(conditions as above) showed the signals of **27b** (t_R = 7.53 min), acetone (t_R = 4.55 min), and acetic anhydride (t_R = 15.93 min), as confirmed by injection of authentic samples.

Reduction of 29 with Triphenylphosphine at -30 °C. A solution of 44 mg (0.188 mmol) of **29** (mixture of racemic and meso) in 70 μL of $CDCl_3$ was admixed with 79 mg (0.30 mmol) of triphenylphosphine at -30 °C and left at this temperature. ^1H NMR analysis ($CDCl_3$, Me_4Si) of samples after 13 and 36 h showed the presence of **27b** (δ 2.33, s), **30** (δ 2.29, s),[18] acetone (δ 2.17, s), and acetic anhydride (δ 2.23, s) in molar ratios of 20:9:49:1 and 31:5:65:1, respectively.

Thermal Decomposition of 29 in Dichloromethane. (a) Isolation of 38 and 39. A solution of 1.2 g (5.1 mmol) of **29** (mixture of racemic and meso) in 10 mL of dichloromethane was heated to 50 °C for 40 h, and the solvent was removed at room temperature and 15 Torr. The liquid residue was dissolved in 30 mL of diethyl ether and washed with aqueous sodium bicarbonate, and the ether was removed at room temperature and 15 Torr to leave 1.88 g of a residue. It was separated by column chromatography (silica gel, pentane/diethyl ether, 4:1) to give 240 mg of **39** and a fraction containing impure **38**. The latter was purified by preparative GLC (glass column, 0.7 × 400 cm, 5% Carbowax 20 M on Chromosorb G; 130 °C for 15 min, 130-180 °C at 16 °C/min).

2,3-Dimethyl-1,3-dioxolan-4-one (38): ^1H NMR ($CDCl_3$, Me_4Si) δ 1.59 (s, 6 H), 4.35 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.90 (q, q, J = 128 and 2.9 Hz), 63.65 (t, J = 153 Hz, 112.67 (br s), 171.37 (t, J = 3.8 Hz); GLC (conditions as above) t_R = 20.50 min. The data agree with those of independently prepared[31] authentic **38**.

Acetyl 1-methyl-1-acetoxyethyl peroxide (39): colorless liquid; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.75 (s, 6 H), 2.06 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.50, 22.02, 23.07, 109.32, 167.56, 168.90. Anal. Calcd for $C_7H_{12}O_5$: C, 47.73; H, 6.87. Found: C, 47.57; H, 6.89.

(b) Determination of Product Distribution. The reactions were carried out in NMR tubes which were closed by ground-glass stoppers, and the products were analyzed by ^1H NMR spectroscopy. The following results were obtained: Heating of 15 mg of **29** in 3 mL of $CDCl_3$ to 40 °C for 2.5 days gave acetone, acetic acid, **38**, and **39** in relative amounts of 42, 29, 6, and 23%. Heating of 93 mg of **29** in 3 mL of $CDCl_3$ to 40 °C for 2.4 days gave the same products in relative amounts of 41, 38, 17, and 4%.

Reduction of 39 with $LiAlH_4$. To 5 drops of **39** in diethyl ether was added solid $LiAlH_4$, and the mixture was left at room temperature for 30 min. Then, water and diluted sulfuric acid were added sequentially, and the mixture was continuously extracted with ether. GLC analysis (glass column, 0.3 × 500 cm, 5% Carbowax 20 M on Chromosorb G; 60 °C) of the extract showed the presence of ethanol (t_R = 8.00 min) and 2-propanol (t_R = 7.63 min). This was confirmed by injection of authentic samples and by GC/MS analysis of the extract: m/e (relative intensity) 46 (29) M^+, 45 (61) $(M - H)^+$, 31 (100) $(M - CH_3)^+$ for ethanol and 59 (3) $(M - H)^+$, 45 (100) $(M - CH_3)^+$ for 2-propanol.

Ozonolysis of 3-Methyl-1,2-butadiene. 3-Methyl-1,2-butadiene (1.9 g, 28 mmol) was loaded on 93 g of polyethylene and ozonized at -75 °C for 4 h. A small sample was extracted with $CDCl_3$. ^1H NMR analysis of the extract showed the presence of acetone and **38** in a molar ratio of 17:1, along with unreacted substrate. The major part of the polyethylene was extracted with diethyl ether, and the ether was distilled off through a 7-cm Vigreux column at normal pressure. From the residue of ca. 1 mL, a sample of pure **38** was isolated by preparative GLC (glass columnm, 0.7 × 400 cm, 5% Carbowax 20 M on Chromosorb G; 120 °C for 13.5 min, 120-180 °C at 18 °C/min).

Supplementary Material Available: Tables 1-3 giving fractional crystallographic coordinates, B values, bond distances and angles, and anisotropic thermal parameters for *meso*-**29** (3 pages). Ordering information is given on any current masthead page.

(31) Willstätter, R.; Königsberger, F. *Chem. Ber.* **1923**, *56*, 2108.
(32) Johnson, C. A. *ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*; ORNL-3794, 2nd rev. with supplemental instructions, Oak Ridge National Laboratory, 1979.

Formation of Olefins via Pyrolysis of Sulfonate Esters[1]

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Esters of 8-quinolinesulfonic acid and 2-pyridinesulfonic acid were synthesized from alcohols and the acid chlorides. The secondary esters decomposed cleanly at moderate temperatures to give olefins in high yield. Product studies were consistent with carbocation formation and abstraction by a ring nitrogen to give olefin. The importance of a basic group was confirmed by pyrolysis of a series of para-substituted cyclohexyl benzenesulfonates, p-$XC_6H_4SO_3R$. The compounds with X = NHEt and NHCOMe reacted cleanly to give olefin in good yield. When X = NO_2, Br, CH_3, or OCH_3, olefin was formed in low yield along with considerable amounts of tar.

Although it has been known for many years that heating of sulfonate esters can lead to the formation of olefins,[2] such reactions generally give poor yields and considerable decomposition. We have discovered that secondary esters of 8-quinolinesulfonic acid and 2-pyridinesulfonic acid decompose cleanly at moderate temperatures to give olefins in high yield (eq 1 and 2). In this paper we present examples of this reaction and evidence in support of its mechanism.

The esters were synthesized in good yield by the reaction of alcohols with the corresponding sulfonyl chloride in pyridine or triethylamine except where noted (Table I).

(1) This work was supported in part by a grant from the Research and Scholarly Development Committee of Grand Valley State University.
(2) (a) Foldi, Z. *Chem. Ber.* **1927**, *60*, 656. (b) Drahowzal, F.; Klamann, D. *Monatsh. Chem.* **1951**, *82*, 467. (c) Gough, G. A. C.; Hunter, H.; Kenyon, J. *J. Chem. Soc.* **1926**, 2066.

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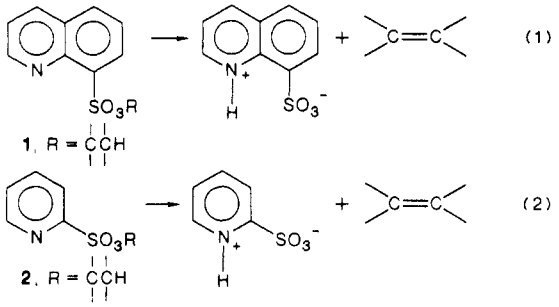


Pyrolysis reactions were run by placing the ester in a flask connected with a short tube to a receiver cooled in liquid nitrogen or dry ice. The entire apparatus was evacuated, and the reaction flask was heated in an oil bath. Olefin distills as it is formed and is collected in high purity without the necessity of workup. The sulfonic acid is left behind in the reaction flask. Table II shows that olefin was isolated in high yield from the secondary esters.

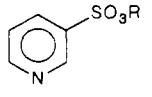
At the outset two mechanisms were considered. The first is a concerted elimination as in the pyrolysis of acetates or amine oxides[3] (Scheme I). The second involves a carbocation intermediate and is essentially an E1 elimination without a solvent (Scheme II).

The pyrolysis of neomenthyl 8-quinolinesulfonate (**1e**), which requires a syn elimination, serves as a good test of the concerted mechanism. In the neomenthyl ester there is only one cis-β hydrogen, and this mechanism would require formation of a single olefin, 2-menthene.[4] In fact, pyrolysis of this ester gave mostly 3-menthene but no 2-menthene. These results clearly preclude a concerted mechanism but are consistent with ionic intermediates.[5]

Further evidence against a concerted mechanism comes from reactions of the *exo*-norbornyl esters **1c** and **2c**. Both esters give a mixture of norbornene and nortricyclene with the latter predominating. While norbornene would be expected in a concerted elimination, formation of nortricyclene would be geometrically impossible in such a reaction from an *exo*-norbornyl ester. On the other hand, nortricyclene can be formed from *exo*-norbornyl substrates by E1 as well as E2 mechanisms.[6]

Results of the pyrolysis of esters of primary alcohols are clearly consistent with a carbocation intermediate. These esters require temperature up to 100 °C higher for olefin formation than the esters of secondary alcohols. In addition, rearranged products are formed. The 1-octyl esters **1g** and **2e** gave mixtures of 1- and 2-octene, and the cyclohexylmethyl esters **1h** and **2f** formed methylenecyclohexane and 1-methylcyclohexene. In a control experiment it was shown that methylenecyclohexane does not rearrange under the conditions of the pyrolysis.

Finally, it is instructive to consider the pyrolysis of *trans*-4-*tert*-butylcyclohexyl 3-pyridinesulfonate (**3**). It



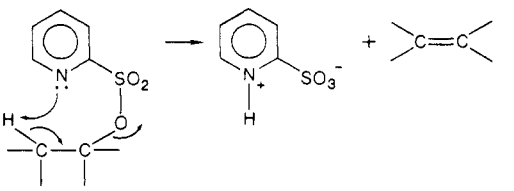
3, R = *trans*-4-*tert*-butylcyclohexyl

Table I. Synthesis of Sulfonate Esters

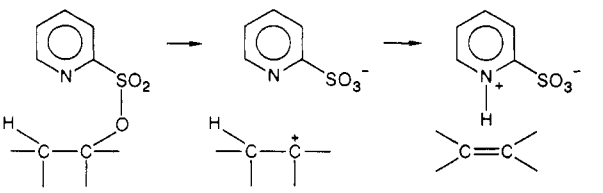
product[a]	% yield[b]	mp, °C
8-Quinolinesulfonates		
1a, R = cyclohexyl	88	122.8–123.2
1b, R = *trans*-4-*tert*-butylcyclohexyl	91	138–139
1c, R = *exo*-norbornyl	65	118–119
1d, R = *l*-menthyl	83	135.5–136
1e, R = *d,l*-neomenthyl[c]	73	101 dec
1f, R = 2-octyl	89	41.2–42.0
1g, R = 1-octyl	62	*d*
1h, R = cyclohexylmethyl	80	76.0–77.0
2-Pyridinesulfonates		
2a, R = cyclohexyl	85	*d*
2b, R = *trans*-4-*tert*-butylcyclohexyl	90	79.5–80.0
2c, R = *exo*-norbornyl	83	*d*
2d, R = 2-octyl	86	*d*
2e, R = 1-octyl	77	*d*
2f, R = cyclohexylmethyl	80	*d*
3-Pyridinesulfonate		
3, R = *trans*-4-*tert*-butylcyclohexyl	77	108–109
p-Acetamidobenzenesulfonate		
4a, R = cyclohexyl	79	125–125.5 lit.[e] 125
p-(Ethylamino)benzenesulfonate		
4b, R = cyclohexyl[f]	79	77–78
Dansylate		
5, R = cyclohexyl	77	84.5–86.5

[a] Satisfactory analyses were obtained for all new solid compounds. Liquids were characterized by IR and NMR data. [b] Based upon alcohol except for **4b**. [c] *d,l*-Neomenthol was treated with *n*-BuLi in THF followed by addition of the sulfonyl chloride. [d] Liquid. [e] Horner, L; Schmitt, R.-E. *Phosphorous Sulfur* **1978**, *5*, 223. [f] Synthesized by reduction of **4a** with $LiAlH_4$, yield based on **4a**.

Scheme I



Scheme II



decomposes in the same temperature to give the same product as the corresponding 8-quinolinesulfonate (**1b**) and 2-pyridinesulfonate (**2b**). It is thus reasonable to conclude that all three compounds react by the same mechanism. However, since a cyclic transition state is geometrically impossible for the 3-pyridinesulfonate, a concerted mechanism may be ruled out for all three compounds.

None of the evidence presented here supports a concerted syn elimination in the pyrolysis of these sulfonate esters. On the other hand, the products formed in these reactions are consistent with initial formation of an ion pair followed by abstraction of a hydrogen by a basic ring nitrogen. An intermolecular E2 elimination is another possible mechanism for the secondary esters. However, an E2 mechanism cannot account for rearrangements in the reaction of the primary esters or the formation of two products in the reaction of the menthyl ester **1d**.[7]

(3) (a) DePuy, C. H.; King, E. R. *Chem. Rev.* **1960**, *60*, 431. (b) Cope, A. C.; Trumbull, E. R. *Org. React.* **1960**, *11*, 317.
(4) See: (a) Huckel, W.; Rucker, D. *Ann. Chem.* **1963**, *666*, 30. (b) Cope, A. C.; Acton, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 1955.
(5) Elimination from neomenthylammonium hydroxide in water by an E1 mechanism gives 98% of 3-menthene and 2% of 2-menthene. The reaction of menthylammonium hydroxide gives 14% of 3-menthene and 86% of 2-menthene. Huges, E. D.; Wilby, J. *J. Chem. Soc.* **1960**, 4094.
(6) (a) Kwart, H.; Takeshita, T.; Nyce, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 2606.

Table II. Pyrolysis of 8-Quinolinesulfonates and Pyridinesulfonates

compd	pyrolysis temp, °C	olefin yield, %[a]	pressure, mm	time, min	products
			8-Quinolinesulfonates		
1a	150	92	19	45	cyclohexene
1b	145	87	27	75	4-*tert*-butylcyclohexene
1c	140	89	18	60	norbornene (34%) nortricyclene (66%)
1d	135–144	95	0.3–0.5	30	3-menthene (70%) 2-menthene (29%)
1e	96–112	98	0.3	40	3-menthene (93%)[b]
1f	150	86	0.3	60	1-octene (50%) 2-octene (50%)
1g	220	37	6	90	1-octene (98%) 2-octene (2%)
1h	230	66	11	135	methylenecyclohexane (35%) 1-methylcyclohexene (65%)
			2-Pyridinesulfonates		
2a	108	95	0.8	100	cyclohexene
2b	125	88	17	120	4-*tert*-butylcyclohexene
2c	110	75	11	30	norbornene (2%) nortricyclene (98%)
2d	115	88	19	75	1-octene (38%) 2-octene (62%)
2e	225	46	1.5	60	1-octene (59%) 2-octene (41%)
2f	200	80	0.3	75	methylenecyclohexane (25%) 1-methylcyclohexene (70%)
			3-Pyridinesulfonate		
3	125	100	25	120	4-*tert*-butylcyclohexene

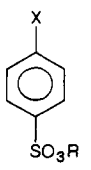
[a] Based on sulfonate ester. [b] No 2-menthene is observed.

Table III. Pyrolysis of Arenesulfonates 4 and 5, R = Cyclohexyl[a]

compound	pyrolysis temp, °C	olefin yield, %	product (% purity)
4a, X = $NHCOCH_3$[b,c]	135–140	99	cyclohexene (99)
4b, X = $NHCH_2CH_3$[b]	175–180	91	cyclohexene (98)
4c, X = NO_2[d,e]	100–105	29	cyclohexene (93)
4d, X = Br[f]	120–126	43	cyclohexene (98)
4e, X = CH_3[g,h]	150–156	58	cyclohexene (98)
4f, X = OCH_3[c,g]	141–146	55	cyclohexene (97)
5, X = $N(CH_3)_2$	161–164	69	cyclohexene (99)

[a] All pyrolyses were run for 30 min at aspirator pressure, ca. 25 mm. [b] The sulfonic acid byproduct was characterized by NMR and IR data. [c] Table I, ref *e*. [d] The decomposition was quite violent. [e] Bartlett, P. D.; Closson, W. D.; Cogdell, T. J. *J. Am. Chem. Soc.* **1965**, *87*, 1308. [f] Winstein, S.; Grunwald, E.; Graham, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 821. [g] The sulfonic acid that was produced codistilled with the olefin. Yield of olefin was determined by gas chromatography. [h] Huckel, W.; Neunhoeffer, O.; Gercke, A.; Frank, E. *Ann. Chem.* **1929**, *477*, 143.

Regardless of mechanism, the ring nitrogen is probably functioning as a base in these reactions. If this is the case, other sulfonate esters that contain basic groups should react similarly to form olefins. To test this hypothesis we pyrolyzed several substituted benzene- and naphthalenesulfonates (Table III). All of the esters that lacked a basic substituent gave low yields of olefin with considerable tar formation. The dansyl ester **5**, which contains a dimethylamino group, decomposed cleanly without leaving a tarry residue but did not give an especially good yield of olefin. On the other hand, the benzenesulfonate substituted with an ethylamino group (**4b**) gave olefin cleanly and in good yield. Surprisingly, the *p*-acetamidobenzenesulfonate **4a** also gave an excellent yield of olefin despite the low basicity of the acetamido group. It might be noted in addition that the benzenesulfonate esters with electron-withdrawing groups required lower pyrolysis temperatures than those with electron-donating groups, reflecting the relative stabilities of the sulfonate anions formed in the initial ionization.



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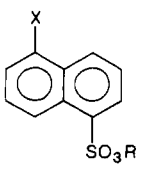

5

Pyrolysis of secondary 8-quinolinesulfonates and 2-pyridinesulfonates thus offers a simple, efficient method for converting alcohols to olefins. Most of these esters were synthesized from alcohols in good yields. The 8-quinolinesulfonate esters are more convenient to make since most were solids, and the acid chloride is commercially available. Pyrolysis of the esters is accomplished under mild, neutral conditions in good yield. A major advantage of this reaction is that the olefin is isolated in high purity without further purification. Overall conversion of alcohol to olefin was achieved in yields as high as 71%. The results of Table III indicate that it should be possible to extend this reaction to other sulfonate esters. The *p*-acetamidobenzenesulfonates look especially promising since they can be synthesized using *N*-acetylsulfanilyl chloride, which is relatively inexpensive. This method of olefin synthesis should be most successful with symmetrical secondary alcohols that can give only one olefin.

Experimental Section

Melting points were recorded on Büchi and Thomas-Hoover melting point apparatuses and are uncorrected. Infrared data were obtained on the following spectrophotometers: Perkin-Elmer 137, Beckman Acculab 2, and Pye-Unicam SP1000. NMR spectra were obtained on Varian A-60 and Perkin-Elmer R-24B spectrophotometers. GC analyses were performed on an F and M Model 300 gas chromatograph using a 25% TCEP column or a Varian Aerograph 2700 instrument using a 1.5% OV-101 column (5 ft × 0.125 in.). Microanalyses were performed by Alfred

(7) The E2 elimination of menthyl chloride with NaOEt gives only 2-menthene. (a) Hughes, E. D.; Ingold, C. K.; Rose, J. B. *J. Chem. Soc.* **1953**, 3839. (b) Huckel, W.; Tappe, W.; Legutke, G. *Ann. Chem.* **1940**, *543*, 191.

Bernhardt Mikroanalytisches Laboratorium, Mulheim (Ruhr), Germany, Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Galbraith Laboratories, Knoxville, TN.

Preparation of 8-Quinolinesulfonate Esters. The preparation of cyclohexyl 8-quinolinesulfonate (**1a**) is typical of the procedure used for other 8-quinolinesulfonates. 8-Quinolinesulfonyl chloride (Aldrich, 2.40 g, 10.5 mmol) was added to a solution of 405 mg (4.05 mmol) of cyclohexanol in 5 mL of anhydrous pyridine at 5 °C. The resulting solution was kept at −10 °C for 18 h, during which time crystals formed. The crystals were dissolved by addition of 5 drops of water with cooling. Addition of more water caused formation of a white precipitate, which was collected, washed with water and a small amount of dilute sodium bicarbonate solution, and dried under reduced pressure. The crude product was recrystallized from acetone–water, giving 1.04 g (88%) of **1a**: mp 122.8–123.2 °C; IR ($CHCl_3$) 1340, 1170, 943–935 cm^{-1}; NMR ($CHCl_3$) δ 1.0–2.0 (m, 10 H), 5.0 (m, 1 H), 7.4–9.2 (m, 6 H).

The two primary 8-quinolinesulfonates **1g** and **1h** were prepared in the same manner, but the reaction time was reduced to 2.5–3 h. Since **1g** was a liquid, it was isolated by extraction with ether.

The IR spectra of the quinolinesulfonate esters show S–O peaks at 1340 and 1170 cm^{-1}. The NMR spectra show six aromatic hydrogens at δ 7.4–9.2 and a signal for carbinol hydrogens at 4.8–5.2 for secondary esters and 4.1–4.4 for primary esters.

***d,l*-Neomenthyl 8-Quinolinesulfonate (1e).** *d,l*-Neomenthol was prepared by reduction of *d,l*-menthone with aluminum isopropoxide and was recovered via the *p*-nitrobenzoate. A solution of 250 mg (1.6 mmol) of *d,l*-neomenthol in 5 mL of THF under nitrogen was cooled in ice, and 1.9 mmol of *n*-BuLi was added in pentane solution. The solution was stirred at 0 °C for 30 min, and then 455 mg (2.0 mmol) of 8-quinolinesulfonyl chloride in 5 mL of THF was added over 15 min. After 4.25 h at 0 °C, water was added and the resulting mixture was extracted with ether. The ether solution was washed with water and 10% sodium bicarbonate solution and dried with magnesium sulfate. Evaporation of the solvent yielded 553 mg of a yellow solid, which was twice recrystallized from benzene–pentane, giving 414 mg (73%) of pale yellow needles, which decomposed from 101 °C without melting: IR ($CHCl_3$) 1340, 1170, 893 cm^{-1}; NMR ($CDCl_3$) δ 0.3–2.0 (m, 17 H), 0.53 (d, J = 5 Hz), 0.68 (d, J = 2 Hz), 5.14 (m, 1 H), 7.3–9.2 (m 6 H).

Preparation of 2-Pyridinesulfonyl chloride.[8] A solution of 447 mg (4.02 mmol) of 2-mercaptopyridine (Aldrich) in 5.2 mL of concentrated hydrochloric acid and 1.5 mL of water was cooled to 2–5 °C. Chlorine was bubbled into this solution for 30 min, taking care to maintain the temperature at 5 °C. Water was added followed by three extractions with cold ether. The organic extracts were washed with cold sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Evaporation of the ether with a stream of dry nitrogen gave 696 mg (97%) of a light yellow liquid, which was shown to be pure by TLC on silica gel PF_{254} with ether as eluant. Its IR (strong sulfonyl peaks at 1180 and 1370 cm^{-1}) and NMR spectra are fully consistent with its structure, and a solid derivative (compound **2b**) gave a satisfactory elemental analysis.

Preparation of 2-Pyridinesulfonate Esters. The preparation of cyclohexyl 2-pyridinesulfonate (**2a**) is typical of the procedure for preparation of the other secondary 2-pyridinesulfonate esters **2c** and **2d**. To approximately 0.5 mL of anhydrous triethylamine was added 115 mg (1.15 mmol) of cyclohexanol. After this solution was cooled to 5 °C, 219 mg (1.24 mmol) of freshly prepared 2-pyridinesulfonyl chloride was added in one portion. The resulting mixture was kept at 2 °C for 3 h, and then a few milliliters of water were added with cooling. This was extracted three times with ether, and then the ether extracts were washed with dilute sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and evaporated to a maroon liquid of constant weight, 234 mg (85%): IR (neat) 1360, 1190, 935–917 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.0 (m, 10 H), 4.8 (m, 1 H), 7.6–8.8 (m, 4 H).

The primary 2-pyridinesulfonates **2e** and **2f** were prepared from 1 mmol of alcohol, 2 mmol of triethylamine, and 1.25 mmol of 2-pyridinesulfonyl chloride in 1 mL of dry benzene. After the solution was stirred at 2 °C for 16–19 h, it was filtered, and solvent was evaporated to give the ester.

Compounds **2b** and **3** were prepared in the same manner as the 8-quinolinesulfonate esters with pyridine as a solvent with a reaction time of 1.75 h.

The IR spectra of the 2-pyridinesulfonate esters show S–O peaks at 1360 and 1190 cm^{-1}. The NMR spectra show four aromatic hydrogens at δ 7.6–8.8 and signal for carbinol hydrogens at 4.8–5.2 for secondary esters and 4.1–4.4 for primary esters.

Preparation of 3-Pyridinesulfonyl Chloride.[9] To 1.03 g (6.48 mmol) of 3-pyridinesulfonic acid was added 2.08 g (10.0 mmol) of phosphorus pentachloride and 1 mL of phosphorus oxychloride. After refluxing under nitrogen for 3 h, excess phosphorus oxychloride was removed in vacuo to give a yellow liquid. A few drops of ice water were added with cooling. Extraction with three portions of ether, washing with dilute sodium bicarbonate solution, drying over anhydrous magnesium sulfate, and evaporation of the ether gave 824 mg (72%) of a slightly yellow liquid, which showed only one spot on TLC and peaks in the IR at 1185 and 1380 cm^{-1} due to the sulfonyl group. A solid derivative (compound **3**) gave a satisfactory elemental analysis.

Preparation of Cyclohexyl *p*-(Ethylamino)benzenesulfonate (4b). A solution of 3.00 g (10.1 mmol) of **4a** in 75 mL of dry THF was added dropwise with stirring over 2 h at room temperature to 0.77 g (20 mmol) of lithium aluminum hydride in 23 mL of THF. After an additional 6 h of stirring, 7 mL of water was added followed by 14 mL of 15% sodium hydroxide solution. After filtration, methylene chloride was added to the solution, and the water layer was separated. Solvent was removed in a stream of nitrogen, and the crude product was recrystallized from ethanol–water to give 2.26 g of **4b**: mp 77–78 °C; IR (KBr) 3380, 1340, 1160 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (t, J = 7 Hz), 1.0–2.0 (br m, 13 H), 3.22 (q, J = 7 Hz, 2 H), 4.2–4.6 (br m, 2 H), 6.60 (d, J = 9 Hz, 2 H), 7.66 (d, J = 9 Hz 2 H).

Preparation of Cyclohexyl Dansylate (5). The same procedure was used as that for the synthesis of the 8-quinolinesulfonate esters with 0.357 g (3.56 mmol) of cyclohexanol and 1.0 g (3.7 mmol) of dansyl chloride in 4.0 mL of pyridine. After 44 h at −10 °C, ice water was added, the mixture was extracted twice with ether, and the solvent was evaporated with a stream of nitrogen. The crude product was recrystallized from ethanol–water to give 0.957 g (80.6%) of **5**: mp 78–79 °C; IR (KBr) 1349, 1175, 888 cm^{-1}; NMR ($CDCl_3$) δ 1.0–1.9 (br m, 10 H), 2.85 (s, 6 H), 4.4–4.8 (br m, 1 H), 7.2–7.8 (m, 3 H), 8.3–8.8 (m, 3 H).

Pyrolysis of Sulfonate Esters. The following procedure is typical of all other pyrolyses. Cyclohexyl 8-quinolinesulfonate (50.3 mg, 1.72 mmol) was placed in a flask connected by a short tube to a receiver. After the pressure in the system was reduced to 19 mm, the receiver was immersed in a dry ice–acetone bath. The flask containing the ester was placed in a preheated (ca. 120 °C) oil bath, the temperature of which was raised to 150 °C and maintained there for 45 min. The product was 129 mg (91.5%) of a colorless liquid, which was shown to be cyclohexene by comparison of its IR and NMR spectra and GC retention time with those of authentic cyclohexene.

In pyrolyses run at lower pressures, the receiver was cooled with liquid nitrogen.

The white crystalline residue in the reaction vessel was shown to be 8-quinolinesulfonic acid: IR (KBr) 1050, 1175–1205, and 1240 cm^{-1}; mp >300 °C; vigorous bubbling with dilute sodium bicarbonate.

Registry No. **1a**, 117800-87-0; **1b**, 117800-91-6; **1c**, 117800-92-7; **1d**, 117800-93-8; **1e**, 117893-71-7; **1f**, 117828-23-6; **1g**, 117800-94-9; **1h**, 62862-08-2; **2a**, 117800-88-1; **2b**, 117800-95-0; **2c**, 117828-24-7; **2d**, 117800-96-1; **2e**, 117800-97-2; **2f**, 117800-98-3; **3**, 117800-89-2; **4a**, 69564-59-6; **4b**, 117800-99-4; **4c**, 788-92-1; **4d**, 18939-93-0; **4e**, 953-91-3; **4f**, 69564-57-4; **5**, 117800-90-5; cyclohexene, 110-83-8; 4-*tert*-butylcyclohexene, 2228-98-0; norbornene, 498-66-8; nortricyclene, 279-19-6; 3-menthene, 500-00-5; 2-menthene, 5256-65-5; 1-octene, 111-66-0; 2-octene, 111-67-1; methylenecyclohexane, 1192-37-6; 1-methylcyclohexane, 591-49-1; 8-quinolinesulfonyl

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chloride, 18704-37-5; cyclohexanol, 108-93-0; DL-menthone, 1074-95-9; *p*-nitrobenzoate, 117893-72-8; DL-neomenthol, 3623-51-6; 2-mercaptopyridine, 2637-34-5; 2-pyridinesulfonyl chloride, 66715-65-9; 3-pyridinesulfonyl chloride, 16133-25-8; 3-pyridinesulfonic acid, 636-73-7; dansyl chloride, 605-65-2; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; *exo*-norbornol, 497-37-0; L-menthol, 2216-51-5; 2-octanol, 123-96-6; 1-octanol, 111-87-5; cyclohexylmethanol, 100-49-2.

Structural and Complexation Properties of 2,11-Diselena[3.3](2,6)pyridinophane

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2,11-Diselena[3.3](2,6)pyridinophane ($PyPySe_2$) has been synthesized in excellent yield by the high dilution method. Its conformational behavior in solution has been unambiguously determined by variable temperature (VT) ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR. $PyPySe_2$ exists predominantly in the syn conformation, which undergoes flip of the pyridine rings and twist of the methylene bridges. The syn forms arising from pyridine flips cannot be distinguished by VT NMR as the energy barrier is low for this process. The syn forms arising from methylene twists can be differentiated by the nonequivalency of the bridge protons in VT NMR. The coalescence temperature for the bridge protons yields an activation barrier, $\Delta G^{\ddagger}$, of 37.4 kJ mol^{-1} for this process. The activation barrier for this process in the phenyl analogue is 30.4 kJ mol^{-1}. The difference in the activation barriers (7 kJ mol^{-1}) is due to the electrostatic interaction of the nitrogen lone pairs in the transition state of the methylene twist where the two pyridine rings are horizontal with respect to each other. $PyPySe_2$ complexed Ni^{2+} and Cu^{2+} in CH_3NO_2 with these complexes exhibiting similar stability constants, indicating that both metal ions fit equally well in the cavity of the heterophane. The stability constant values indicate a typical host–guest interaction. The X-ray structure determined from a single crystal of $[NiPyPySe_2(H_2O)_2][ClO_4]_2 \cdot CH_3NO_2$ belonging to the *Pnma* space group shows that the heterophane is in a syn conformation and highly symmetrical. This is in contrast to the Ni^{2+} complex of the thia analogue where the heterophane is distorted from the syn conformation. Interesting differences in the spectral and conductivity properties of the Cu(II) complex are observed when the coordinated H_2O is replaced by Cl^-. The heterophane and its metal and charge-transfer complexes are semiconductors at room temperature with the $CuPyPySe_2Cl_2$ complex exhibiting the best conductivity.

Introduction

Cyclophanes have attracted the attention of chemists for some time. Their synthesis, conformation, electronic structure, and host–guest chemistry have been the subjects of many investigations.[1] Heterophanes containing nitrogen, oxygen, and sulfur in the bridge have also been widely studied.[1] There have been, however, only a few reports of cyclophanes with selenium in the bridge.[2] Cyclophanes with selenium in the bridge are attractive for several reasons, namely, (1) selenium in the bridge provides an additional tool for the investigation of the conformational properties of the cyclophanes by ^{77}Se NMR [Such a tool is absent in the case of nitrogen, oxygen, and sulfur atoms in the bridge.], (2) selenium is more polarizable than nitrogen, oxygen, and sulfur, which could influence the complexation properties of selenacyclophanes with metal ions and charge-transfer complexation with electron acceptors like tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE), and (3) the presence of selenium provides the possibility for novel conductivity properties of the cyclophanes and their complexes. We have initiated in our laboratory an investigation of the chemistry of selenacyclophanes for these reasons. We have synthesized 2,11-diselena[3.3](2,6)pyridinophane in >95% yields, characterized its conformational behavior by ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR, investigated its complexation properties with transition-metal ions and electron acceptors, and determined the conductivity properties of these complexes. The crystal and molecular structure of its nickel(II) complex was also determined. This, to our knowledge, is the first report of the complexation and conductivity properties of selenacyclophanes.

Results and Discussion

The procedure we have adopted for the synthesis of $PyPySe_2$ provides >95% yield in comparison to the procedure used by Mitchell for the synthesis of 2,11-diselena[3.3]metacyclophane with xylylene bromide and Na_2Se, which gave the corresponding product in 7% yield.[10]

Conformational Properties of $PyPySe_2$. The conformational characteristics of metacyclophanes with and without heteroatoms in the bridge have been investigated in detail.[11] Relatively fewer investigations on the structurally analogous [3.3](2,6)pyridinophanes have been re-

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