$$CH_3S(O)OCH_3 + Cl_2 \longrightarrow CH_3SO_2Cl + CH_3Cl \quad (3)$$

tion but takes place at a very slow rate or is inhibited at −20°. Some of the sulfonyl chloride may also result from the attack of methanesulfenyl chloride on the alkoxide oxygen of the sulfinic ester[8] (eq 4).

$$CH_3S(O)OCH_3 \xrightarrow{CH_3SCl} [CH_3S(O)OSCH_3] + CH_3Cl \quad (4)$$
$$\xrightarrow{CH_3SCl} CH_3SO_2Cl + CH_3SSCH_3$$

The thiolsulfonic ester by-product has two possible sources. Thiolsulfinic esters, RS(O)SR, among the postulated intermediate compounds referred to above, are known to disproportionate in the presence of acid[7] into the corresponding thiosulfonic esters and disulfides (eq 5).

$$2RS(O)SR \longrightarrow RSO_2SR + RSSR \quad (5)$$

We have also demonstrated that sulfenyl chlorides react with sulfinic esters by attack at the sulfoxide sulfur to yield thiosulfonates[8] (eq 6).

$$CH_3S(O)OCH_3 + CH_3SCl \longrightarrow CH_3SO_2SCH_3 + CH_3Cl \quad (6)$$

The experimental procedure outlined below is based on the chlorination of methyl disulfide in methanol. The limits to the applicability of the reaction have not yet been determined. Our experience suggests that sulfinic esters with higher molecular weights may be obtained in better yields. Using procedures similar to or slightly modified from those described, the following sulfinic esters were obtained in the yields indicated: ethyl methanesulfinate, $CH_3S(O)OC_2H_5$, 78%; *n*-butyl methanesulfinate, $CH_3S(O)OC_4H_9$-*n*, 84%; and ethyl ethanesulfinate, $C_2H_5S(O)OC_2H_5$, 75%.

Experimental Section

Chlorination of Methyl Disulfide in Methanol. A mixture of methyl disulfide (47.1 g, 0.5 mol) and methanol (67.3 g, 2.1 mol) was placed in a three-neck flask fitted with mechanical stirrer, an inlet tube terminating above the liquid surface, an internal thermometer, and an outlet protected by a drying tube. After the reaction mixture was cooled by means of a Dry Ice–acetone bath to −20°, chlorine was passed in from a small tank previously weighed and supported on a platform balance. Addition of chlorine was regulated so that the temperature was maintained at −20 to −25°. (Lower temperature did not seem to have an adverse effect other than to cause problems due to the separation of crystals, but higher temperatures favored the formation of methanesulfonyl chloride.) As the reaction proceeded, the reddish-orange color of methanesulfenyl chloride developed but faded when the stoichiometric amount of chlorine (106.4 g, 1.5 mol) was approached. The best yields of sulfinic ester and the least amounts of sulfonyl chloride were obtained when the stoichiometric amount of chlorine was used. At the end of the reaction the reaction mixture should be water clear or only faintly colored.

After the addition of chlorine was completed, the cold reaction mixture was transferred immediately to a distilling flask having a thermometer well, and attached to the 18-in. Vigreux column of a vacuum still connected to an efficient water pump. The hydrogen chloride and methyl chloride were removed at reduced pressure with gentle heat. (Because of the toxic nature of methyl chloride, it is important that the water pump be located in a hood.) The methyl chloride, if desired, may be collected in a Dry Ice trap located between the water pump and the still. During the removal of the gaseous products the temperature in the pot remained well below 0°.

The reaction mixture remaining when the pot temperature reached 25° (18 mm), analyzed by nuclear magnetic resonance (nmr) on a Varian A-60, consisted of approximately 86% methyl methanesulfinate, $CH_3S(O)OCH_3$; 6% methanesulfinyl chloride, $CH_3S(O)Cl$; 4% methanesulfonyl chloride, CH_3SO_2Cl; and 4% methyl methanethiolsulfonate, $CH_3S(O_2)SCH_3$.

After removal of the gaseous products, the crude reaction mixture was immediately treated with 10 ml of methanol to convert the sulfinyl chloride present to ester and was then distilled, yielding 71 g of product boiling over a 10° range which included the boiling point of methyl methanesulfinate, 46° (20 mm). This crude product, which gave a strong Beilstein test for chlorine, was diluted with an equal volume of ether and treated with 10 g of *p*-toluidine. After standing for 30 min to permit complete reaction between the sulfonyl chloride impurity and the amine, the amine hydrochloride was removed by suction filtration and the ether solution was treated with an additional 2 g of *p*-toluidine and allowed to stand until it was evident that no further amine hydrochloride would form. Ether was then removed at atmospheric pressure and the residue was distilled under reduced pressure, yielding 50.5 g (54% yield) of colorless, chlorine-free liquid, bp 49–51° (30 mm), $n^{27}D$ 1.4352 (lit.[2] $n^{25}D$ 1.4360). This fraction remained colorless on standing at room temperature but, had it darkened due to *p*-toluidine contamination, redistillation after adding 2 ml of concentrated sulfuric acid would have given a stable product.

Acknowledgment. This research has been made possible by a grant from the Faculty Research Fund of the University of Maine.

Registry No. Methyl disulfide, 624-92-0; methanol, 67-56-1; $CH_3S(O)OCH_3$, 666-15-9; $CH_3S(O)OC_2H_5$, 819-75-0; $CH_3S(O)OC_4H_9$-*n*, 675-87-6; $C_2H_5S(O)OC_2H_5$, 673-54-1.

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Diels–Alder Cycloadditions of Sulfonyl Cyanides with Cyclopentadiene. Synthesis of 2-Azabicyclo[2.2.1]hepta-2,5-dienes

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Received September 25, 1973

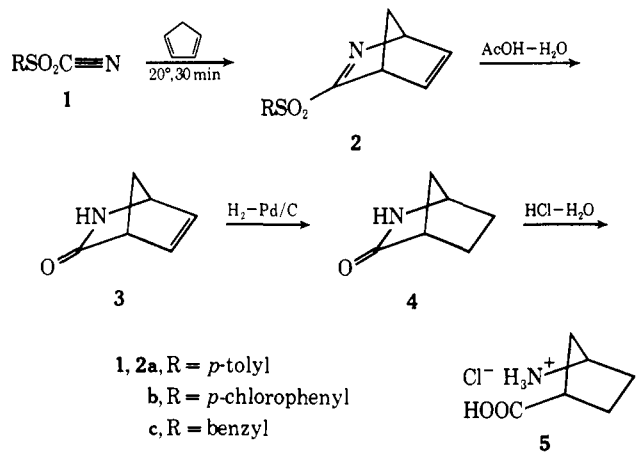
Diels–Alder cycloadditions of nitriles with dienes have been known for many years.[1] To date, however, the expected primary cycloadducts have not been isolated. Rather, at the temperatures at which these reactions usually are carried out (200–400°), aromatization to pyridine derivatives occurs,[2] either by dehydrogenation of the initially formed 2,5-dihydropyridines,[1] or, in case of bicycloadducts, by various types of ring-opening reactions.[1,3,4] Loss of carbon monoxide from the cycloadducts of cyclopentadienones is a typical example of the latter process.[1]

Recently, we established that sulfonyl cyanides are good dienophiles.[5] For example, tosyl cyanide (**1a**) reacts at room temperature with 2,3-dimethylbutadiene, but even under these mild conditions the primary cycloadduct was not observed.[6] We now wish to report the even faster reaction between cyclopentadiene and a number of sulfonyl cyanides. At room temperature, tosyl cyanide (**1a**), dissolved in cyclopentadiene, is converted in 30 min into 3-tosyl-2-azabicyclo[2.2.1]hepta-2,5-diene (**2a**), isolated in 95% yield. This is the first example of the formation of a primary Diels–Alder cycloadduct of a nitrile not accompanied by aromatization. *p*-Chlorobenzenesulfonyl cyanide (**1b**) and phenylmethanesulfonyl cyanide (**1c**) react similarly to **2b** and **2c** (84 and 73% yield, respectively). Compounds **2** are of particular interest because of their 2-azanorbornadiene structure, which has not been reported previously.

The cycloadducts 2 are rather unstable and decompose readily at room temperature, especially when exposed to air. The instability may be partly due to the presence of a C-sulfonyl imino structural unit, which has been reported thus far only in compounds stabilized by α-heteroatoms.[5a] This functionality is apparently sensitive to hydrolysis.[5a]

The proof of structure was elaborated for **2a** as indicated in Scheme I. As expected **2a** was hydrolyzed smoothly with acetic acid and water (or, likewise, with aqueous sodium hydroxide in dioxane) to the unsaturated lactam **3** (64% yield), which was reduced catalytically to the saturated lactam **4** (in 89% yield). Acid-catalyzed hydrolysis of **4** gave in 82% yield compound **5**, identical with an authentic sample.[7]

Scheme I



1

2

3

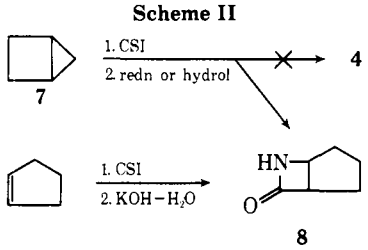
4

5

1, 2a, R = *p*-tolyl
b, R = *p*-chlorophenyl
c, R = benzyl

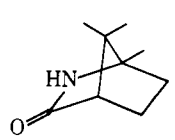
The spectral data of **2–5** (see Experimental Section) agree with the proposed structures. However, for **4** there is a conflict with literature data. Recently, the groups of Moriconi[8] and Paquette[9a] independently assigned structure **4** to a product obtained through the addition of chlorosulfonyl isocyanate (CSI) to bicyclo[2.1.0]pentane (**7**, Scheme II). Their spectral data do not agree with those

Scheme II



8

for our compound, which is correctly represented by structure **4**. We find a C=O stretch at 1690 cm^{-1}, consistent with a γ-lactam structure. Lactam **6** of comparable struc-



6

ture is reported[10] to have a C=O band at 1700 cm^{-1}. The compound obtained by Moriconi and Paquette shows, as the most striking difference, a C=O stretch in the 1745–1750-cm^{-1} region, indicating a β-lactam structure rather than a γ-lactam. By repeating experiments, we have demonstrated that the product[9a] from CSI and bicyclopentane is actually β-lactam **8**, previously obtained by Bestian,[11] *et al.*, *via* CSI addition to cyclopentene. Apparently, in the experiments of Moriconi and Paquette **7** was isomerized to cyclopentene prior to addition of CSI, or, alternatively, a carbonium ion rearrangement took place in the zwitterionic intermediate formed from **7** and CSI.[8,9]

Further evidence for our structure **4** was achieved by lactamization of the known *cis*-3-aminocyclopentanecarboxylic acid[7] (free amino acid corresponding to **5**) by the method of Noyes and Potter[12] to give a compound identical by ir, pmr, and glc with the product of hydrogenation of **3** discussed above.

Experimental Section

3-Tosyl-2-azabicyclo[2.2.1]hepta-2,5-diene (2a). A solution of tosyl cyanide[13] (**1a**, 1.00 g, 5.52 mmol) in 15 ml of freshly prepared, and dried ($MgSO_4$), cyclopentadiene was, after standing for 30 min at room temperature, evaporated to dryness *in vacuo* without heating. The solid residue was washed with cold, anhydrous ether, providing 1.30 g (95% yield) of **2a** as a white solid, mp 76–78°, which was crystallized under nitrogen from dichloromethane–petroleum ether (bp 40–60°) at a temperature not exceeding 20° to give an analytical sample: mp 79–81°; ir (KBr) 1310, 1290, and 1155 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 2.04 (d, 1, J = 8 Hz, CHH), 2.26 (d, 1, J = 8 Hz, CHH), 2.48 (s, 3, CH_3), 4.4 (m, 1, CH), 5.4 (m, 1, CH), 6.8 (m, 2, CH=CH), 7.2–7.9 (4, aromatic).

Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.31; N, 5.66; S, 12.96. Found: C, 62.8; H, 5.3; N, 5.7; S, 12.6.

3-*p*-Chlorophenylsulfonyl-2-azabicyclo[2.2.1]hepta-2,5-diene (2b) was prepared, analogously to **2a**, from *p*-chlorobenzenesulfonyl cyanide[13] (**1b**) in a yield of 84%: mp 71–74°; ir (Nujol) 1320 and 1150 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 2.00 (d, 1, J = 8 Hz, CHH), 2.23 (d, 1, J = 8 Hz, CHH), 4.5 (m, 1, CH), 5.3 (m, 1, CH), 6.7–7.0 (m, 2, CH=CH), 7.4–7.9 (4, aromatic).

Anal. Calcd for $C_{12}H_{10}ClNO_2S$: C, 53.83; H, 3.76; Cl, 13.24; N, 5.24; S, 11.98. Found:[14] C, 5.31; H, 4.0; Cl, 13.4; N, 5.2; S, 11.8.

3-Benzylsulfonyl-2-azabicyclo[2.2.1]hepta-2,5-diene (2c) was prepared, analogously to **2a**, from phenylmethanesulfonyl cyanide[15] (**1c**). Crude **2c** was precipitated from the reaction mixture by addition of petroleum ether without removal of the excess of cyclopentadiene. The yield after crystallization was 73%: mp 56–58°; ir (Nujol) 1310 and 1140 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 1.9–2.3 (m, 2, CH_2), 4.3 (m, 1, CH), 4.54 (s, 2, CH_2SO_2), 5.5 (m, 1, CH), 6.6–7.0 (m, 2, CH=CH), 7.2–7.5 (m, 5, aromatic).

Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.31; N, 5.66; S, 12.96. Found:[14] C, 62.3; H, 5.5; N, 5.5; S, 13.0.

2-Azabicyclo[2.2.1]hept-5-en-3-one (3). Azanorbornadiene **2a** (0.89 g, 3.60 mmol) was dissolved in 5 ml of acetic acid. A white solid, which formed immediately, was separated after addition of the mixture to 25 ml of ice-water. The solid (0.35 g, 66% yield) was identified by melting point, 90–92° dec (lit.[16] mp 87° dec), and ir as *p*-tolylsulfinyl *p*-tolyl sulfone. The mother liquor was extracted, after neutralization (<20°) with concentrated sodium hydroxide, with dichloromethane (4 × 100 ml). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give a yellow oil (0.34 g), which was sublimed at 60–80° (0.1 mm), affording 0.25 g (64%) of **3** as a white solid, mp 51–53°. Resublimation gave an analytical sample: mp 54–55°; ir (KBr) 3240 (br, NH), 1690 cm^{-1} (C=O); pmr ($CDCl_3$) δ 2.20 (d of t, 1, J = 8 and 2 Hz, CHH), 2.39 (d of 5, 1, J = 8 and 2 Hz, CHH), 3.2 (m, 1, CH), 4.4 (m, 1, CH), 6.6–6.9 (m, 2, CH=CH), 6.2 (br, 1, NH).

Anal. Calcd for C_6H_7NO: C, 66.06; H, 6.46; N, 12.83. Found: C, 66.1; H, 6.5; N, 12.9.

2-Azabicyclo[2.2.1]heptan-3-one (4). A solution of **3** (250 mg, 2.29 mmol) in 50 ml of ethyl acetate was reduced in a Parr apparatus (using 500 mg of 5% Pd/C and 3 atm H_2) for 60 hr at room temperature. After filtration and removal of solvent *in vacuo*, the residual colorless oil[17] (227 mg, 89%) gave a white, hygroscopic solid upon sublimation at 80° (0.05 mm), mp 106–109°, which liquefied immediately when exposed to air: ir (neat) 3260 (br, NH), 1690 cm^{-1} (C=O); pmr (CCl_4) 1.2–2.1 (m, 6, 3 CH_2), 2.6 (m, 1, CH), 3.9 (m, 1, CH), 7.8 (br, 1, NH); mass spectrum (70 eV) m/e (rel intensity) 111 (M^+, 100), 83 (67), 77 (65), 55 (44), 44 (30).

Anal. Calcd for C_6H_9NO: C, 64.86; H, 8.15; N, 12.60. Found: C, 64.8; H, 8.3; N, 12.9.

Lactam **4** was synthesized independently from *cis*-3-aminocyclopentanecarboxylic acid according to the method of Noyes and

Potter.[12] A solution of *cis*-3-aminocyclopentanecarboxylic acid[7] (200 mg, 1.55 mmol) in 1 ml of acetic anhydride was refluxed for 0.5 hr. After removal of the solvent *in vacuo*, dichloromethane was added and the solution was filtered. Evaporation of dichloromethane afforded *N*-acetyl-2-azabicyclo[2.2.1]heptan-3-one as a colorless oil (185 mg, 78%): ir (neat) 1750 (lactam C=O) and 1690 cm^{-1} (amide C=O); pmr (CCl_4) δ 1.4–2.1 (m, 6, 3 CH_2), 2.31 (s, 3, CH_3), 2.8 (m, 1, CH), 4.7 (m, 1, CH); mass spectrum (70 eV) *m/e* 153 (M^+).

A portion of this oil (168 mg) was heated at 30–40° with 0.5 g of 10% potassium hydroxide for 20 min. The solution was extracted with ether (2 × 25 ml), and the extract was dried ($MgSO_4$) and concentrated *in vacuo*, giving 26 mg (*ca.* 21%) of 4 as a colorless oil, identical with the compound described above by ir, pmr, and glc retention time.

From the water layer, an additional product, *cis*-3-acetylaminocyclopentanecarboxylic acid, was obtained by acidifying the water layer with concentrated hydrochloric acid and, thereafter, extracting with dichloromethane (50 ml). The extract was dried ($MgSO_4$) rapidly and concentrated to *ca.* 3 ml and the white precipitate (92 mg, 46%) was collected, mp 136–139°. An analytical sample, mp 144–146°, was obtained from ethanol-ether-petroleum ether: ir (KBr) 3350 (NHCO), 3000–2200 (COOH), 1705 (COOH), 1615 (amide I), 1560 cm^{-1} (amide II); pmr ($CDCl_3$) δ 1.5–2.3 (m, 9, CH_3, 3 CH_2), 3.0 (br, 1, CH), 4.4 (br, 1, CH), 6.2 (br, 1, NH), 8.8 (br, 1, COOH).

Anal. Calcd for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.1; H, 7.7; N, 8.4.

***cis*-3-Aminocyclopentanecarboxylic Acid Hydrochloride (5).** A solution of lactam 4 (45 mg, 0.40 mmol) in 10 ml of 5% hydrochloric acid was, after standing for 3 days at room temperature, concentrated *in vacuo*. Addition of acetone to the yellow oil gave 55 mg (82%) of 5 as a white solid, mp 142–145° (lit.[7] mp 145–146°), which was identical with an authentic sample[7] by mixture melting point, ir, and pmr: ir (KBr) 3300–2500 (v br, $-CO_2H$ and $-NH_3^+$), 1700 cm^{-1} (C=O); pmr (CD_3OD) δ 1.4–2.6 (m, 6, 3 CH_2), 3.0 (t-like m, 1, CH), 3.7 (t-like m, 1, CH).

Registry No. 1a, 19158-51-1; **1b,** 24225-00-1; **1c,** 49805-26-7; **2a,** 49805-27-8; **2b,** 49805-28-9; **2c,** 49805-29-0; **3,** 49805-30-3; **4,** 24647-29-8; **5,** 24647-29-8; cyclopentadiene, 542-92-7; *cis*-3-aminocyclopentanecarboxylic acid, 49805-32-5; *N*-acetyl-2-azabicyclo-[2.2.1]heptan-3-one, 49805-33-6; *cis*-3-acetylaminocyclopentanecarboxylic acid, 49805-34-7.

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(2) The reaction mixture obtained at 380° from cyanogen bromide and perfluoro-1,3-cyclohexadiene is reported[3] to contain, in addition to perhalopyridine, the primary adduct 3-bromo-1,4,5,6,7,7,8,8-octafluoro-2-azabicyclo[2.2.2]bicycloocta-2,5-diene in low yield (9%). This, together with a similar result from 1,3-dicyanoperfluoropropane,[3] is the only exception that has come to our knowledge.

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(17) Glc analysis (SE-30, 6 ft × 0.125 in.) of this oil at 150 and 200° showed one single peak; no impurities were detected by pmr and ir either.

Trifluoroacetic Acid Cleavage of *N*-*tert*-Butylamides. A New Synthesis of Primary Sulfamides

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Received October 1, 1973

During the preparation of some sulfamides, we observed cleavage of the *tert*-butyl group from *tert*-butylsulfamides on treatment with trifluoroacetic acid at room temperature. Since *tert*-butylsulfamides are readily available from *tert*-butylsulfamoyl chloride[1] and amines, their dealkylation with trifluoroacetic acid would constitute an attractive route to primary sulfamides. We have also investigated the use of the *tert*-butyl group as a blocking group for sulfamides, sulfonamides, and benzamides.

Known methods[2,3] of synthesis of primary sulfamides include reaction of sulfamoyl chloride with amines, heating sulfamide or *o*-nitrophenylsulfamide with amines, and treating substituted sulfamoyl chlorides with ammonia. These methods have serious limitations; *e.g.*, both the sulfamide and sulfamoyl chloride methods quite often give poor yields of the desired products, the use of sulfamide and *o*-nitrophenylsulfamide usually requires drastic conditions, and many substituted sulfamoyl chlorides, particularly aromatic ones, are unknown.

Although *tert*-butyl and benzyl groups have been used previously as blocking groups for sulfonamides and benzamides, hot methanesulfonic acid or concentrated sulfuric acid[4,5] has generally been required for their removal. Similarly, hot concentrated hydrochloric acid has been used to cleave the alkyl group from *N,N*-di-*tert*-butylsulfamide.[6] However, these conditions are quite vigorous and can cause N–S bond cleavage in sulfamides.[7]

We have prepared various *tert*-butylsulfamides in good yields (Table I, compounds 3–8) from *tert*-butylsulfamoyl chloride[1] (1) and amines *via* the sulfonylamine 2[8] (eq 1). Generation of 2 *in situ* by adding 1 to an ether solution of triethylamine and the appropriate amine at −50° provides better yields of sulfamides than with prior formation of 2.[8] The dimethylsulfamide 14 was prepared by exhaustive methylation of 5.

$$t\text{-}C_4H_9NHSO_2Cl \xrightarrow{Et_3N} [t\text{-}C_4H_9{=}SO_2] \xrightarrow{RNH_2} t\text{-}C_4H_9NHSO_2NHR \quad (1)$$

1 2 3–8

Treatment of the *tert*-butylsulfamides with trifluoroacetic acid at room temperature gave the dealkylated products 9–13 and 15 in high yields (Table I). Similarly, compound 8 gave a nearly quantitative yield of sulfamide.

The mechanism (eq 2) for the cleavage probably involves rapid protonation of the nitrogen bearing the *tert*-

$$(CH_3)_3\overset{+}{C}NHSO_2NHR \rightleftharpoons \begin{matrix}(CH_3)_3C\\ |\\ H\end{matrix}\!\!NHSO_2NHR$$

$$NH_2SO_2NHR + [(CH_3)_3C^+] \xrightarrow{CF_3CO_2^-} CF_3CO_2C(CH_3)_3 \quad (2)$$

24

butyl group followed by loss of the *tert*-butyl carbenium ion to give the primary sulfamide. The *tert*-butyl carbenium ion then combines with trifluoroacetate anion to give *tert*-butyl trifluoroacetate (24). This ionic reaction would be favored by the strongly ionizing trifluoroacetic acid solvent.[9] Support for this mechanism was obtained from the nmr spectra where the only change observed was a 15 Hz downfield shift of the *tert*-butyl peak, which is consistent