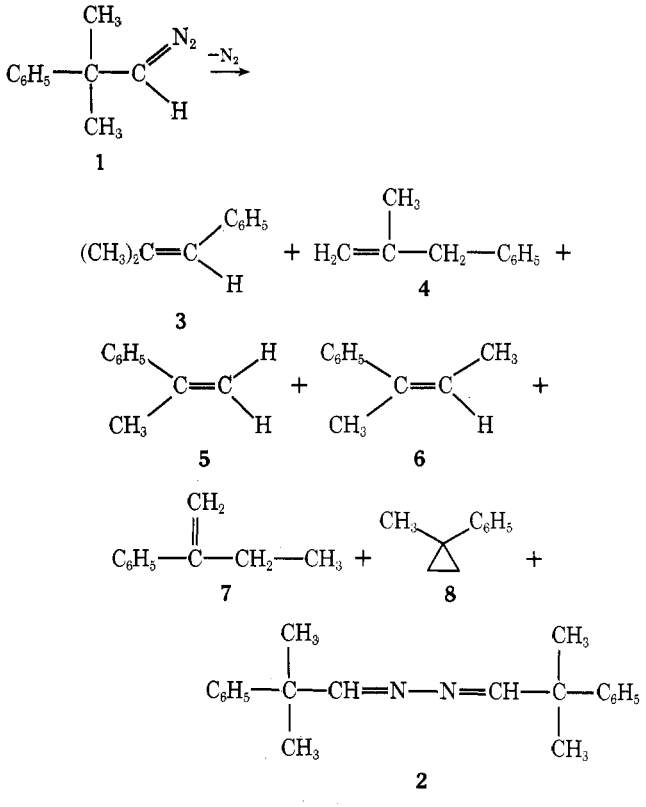
The literature of chemistry contains many examples of carbenes whose singlet and triplet states exhibit different chemical reactions.[1] A classical example of this phenomenon is seen in the addition of carbenes to cis or trans olefins. Singlet carbenes add predominantly stereospecifically, whereas triplet carbenes form cyclopropanes in a nonstereospecific manner.[2]

Some intramolecular carbene reactions are also dependent upon carbene multiplicity. When competing reactions are available, the rearrangements of hydrogen atoms[3] and phenyl groups[4] proceed more favorably to singlet rather than triplet carbenes. However, the experimental evidence does not exclude some triplet contribution to these rearrangement processes.

The carbene produced by the decomposition of 2-methyl-2-phenyldiazopropane (**1**) is suited to the study of three competing intramolecular reactions: phenyl rearrangement, methyl rearrangement, and C–H insertion. The thermal decomposition of **1** in dry hexane at 59 °C has been reported[5] to yield an azine ($C_{20}H_{24}N_2$), **2**, and six products of formula $C_{10}H_{12}$: 2-methyl-1-phenylpropene (**3**); 2-methyl-3-phenylpropene (**4**); *cis*-2-phenyl-2-butene (**5**); *trans*-2-phenyl-2-butene (**6**); 2-phenyl-1-butene (**7**); and 1-methyl-1-phenylcyclopropane (**8**). Products **3** and **4** are formed by phenyl rearrangement; olefins **5**, **6**, and **7** are methyl migration products; and cyclopropane **8** is a product of intramolecular C–H insertion. The object of the present study was to determine how the relative yields of these products might be affected by reaction conditions which would selectively favor carbene reaction from either the singlet or triplet state.



The ground state of alkylcarbenes appears to be the triplet.[6] However, the thermal or direct photochemical decomposition of diazoalkanes initially produces the excited singlet state of the carbene.[1] Methods of inducing triplet behavior in the carbene include the use of triplet photosensitizers to directly produce the triplet carbene, and the use of heavy atom solvents to quench the initially formed singlet to the ground state triplet.[7] The products of the decomposition of **1** under varying reaction conditions are summarized in Tables I and II.

While the origins of individual products in Table II are open to speculation, certain trends in migratory aptitudes and C–H insertion are evident. In comparing thermal decompositions I and II with reaction III, it is seen that the use of a heavy atom solvent decreases the relative amounts of methyl rearrangement and cyclopropane formation. The same trend is noted when comparing direct photolysis IV with photosensitized decompositions V and VI. Triplet sensitization increases phenyl migration at the expense of the competing intramolecular processes.

It is possible that phenyl rearrangement, methyl rearrangement, and C–H insertion all proceed to both the singlet and triplet states of the carbene. In any case, reaction conditions which favor triplet carbene production decrease the relative rates of methyl migration and C–H insertion while increasing the relative rate of phenyl rearrangement. The distinction between singlet and triplet behavior may be blurred by rapid intersystem crossing.[4b]

Tetraphenylethylene-catalyzed diazo decompositions have recently been reported by Ho, Conlin, and Gaspar.[8] The relative product yields of the tetraphenylethylene-catalyzed decomposition of **1** (reactions VII and VIII) resemble product yields from triplet carbene reactions (III, V, and VI) more closely than they resemble singlet carbene product yields (I, II, and IV). An explanation for this obser-