

(400 ml). The solution was concentrated on a steam bath to a residue that crystallized from glacial acetic acid as colorless prisms (50.6 g, 81%), mp 167.5–169.5°.

Anal. Calcd for $C_{16}H_{16}Br_2O_4$: C, 44.47; H, 3.73; Br, 36.99. Found: C, 44.64; H, 3.81; Br, 37.08.

2,4,9-Trimethyl-7H-furo[3,2-f][1]benzopyran-7-one (IXb).—6-Acetoxy-5-(2',3'-dibromopropyl)4,7-dimethylcoumarin (50.6 g, 0.117 mole) was heated under reflux for 105 min with a solution of sodium (15.0 g) in absolute ethanol (1 l.). The cooled solution was poured into a mixture of ice (ca. 2 kg) and 5% hydrochloric acid (ca. 1.5 l.) and the precipitate was washed with 5% aqueous sodium hydroxide and recrystallized from 95% ethanol to obtain colorless prisms (16.3 g, 61%), mp 218–220°.

Anal. Calcd for $C_{14}H_{12}O_8$: C, 73.67; H, 5.30. Found: C, 73.26; H, 5.75.

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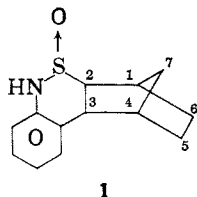
The Addition of N-Sulfinylaniline to Bicycloalkenes

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The reaction between N-sulfinylaniline^{2,3} and norbornene has been reported⁴ to yield adduct 1. It was not possible however to assign an *exo* or *endo* configura-



tion to adduct 1 based on its nmr spectrum. It has been well established that *exo* adducts are formed exclusively when norbornene is treated with suitable reagents such as aryl azides,⁵ or nitrosyl chloride.⁶ The *exo* configuration for 1 is therefore likely *a priori*; definite proof of this configuration will be presented below.

Refluxing equimolar quantities of N-sulfinylaniline and norbornadiene yielded two products, adduct 2 with mp 186–187° (42% yield), and an adduct 3, mp 306–307° (22% yield). Elemental analyses indicated that the former compound was a 1:1 adduct, and the latter a 2:1 adduct. The infrared spectra of both adducts exhibited N–H and S–O stretching frequencies.

(1) Abstracted from the Ph.D. dissertation of A. Macaluso presented to Tulane University, 1965.

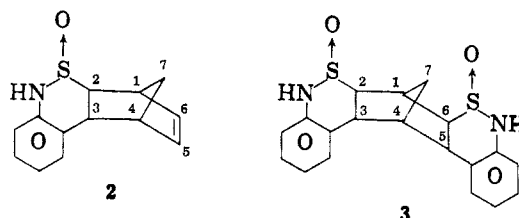
(2) G. Kresze, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1966, Chapter 13.

(3) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem. Intern. Ed. Engl.*, **1**, 89 (1962).

(4) G. R. Collins, *J. Org. Chem.*, **29**, 1688 (1964). This paper was published when the experiments described here were essentially completed.

(5) J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 42 (1954).

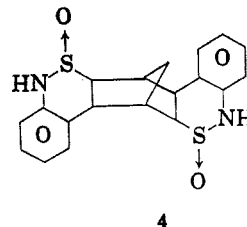
(6) J. Meinwald, Y. C. Meinwald, and T. N. Baker, Jr., *J. Am. Chem. Soc.*, **85**, 2513 (1963).



The hydrogenation of 2 at room temperature with palladium-over-carbon catalyst yielded 1 which established that compounds 1 and 2 have either both the *exo* configuration or both the *endo* configuration. That 2, and consequently 1, is the *exo* adduct may be concluded by examining its nmr spectrum,⁷ which may be interpreted as follows: a multiplet from 2.65 to 3.20, which integrates for four phenyl protons; $H_{5,6}$, signal at 3.49; $H_{2,3}$ at 6.65–6.68; H_1 at 6.70; H_4 at 6.99; $H_{7\text{syn}}$ at 7.90; and $H_{7\text{anti}}$ at 8.45. The signal at 6.70 was designated for H_1 since the presence of sulfur was considered to effect the bridgehead proton H_1 more so than the phenyl group effects the bridgehead proton H_4 .

Consistent values for the major coupling constants between various protons of norbornane derivatives have been reported.^{8–10} The coupling constant for H_1 and $H_{2\text{exo}}$ was reported to fall in the range 3.8–5.6 cps, while the J value for H_1 and $H_{2\text{endo}}$ was approximately 1 cps. The presence of an *exo* proton in compound 2 should thus cause quite noticeable splitting with the bridgehead proton. In the observed spectrum however the bridgehead protons ($H_{1,4}$) are only very slightly split, $J < 1$ cps, indicative of the presence of an *endo* proton on C-2. It is clear then that compound 2 has the *exo* configuration. This also holds true for adduct 1 since it may be formed by the hydrogenation of 2.

For compound 3 the nmr spectrum may be interpreted as follows: a multiplet from 2.45 to 3.10 which integrates for eight phenyl protons; $H_{2,3,5,6}$ signal at 6.02; H_1 at 6.69; H_4 at 7.42; and $H_{7\text{anti}}$, $H_{7\text{syn}}$ at 7.90. The bridgehead protons ($H_{1,4}$) are very slightly split, $J < 1$ cps, and thus indicative of *exo* addition. The nonequivalence of H_1 and H_4 confirmed the structure of the adduct as 3, since in the alternate possibility (4) the bridgehead protons become equivalent.



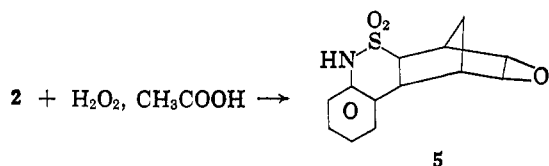
Treatment of adducts 1, 2, and 3 with lithium aluminum hydride in tetrahydrofuran at room temperature or at reflux led to essentially quantitative recovery of the starting materials. Adduct 2 when treated with 30% hydrogen peroxide in acetic acid yielded the epoxy

(7) All peak assignments are given in τ units.

(8) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

(9) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 559 (1964).

(10) (a) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); (b) J. C. Davis and T. T. Van Auken, *ibid.*, **87**, 3900 (1965).



sulfonamide (5), identified by the presence of the SO₂ band and epoxide stretching frequencies in the infrared.

Treatment of 5-methylene-2-norbornene with *N*-sulfinylaniline yielded a single product (6). Elemental analysis was indicative of a 1:1 adduct; the infrared spectrum showed the presence of the N-H, S-O, and terminal methylene stretching frequencies. The presence of an *exo*-methylene group in 6 was also confirmed by the nmr spectrum, which may be interpreted as follows: a multiplet signal at 2.65 which integrated for four phenyl protons; a well-defined quartet from 6.05 to 6.65 for two terminal methylene protons; H_{2,3} signal at 7.13; H₄ at 7.60; and H₁, H₆, H_{7 syn}, H_{7 anti} at 8.11.

p-Methyl-*N*-sulfinylaniline yielded analogous *exo* adducts with norbornene (adduct 7) and 5-methylene-2-norbornene (adduct 8). With norbornadiene only a 1:1 *exo* adduct was isolated (adduct 9). Reactions of the bicyclic alkenes with 2,6-dimethyl-*N*-sulfinylaniline were examined since blocking of the *ortho* positions might induce addition across the N=S bond with the homoconjugated norbornadiene in a 1,4 fashion. Adduct formation was not observed, however.

Experimental Section

Elemental analyses were by Galbraith Laboratoris Inc., Knoxville, Tenn. All nmr spectra were obtained with a Varian A-60 spectrometer with tetramethylsilane as internal standard; peak assignments were in τ units. Infrared spectra were determined in potassium bromide pellets with a Beckman IR-5. A Wilkens Instrument Autoprep Model A-700 with helium as carrier gas was used for chromatography work.

N-sulfinylaniline and derivatives were prepared from the corresponding amines and thionyl chloride.³ The bicyclic alkenes were obtained commercially.

Compound 1 was prepared as described previously, mp 229–231° (lit.⁴ 230–231°).

Compounds 2 and 3 were prepared by adding *N*-sulfinylaniline (13.9 g 0.1 mole) dropwise with stirring to norbornadiene (9.2 g 0.1 mole) and refluxing the mixture for 20 min under a dry nitrogen atmosphere. Upon cooling a precipitate was formed which was isolated by filtration. Recrystallization from carbon tetrachloride afforded 9.7 g (42%) of compound 2 as colorless needles, mp 186–187°. Pertinent infrared data are as follows: NH stretching frequency, 3190 cm⁻¹; SO stretching frequency, 1053 cm⁻¹.

Anal. Calcd for C₁₃H₁₃NOS: C, 67.50; H, 5.67; N, 6.06; S, 13.86. Found: C, 67.19; H, 5.67; N, 5.88; S, 13.64.

A second solid material was recrystallized from methanol to yield 8.2 g (22%) of compound 3 as colorless needles, mp 306–308°. Infrared stretching frequencies are as follow: NH, 3160 cm⁻¹; SO, 1050 cm⁻¹.

Anal. Calcd for C₁₅H₁₅N₂O₂S₂: C, 61.59; H, 4.89; N, 7.56; S, 17.30. Found: C, 61.41; H, 5.01; N, 7.50; S, 17.28.

When the reaction mixture was refluxed for 45 min the yields of 2 and 3 were 7.1 g (31%) and 14.1 g (38%), respectively.

Compound 2 (0.18 g 0.7 mmole) was dissolved in glacial acetic acid (20 ml) and added to 0.027 g of 10% palladium-over-carbon catalyst. The hydrogenation was performed according to the procedure of Pack and co-workers. The reaction mixture was filtered and the filtrate was neutralized with sodium bicarbonate to produce a colorless, crystalline mass. Isolation of the precipitate yielded 0.16 g (88%) of compound 1, identified by mixture melting point and infrared and nmr spectra.

Compound 5 was obtained by dissolving 2 (2.3 g 0.01 mole) in glacial acetic acid (5 ml) to which was added slowly hydrogen

peroxide (30%, 5 ml). The reaction mixture was allowed to stand for 24 hr, and then poured over cracked ice. The formed precipitate was isolated, yielding 1.7 g (65%) of 5, mp 122–124°. Pertinent infrared data are as follows: SO₂, 1140 and 1120 cm⁻¹; NH, 3290 cm⁻¹.

Anal. Calcd for C₁₃H₁₃NO₂S: C, 59.17; H, 4.98; N, 5.32; S, 12.18. Found: C, 59.30; H, 5.15; N, 5.40; S, 12.18.

Compound 6 was obtained from 5-methylene-2-norbornene and *N*-sulfinylaniline by the procedure described for 2. Reflux time was 20 min. Recrystallization of crude product from carbon tetrachloride yielded 37% of 6, mp 222–224°. Pertinent infrared stretching frequencies are as follows: NH, 3153 cm⁻¹; SO, 1048 cm⁻¹.

Anal. Calcd for C₁₄H₁₄NOS: C, 68.54; H, 6.16; N, 5.71; S, 13.07. Found: C, 68.26; H, 6.18; N, 5.48; S, 13.06.

Compound 7 was obtained from norbornene and *p*-methyl-*N*-sulfinylaniline by the procedure described for 2 in 30% yield with a reaction time of 5 hr, mp 235–236° (from ethanol). Pertinent infrared stretching frequencies are as follows: NH, 3220 cm⁻¹; SO 1060 cm⁻¹. Increase of reaction time to 60 hr improved the yield slightly to 34%. Decomposition begins to occur 210–212° (lit.⁴ 211–214°).

Compound 8 was obtained from norbornadiene and *p*-methyl-*N*-sulfinylaniline by the procedure described for 2 in a 36% yield, mp 205–206.5° (from ethanol). Decomposition begins to occur at 170–174°. Pertinent infrared stretching frequencies are as follows: NH, 3220 cm⁻¹; SO, 1060 cm⁻¹; nmr spectrum (in DCCl₄) 2.45 (NH), 3.00–3.40 (three-phenyl protons), 3.60 (H_{5,6}), 6.90 (H_{2,3}), 7.05 (H₁), 7.15 (H₄), 7.75 (methyl protons), 8.00–8.20 (H_{7 syn}), 8.70–8.85 (H_{7 anti}).

Anal. Calcd for C₁₄H₁₆NOS; C, 68.54; H, 6.16; N, 5.71; S, 13.07. Found: C, 68.32; H, 6.32; N, 5.42; S, 13.34.

Compound 9 was prepared from 5-methylene-2-norbornene by the procedure described for 2 in 30% yield, mp 218–219° (from ethanol). Decomposition begins to occur at 142–147°. Pertinent infrared stretching frequencies are as follows: NH, 3172 cm⁻¹; SO, 1057 cm⁻¹; nmr spectrum (in TFA) 2.83–3.20 three phenyl protons), 6.25–6.55 (doublet, terminal methylene protons), 7.05–7.20 (multiplet, H_{2,3}), 7.60 (broad, H₄ and methyl protons), 8.00, (H_{1,6,7 syn}, 7 anti).

Anal. Calcd for C₁₅H₁₇NOS: C, 69.46; H, 6.61; N, 5.40; S, 12.36. Found: C, 69.30; H, 6.68; N, 5.54; S, 12.57.

Constituents of *Helenium* Species. XX. Virginolide, a New Guaianolide from *Helenium* *virginicum* Blake^{1,2}

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In 1936, Blake³ reported the discovery in Augusta County, Va., of a *Helenium* colony closely related to, but apparently different from, *Helenium autumnale* L. and accorded it separate species status as *Helenium virginicum* Blake. This separation has been questioned.⁴

Through the courtesy of Dr. B. H. Braun we came into possession of *H. virginicum* which had been collected near the type locality. It appeared possible

(1) Supported in part by grants from the United States Public Health Service (GM-05814) and the Mallinckrodt Chemical Works.

(2) Previous paper: A. Romo de Vivar, L. Rodriguez-Hahn, J. Romo, M. V. Lakshmikantham, R. N. Mirrington, J. Kagan, and W. Herz, *Tetrahedron*, **22**, 3279 (1966).

(3) S. F. Blake, *Claytonia*, **3**, 13 (1936).

(4) Private communication from the late Dr. H. F. L. Rock, Department of Biology, Vanderbilt University, who concluded that this geographically severely restricted material possesses "no sound morphological features which are distinctive."