After recovery of 2–3 g. of starting ester, there was obtained 4.4 g. of adiponitrile and 5.9 g. of crude product, b.p. 180–190° (0.24 mm.). Redistillation yielded **methyl α-acetamido-δ-cyanovalerate** (IX), b.p. 166–174° (0.20 mm.), $n^{25}$D 1.4680.

*Anal.* Calcd. for $C_9H_{14}N_2O_3$: C, 54.53; H, 7.12; N, 14.14; mol. wt., 198. Found: C, 54.87; H, 6.87; N, 14.25; mol. wt., 197.

**IX Conversion to *dl*-Lysine Monohydrochloride.**—A suspension of 3.8 g. of IX, 0.75 g. of Raney nickel,[14] and 1.0 g. of anhydrous sodium acetate in 15 ml. of acetic anhydride was shaken at room temperature with hydrogen at 50-lb. initial pressure for 4 hr. in a Parr apparatus. The mixture was filtered. Volatile materials were removed *in vacuo*. The sirupy residue was heated under reflux with 20 ml. of concentrated HCl for 7 hr. Volatile products were again removed *in vacuo*. The residual sirup was dissolved in 20 ml. of hot absolute ethanol, treated with charcoal, and filtered. Addition of an excess of dry ether precipitated 5.5 g. of a gum which was dissolved in 30 ml. of hot absolute ethanol and treated with 1.0 ml. of pyridine. After refrigeration, a small quantity of pyridine hydrochloride was removed. Addition of 10 drops of pyridine precipitated crude *dl*-lysine monohydrochloride. Further crops were obtained from the filtrate by careful addition of pyridine. The crude product was dissolved in 3 ml. of water, treated with charcoal, and filtered. Addition of 25 ml. of absolute ethanol followed by refrigeration yielded pure white crystals, 0.37 g., m.p. 264°.

In another preparation in which Adams' catalyst was used instead of Raney nickel the purified product melted at 267°.

**Suberonitrile.**—The catholyte contained 98 g. (1.8 moles) of acrylonitrile and 18.3 g. (0.23 mole) of freshly distilled 1-cyano-1,3-butadiene dissolved in 115 g. of 80% tetraethylammonium *p*-toluenesulfonate. The cathode voltage was regulated manually at −1.69 to 1.71 v. (*vs.* the saturated calomel electrode). The initial amperage was 3.0 and this was gradually reduced to 0.25 toward the end of the run. A total of 10.6 amp.-hr. (coulometer) was used. The temperature was maintained at 25° and the pH at *ca.* 8. The residual liquid, after removal of materials volatile at 30 mm. on the water bath, weighed 25.9 g. It was dissolved in 90 ml. of absolute ethanol containing 1.00 g. of 5% palladium on carbon and hydrogenated at room temperature at an initial pressure of 36 lb. The uptake was 14.25 lb., 0.166 mole (calcd. for hydrogenation of 1,6-dicyano-2-hexene, 15.4 lb., 0.179 mole). The saturated product (25.3 g.) was distilled. The first cut, 16.5 g., b.p. 150 (2.9 mm.) to 162° (3.2 mm.), $n^{25}$D 1.4428, was virtually pure suberonitrile.

*Anal.* Calcd. for $C_8H_{12}N_2$: C, 70.54; H, 8.88; N, 20.57; mol. wt., 136. Found: C, 70.41; H, 9.09; N, 20.75; mol. wt., 138.

The final cut, b.p. 222 (0.47 mm.) to 226° (0.55 mm.), $n^{25}$D 1.4732, had a molecular weight of 204–210 and 21.3% N, indicating a product with three nitrogen atoms.

**Ethyl 7-Cyanoheptanoate.**—The catholyte contained 88 g. (0.88 mole) of ethyl acrylate (stabilized by hydroquinone), 8.7 g. (0.11 mole) of cyanobutadiene, 43 g. of acetonitrile, and 99 g. of 80% tetraethylammonium *p*-toluenesulfonate. The cathode voltage was regulated at −1.67 to −1.70 v. which required gradually lowering the amperage from 2.7 to 0.25. A total of 5.0 amp.-hr. was passed. The operating temperature was 30–35°. The recovered crude product (12.4 g.) was hydrogenated as above and the saturated products were fractionated through a 2-ft. jacketed Vigreux column. The fractions (4.1 g.) containing the product of mixed coupling, b.p. 155–175° (18 mm.), were combined and refractionated to yield pure product boiling at 162–164° (18 mm.), $n^{25}$D 1.4342.

*Anal.* Calcd. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.44; H, 9.74; N, 7.43.

Higher boiling fractions contained mixtures of the cyano ester and sebaconitrile.

**Diethyl α,α'-Bis(2-cyanoethyl)succinate.**—The catholyte contained 100 ml. of acrylonitrile, 1.5 ml. of diethyl fumarate, 1.0 ml. of water, and 50 g. of tetraethylammonium *p*-toluenesulfonate. The anolyte contained 20 g. of 60% quaternary salt. During the electrolysis the cathode voltage was maintained at −1.48 to −1.50 v. by dropwise addition of 14.9 ml. of diethyl fumarate over a period of 7 hr. The temperature was 25° for the first 90 min. and 40° thereafter. The amperage was in the range of 1.50–0.50, total 6.0 amp.-hr. The crude product (21.0 g.) was fractionated through a 2-ft. Vigreux column. The fraction boiling at 129° (0.45 mm.), $n^{25}$D 1.4430, was pure diethyl α-(2-cyanoethyl)succinate.

*Anal.* Found: C, 58.11; H, 7.53; N, 6.28.

Intermediate fractions were shown by vapor phase chromatographic analysis to consist of mixtures of tetraethyl butanetetracarboxylate and diethyl α-(2-cyanoethyl)succinate. The highest boiling fraction was redistilled and the product collected at 176–178° (0.25 mm.), $n^{25}$D 1.4565.

*Anal.* Calcd. for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19; N, 9.99. Found: C, 59.75; H, 7.18; N, 10.19.

The proton magnetic resonance spectrum was determined at room temperature on the Varian A-60 spectrometer operating at 60 Mc./sec. Spectro Grade chloroform and carbon tetrachloride were used as solvents and tetramethylsilane as internal standard. The spectrum of the sample was obtained in *ca.* 25% solution by volume. The proton magnetic resonance spectra of known model compounds [adiponitrile and diethyl α-(2-cyanoethyl)succinate] were obtained by the same technique. The τ-values and the intensities of the signals of the unknown were used to assign the nonequivalent nuclei in a direct comparison with the model compounds: 8.7 (for 6.2 H of $CH_2\,CH_3$), 8.0 (for 4.1 H of $-CH_2$-CN), 7.4 (for 4.0 H of $-CH_2$—C<), 6.4 (for 1.9 H of >CH-C), and 5.8 (for 3.8 H of —O—$CH_2$—). These data indicated that structure XII was more probable than structure XIII.

**Acknowledgment.**—All instrumental analyses were performed by Donald Beasecker's group The proton magnetic resonance spectra were obtained and interpreted by Louis Boros.

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# Photolysis of Nortricyclanone Tosylhydrazone Sodium Salt

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Photochemical decomposition of nortricyclanone tosylhydrazone sodium salt (1) pursues a course rather different from that of the pyrolysis. 3-Nortricyclyl *p*-tolyl sulfone (5) is formed in yields as high as 50% under *aprotic* conditions. Irradiation of 1 in the presence of free nortricyclanone tosylhydrazone gives nortricyclanone N-tosyl-3-nortricyclylhydrazone (6), identical with a sample prepared by an independent synthesis. Mechanistic implications of these observations are discussed briefly.

Thermal decomposition of *p*-toluenesulfonylhydrazone (tosylhydrazone) salts has become an important method for the generation of carbenes.[1] Dauben's observation that irradiation of camphor tosylhydrazone sodium salt gave high yields of tricyclene, presumably *via* the carbene, suggested that photochemical decomposition of tosylhydrazone salts parallels closely the thermal process.[2] In a study of the behavior of nortricyclanone tosylhydrazone sodium salt (1) we have

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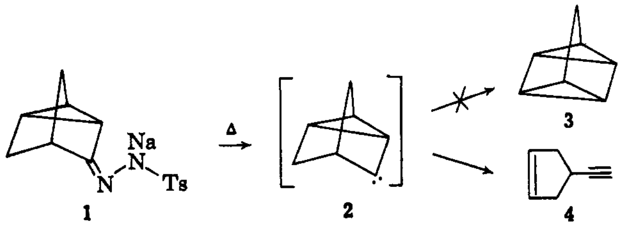
(1) See, for example, E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963).

(2) W. G. Dauben and F. G. Willey, *J. Am. Chem. Soc.*, **84**, 1497 (1962).

found major differences between the pyro- and photolytic reaction pathways.

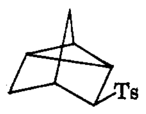
Nortricyclanone was synthesized by bromination of norbornene with N-bromosuccinimide (54% yield)[3] and oxidation of the resulting 3-bromonortricyclene by a modification of Kornblum's[4] alkaline dimethyl sulfoxide procedure.[5] When dissolved at room temperature in dimethyl sulfoxide containing an equivalent of silver fluoborate, the bromo compound was smoothly transformed into the dimethyl-3-nortricyclyloxysulfonium salt. Triethylamine was introduced and the mixture was heated for a short time on the steam bath to complete the oxidation to nortricyclanone (69% yield). Finally, the tosylhydrazone was prepared (87%) from the ketone and tosylhydrazine in hot pyridine.[6]

Near the completion of our work with the tosylhydrazone sodium salt **1**, Cristol[7] reported that thermal decomposition of this substance, which presumably led to nortricyclylidene (**2**), resulted not in ring closure of the carbene to quadricyclene (**3**),[8] but in twofold ring scission to 4-ethynylcyclopentene (**4**, 42% yield).[9] By pyrolyzing **1** at 160° in tetraglyme we had obtained this acetylene in comparable yield and had completely characterized it on the basis of chemical, microanalytical,[10] and spectral evidence. Our data are fully in accord with those of Cristol.[11]

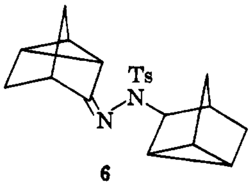


Ts = *p*-toluenesulfonyl

A stirred suspension of **1** in purified tetrahydrofuran or diglyme was irradiated several hours with a Hanovia 450-w. Type L mercury lamp equipped with a Pyrex filter. Although some hydrocarbon **4** was found by g.l.c. (gas–liquid chromatography) in the resulting pale yellow suspension,[12] adsorption chromatography on alumina of the nonvolatile, ether-soluble fraction of the product led to the isolation in as high as 50% yield of a crystalline compound, m.p. 72–74°. The infrared spectrum (chloroform) showed prominent maxima at 7.65 and 8.75 $\mu$ characteristic of sulfones and at 12.0 $\mu$, suggestive of a nortricyclyl residue.[3] Presence of a *p*-tolyl group was indicated by the n.m.r. spectrum (carbon tetrachloride) which featured an AB quartet (doublets at $\tau$ 2.31 and 2.72, $J = 8.0$ c.p.s.) attributable to aryl protons and a singlet at $\tau$ 7.56 corresponding to the methyl. The photolysis product was identified as 3-nortricyclyl *p*-tolyl sulfone (**5**) by spectral and mixture melting point comparison with an authentic sample, which was synthesized by addition of *p*-toluenethiol to norbornadiene followed by hydrogen peroxide oxidation.[13]

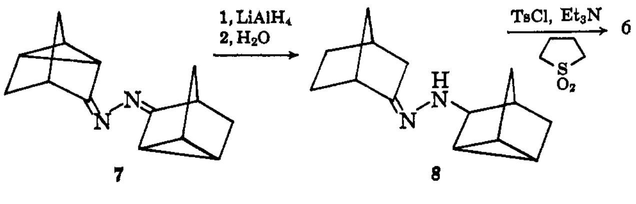


**5**



**6**

In certain of the photolysis runs the sulfone was accompanied by a higher melting (162–163°) substance, $C_{21}H_{24}N_2O_2S$, produced in yields as high as 52%. This compound was neutral, lacked N–H stretching absorption in the infrared spectrum, and exhibited an ultraviolet spectrum virtually identical with that of nortricyclanone tosylhydrazone. Since structure **6**, nortricyclanone N-tosyl-3-nortricyclylhydrazone, fits these data, authentic **6** was synthesized in the following fashion. Nortricyclanone azine (**7**) was prepared from the ketone and anhydrous hydrazine in refluxing ethanol.[14] Reduction of **7** with lithium aluminum hydride in boiling ether proceeded in near-quantitative yield to the nicely crystalline but air-sensitive hydrazone **8** ($\lambda_{max}^{CHCl_3}$ 3.04, 5.95 $\mu$), which was transformed without purification into **6** through the action of tosyl chloride and triethylamine in hot sulfolane.[15] Infrared spectral, melting point, and mixture melting point comparison of **6** with the higher melting photolysis product demonstrated that the two were identical.



Formation of **6** in the photolysis was traced to the presence of free tosylhydrazone, *i.e.*, incomplete conversion to the salt **1**. When a small excess of dry, gran-

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[3] J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

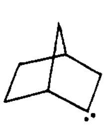
[4] N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

[5] Preparation of the tricyclic ketone from norbornadiene by the method of H. K. Hall, Jr. [*ibid.*, **82**, 1209 (1960), addition of formic acid, methanolysis, and oxidation] resulted in comparable over-all yields.

[6] Attempts to make the tosylhydrazone with HCl catalysis [the general procedure of C. H. De Puy and D. H. Froemsdorf, *ibid.*, **82**, 634 (1960)] led only to 5(?)-chloro-2-norbornanone tosylhydrazone. Thermal decomposition of this compound as its sodium salt gave 3-chloronortricyclene (60%).[8,11]

[7] S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

[8] The tetracyclic substance **3** might have been anticipated on the basis that tricyclenes are formed, often in excellent yield, in reactions proceeding *via* the norbornylidene i and its derivatives. See, for example, D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961), and references contained therein.



i

[9] This event was foreshadowed by observations of L. Friedman and H. Shechter [*ibid.*, **82**, 1002 (1960)]. Pyrolysis of cyclopropanecarboxaldehyde tosylhydrazone sodium salt gave *inter alia* small quantities of ethylene and acetylene, the products of a cleavage entirely analogous with that of **2**. Similarly, ethylene and methylacetylene were minor decomposition products of the sodium salt of methyl cyclopropyl ketone tosylhydrazone.

[10] Satisfactory microanalyses were obtained on all new compounds with the exception of **8**, which was used without purification, as noted.

[11] A. J. Fry, Ph.D. dissertation, University of Wisconsin, 1963.

[12] Cristol[7] found that photochemical decomposition of **1** gave low yields of **4**, but he did not further investigate the reaction mixture.

[13] S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

[14] The azine was also found (4% yield) among the photolysis products of the tosylhydrazone salt **1**.

[15] Sulfolane appears to be an excellent solvent for sulfonylations on nitrogen. Dimethylformamide, also strongly dipolar and aprotic, has been used effectively by Carpino, but, with certain weakly basic amines, formylation (by a modified Vilsmeier reaction) rather than sulfonylation may occur in dimethylformamide.

ular sodium hydride was used to form the salt in tetrahydrofuran or diglyme, **6** was isolated in considerable quantity, but use of excess fresh sodium hydride–mineral oil dispersion gave none. Apparently in the former case coating of the hydride particles with the salt **1** had prevented much of the base from reacting. Deliberate use of insufficient sodium hydride dispersion had the same effect on product composition. The most likely pathway to **6** is alkylation of the weakly acidic sulfonamide function of nortricyclanone tosylhydrazone by diazonortricyclene. Hence isolation of **6** supports the view that diazo compounds are intermediates in the photolysis of sulfonylhydrazone salts.[16]

To our knowledge 3-nortricyclyl *p*-tolyl sulfone (**5**) is the first sulfone prepared by decomposition of a sulfonylhydrazone salt in aprotic media.[17] The compound arises in the thermal as well as the photochemical destruction of **1**, but the yield (10%) is dramatically lower in the pyrolysis. Photolysis runs which give substantial quantities of **6** yield very little sulfone. This is most easily interpreted by assuming that diazonortricyclene is an intermediate on the pathway to sulfone as well as to **6**. Sulfinate ions may react with diazonortricyclene directly; perhaps more likely, the carbene **2** (from the diazo compound) may attack sulfinate ion, giving the reasonably stable sulfone anion which is later protonated. The latter process would be analogous to the trapping of methylene[18] and halocarbenes[19] by triphenylphosphine, since sulfinate ion is "divalent" in the same sense as is a phosphine.[20]

## Experimental[21]

**Nortricyclyl Bromide.**[3]—Norbornene (100 g., 1.065 moles) was dissolved in 650 ml. of carbon tetrachloride, and N-bromosuccinimide (200 g., 1.123 moles) was added, followed by 20 mg. of *p*-toluenesulfonic acid. The initially white suspension was boiled under reflux and stirred vigorously for 5 hr., during which time it became a deep red-brown. After the flask had been cooled for some time in an ice bath, succinimide was separated by filtration and carbon tetrachloride removed by distillation through a Vigreux column. The residual dark brown oil was distilled to afford nortricyclyl bromide, 98.5 g. (0.57 mole, 53.5%), b.p. 60–65° at 12 mm.

**Nortricyclanone. Method A. Oxidation of Nortricyclyl Bromide by Dimethylsulfoxide, Catalyzed by Silver Fluoborate.**—To a solution of silver fluoborate[22] (50 g., 0.285 mole) in 1600 ml. of dry dimethyl sulfoxide was added nortricyclyl bromide (50 g., 0.289 mole), whereupon silver bromide quickly began to precipitate. After 1 hr. at room temperature, precipitation appeared complete. Triethylamine (35 g., 0.347 mole) was added with vigorous swirling, and the mixture quickly darkened. It was allowed to stand, with occasional swirling, for 2 hr., after which it was dark brown. The mixture then was heated on a steam bath for 20 min., allowed to cool, and filtered. The filtrate was diluted with 6 l. of water and extracted with ether until the extracts were colorless. The combined light yellow ether extracts were washed with water and dried over magnesium sulfate. When the ether had been taken off through a Vigreux column, distillation of the residual orange oil afforded nortricyclanone, 21.5 g. (0.199 mole, 68.8%), b.p. 63–65° at 14 mm.

**Method B.** *Via* **Nortricyclanol.**—This alcohol was prepared by addition of formic acid to norbornadiene followed by methanolysis,[5] and also by silver oxide catalyzed hydrolysis of nortricyclyl bromide, described below.

Nortricyclyl bromide (80.5 g., 0.465 mole) and water (22 ml., 1.22 moles) were dissolved in sufficient tetrahydrofuran (350 ml.) to produce a homogeneous solution. Silver oxide (70 g., 0.299 mole) was added all at once; the suspension was boiled under reflux with stirring. Silver bromide began to precipitate almost immediately. After 7 hr., the flask was cooled; a small amount of metallic silver coated its walls. The inorganic residue was removed by filtration and washed with ether. The filtrate was diluted with 1 l. of water and 200 ml. of ether, and the two phases were separated. After the aqueous phase had been extracted several times with ether, the combined organic extracts were washed with water and dried over sodium sulfate. This ether solution of nortricyclanol was used directly in the next step.

Nortricyclanol was oxidized by the method of Brown and Garg.[23] Vigorous stirring was found to be necessary to effect complete oxidation. Yields of nortricyclanone ranged from 55–75%.

**Nortricyclanone Tosylhydrazone.**—Tosylhydrazine (Aldrich Chemical Company, 44.72 g., 0.240 mole) was dissolved in 125 ml. of pyridine, and nortricyclanone (26.00 g., 0.240 mole) was added. The pale yellow solution was heated on the steam bath for 90 min. and then quenched in 800 ml. of cold water. A pale yellow oil separated, but when vigorously scratched with a glass rod it quickly crystallized. After an hour's standing, the off-white crumbly solid was isolated by filtration, washed with water, and dried on a porous plate. Recrystallization from methanol gave 57.5 g. (0.208 mole, 86.5%) of nortricyclanone tosylhydrazone, m.p. 165–165.5° dec. Three additional recrystallizations from methanol afforded an analytical sample, m.p. 165.5–166.0° dec.

*Anal.* Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.84; H, 5.84; N, 10.14; S, 11.61. Found: C, 60.88; H, 5.92; N, 10.19; S, 11.85.

**Photolysis of Nortricyclanone Tosylhydrazone Sodium Salt (1) under Aprotic Conditions.**—Nortricyclanone tosylhydrazone (1.00 g., 3.62 mmoles) was dissolved in 75 ml. of freshly distilled tetrahydrofuran.[24] Sodium hydride (0.10 g., 0.19 g. of a 52% dispersion in mineral oil, 4.2 mmoles) was added and the air above the mixture was replaced by dry nitrogen. The mixture was stirred for several hours to ensure complete conversion of the tosylhydrazone to its sodium salt. The resulting white suspension was stirred magnetically and irradiated for 4 hr., by the end of which time evolution of nitrogen apparently had ceased. The tan suspension was diluted with 600 ml. of water and extracted with ten 100-ml. portions of ether. The combined ether extracts were washed ten times with water, and then dried over magnesium sulfate. The solvent was distilled through a helix-packed column[25a]; the residual light brown oil was chromatographed over 10 g. of Fisher alumina in a 10 × 0.5 in. column. Elution with

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[16] It is well known that diazo compounds are intermediates in the *thermal* decomposition of sulfonylhydrazone salts [see, for example, J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963)]. In the photolysis of camphor tosylhydrazone sodium salt Dauben[2] observed a transient red color which he attributed to the diazo compound.

[17] W. R. Bambord and T. S. Stevens [*J. Chem. Soc.*, 4735 (1952)] obtained phenyl *p*-tolyl sulfone in 14% yield when benzaldehyde tosylhydrazone sodium salt decomposed in hot ethylene glycol. Powell and Whiting[16] and also Friedman and Shechter[16] have shown that this hydroxylic solvent favors carbonium ion formation *via* protonation of the intermediate diazo compound; thus the sulfone probably arises by combination of sulfinate ion with benzyl cation. The nortricyclyldiazonium ion cannot be an intermediate in our reaction since sulfone yields are best when the medium is rigorously aprotic.

[18] V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960).

[19] A. J. Speziale, G. J. Marco, and K. W. Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960); D. Seyferth, S. O. Grim, and T. O. Read, *ibid.*, **82**, 1510 (1960).

[20] A variety of other "potentially divalent" species such as cyanide ion may prove effective at intercepting carbenes in aprotic media.

[21] Except where noted, melting points were determined on a Kofler micro hot stage and are corrected. N.m.r. spectra were measured at 60 Mc./sec. on a Varian Associates A-60 spectrometer using carbon tetrachloride as solvent and tetramethylsilane as internal standard. Photochemical experiments were performed with a Hanovia 450-w. Type L mercury lamp with a water-cooled quartz jacket and Pyrex filter. Microanalyses were carried out by Spang Microanalytical Laboratories, Ann Arbor, Mich.

[22] K. Heyns and H. Paulsen, *Angew. Chem.*, **72**, 349 (1960); G. A. Olah and H. W. Quinn, *J. Inorg. Nucl. Chem.*, **14**, 295 (1960). Silver fluoborate is also available from Chemicals Procurement Laboratories, Inc., 18-17 130th Street, College Point, N. Y.

[23] H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

[24] Tetrahydrofuran and diglyme (dimethyl ether of diethylene glycol) were used interchangeably with no significant effect on the reaction course. They were purified by distillation from lithium aluminum hydride.

[25] (a) G.l.c. analysis of the solution after concentration to a volume of 10 ml. revealed the presence of 4-ethynylcyclopentene (**4**) in 6–8% yield. This should not be taken as an accurate measure of the yield of **4**, as some codistillation of the volatile hydrocarbon with the large volume of solvent may have occurred. (b) In chloroform.

20% benzene in pentane afforded nortricyclanone azine (*vide infra*), m.p. 129–133° (uncor., Hershberg apparatus), 15 mg., 3.9%. Further elution with benzene afforded 3-nortricyclyl *p*-tolyl sulfone, m.p. 72–74°, 0.351 g., 39%. A mixture of this material and an authentic sample of 3-nortricyclyl *p*-tolyl sulfone, m.p. 76–77°, prepared by the method of Cristol, *et al.*,[13] melted at 73–76°, and their infrared spectra were identical.. Yields of the sulfone ranged from 34 to 50% in other runs.

**3-Nortricyclyl *p*-Tolyl Sulfone (5) by Thermal Decomposition of 1.**—Nortricyclanone tosylhydrazone (0.240 g., 0.869 mmole) was dissolved in 15 ml. of diglyme, and excess sodium hydride (0.058 g. of 54% dispersion) was added. The mixture was refluxed for 0.5 hr., cooled, and thrown into 50 ml. of cold water. The resulting oily suspension was extracted several times with pentane; the combined extracts were washed with 10% sodium hydroxide and then with several portions of water, and dried over sodium sulfate. Removal of the solvent at reduced pressure gave 0.096 g. of viscous brown residue, which was chromatographed on 7 g. of Fisher alumina. Elution with benzene afforded 0.023 g. (10%) of crude sulfone. This was recrystallized from ligroin (b.p. 60–68°), yielding 14 mg. of tan crystals whose infrared spectrum was identical with that of authentic material.

**Nortricyclanone N-Tosyl-3-nortricyclylhydrazone (6) by Photolysis.**—Nortricyclanone tosylhydrazone (1.00 g., 3.62 mmoles) was dissolved in 100 ml. of dry diglyme.[24] Dry sodium hydride (0.18 g., 7.5 mmoles) was added; the mixture was magnetically stirred for 15 min. and then irradiated with continued stirring for 3 hr. The resulting white suspension was diluted with 750 ml. of water and extracted with ten 100-ml. portions of pentane. The pentane extracts were washed several times with water and dried over sodium sulfate. Solvent was distilled through a Vigreux column until the residue had been concentrated to a volume of 40 ml. When this residue was chilled to −78°, a white solid, m.p. 137–142°, separated. This was shown (*vide infra*) to be nortricyclanone N-tosyl-3-nortricyclylhydrazone (0.34 g., 0.925 mmole, 51.5%). Four recrystallizations from heptane afforded an analytical sample, m.p. 162–163°.

*Anal.* Calcd. for $C_{21}H_{24}N_2O_2S$: C, 68.44; H, 6.56; S, 8.70. Found; C, 68.12; H, 6.32; S, 8.58.

The n.m.r. spectrum consisted of an AB quartet at $\tau$ 2.45 and 2.76 ($J$ = 8 c.p.s.), singlets at 7.43 and 7.62, and complex absorption from 7.78 to 9.17, relative areas 4:1:3:16, respectively. Presence of nitrogen in this neutral compound was indicated by sodium fusion. The infrared spectrum[25b] exhibited absorption at 5.97 (C=N), 8.60 (sulfonamide), and 12.4 $\mu$ (tricyclene).[3] No N–H stretching absorption was evident. The ultraviolet spectrum was measured in acetonitrile: $\lambda_{max}$ 222 m$\mu$ ($\epsilon$ 11,500), 262 sh (2540), and 274 (1400). That of nortricyclanone tosylhydrazone in the same solvent displayed these features: $\lambda_{max}$ 225 m$\mu$ ($\epsilon$ 14,500), 263 sh (1370), and 274 (675).

**Nortricyclanone Azine (7).**—Nortricyclanone (5.4 g., 0.050 mole) was placed in a 50-ml. three-necked flask fitted with a dropping funnel and condenser; the flask was heated to 80–100° under nitrogen. A solution of hydrazine hydrate (1.25 g., 0.025 mole) in 15 ml. of absolute ethanol containing 3 drops of glacial acetic acid was added to the flask dropwise with stirring. Boiling under reflux was continued for 2 hr. after addition was complete; the solution then was allowed to stand overnight. The solvent was taken off at reduced pressure, and the yellow crystalline residue recrystallized from ligroin (b.p. 60–68°). Nortricyclanone azine was obtained in 66% yield (3.50 g., 0.016 mole). A second recrystallization from ether gave white crystals, m.p. 142–145°. An analytical sample, m.p. 143–143.5° (uncor., Hershberg apparatus) was obtained after four recrystallizations from heptane.

*Anal.* Calcd. for $C_{14}H_{16}N_2$: C, 79.20; H, 7.60; N, 13.20. Found: C, 79.50; H, 7.57; N, 13.14.

**Nortricyclanone 3-Nortricyclylhydrazone (8).**—A slurry of lithium aluminum hydride (0.190 g., 5.0 mmoles) in 10 ml. of ether was boiled under reflux with stirring in a nitrogen atmosphere. To this was added dropwise a solution of nortricyclanone azine (1.06 g., 5.0 mmoles) in ether. The mixture was refluxed for 8 hr. after addition was complete. Water (1 ml.) was added and the mixture was filtered through a Filter Cel–magnesium sulfate pad. The ether was taken off under reduced pressure, affording 1.03 g. of nearly white solid (m.p. 131–132°, uncor., Hershberg apparatus). Recrystallization from ligroin resulted in white rosettes. Presence in the infrared spectrum[25b] of N–H stretching (3.04 $\mu$) and C=N stretching (5.95 $\mu$) absorption bands indicated that this substance was the hydrazone 8. The rosettes, which were quite susceptible to air oxidation, were used directly in the following experiment.

**Nortricyclanone N-Tosyl-3-nortricyclylhydrazone (6) by Tosylation of (8).**—Triethylamine (0.048 g., 0.47 mmole) was dissolved in 2 ml. of sulfolane[26] and tosyl chloride (0.090 g., 0.47 mmole) was added. Nortricyclanone 3-nortricyclylhydrazone (0.101 g., 0.47 mmole) then was introduced. As the temperature was raised, the hydrazone gradually dissolved; solution was complete by the time the temperature had reached 140–150°. After about 3 hr. at this temperature, the dark brown solution was quenched in cold water, whereupon a brown oil separated. The oil was extracted into ether and washed successively with dilute hydrochloric acid, dilute sodium hydroxide, and water. The ether solution was dried over sodium sulfate and stripped under reduced pressure. The heavy brown oil which remained was dissolved in 1:4 benzene–pentane and chromatographed on 5 g. of Fisher alumina. Elution with 1:1 benzene–pentane afforded 0.018 g. of colorless oil, which soon crystallized. After one recrystallization from hexane, nortricyclanone N-tosyl-3-nortricyclylhydrazone was obtained as small white prisms, m.p. 158.5–160°. A mixture of this material with that obtained in the photolytic experiment (*vide supra*), m.p. 155.5–157°, melted at 155–156°, and their infrared spectra were identical.

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(26) The sulfolane (tetramethylene sulfone) was obtained from the Phillips Petroleum Co. and was vacuum distilled before use.