trans-1-(Arenesulfonyl)-2-arylcyclopropanes and Derivatives of Cyclopropanesulfonic Acid

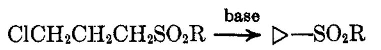
WILLIAM E. TRUCE AND CHRISTIAN T. GORALSKI

Department of Chemistry, Purdue University, Lafayette, Indiana 47907

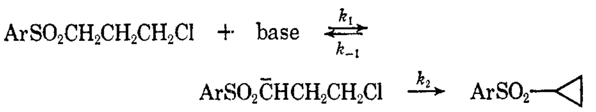
Received October 31, 1968

α,γ dehydrohalogenation as an approach to esters and N,N-disubstituted amides of cyclopropanesulfonic acid and the preparation of *trans*-1-(arenesulfonyl)-2-arylcyclopropanes by the reaction of dimethylsulfonium methylide with *trans*-1-aryl-2-(arenesulfonyl)ethenes are described.

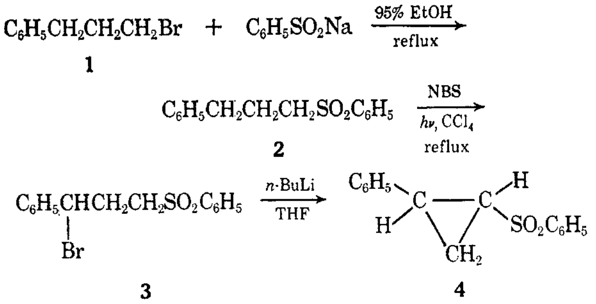
The synthesis of sulfur derivatives of cyclopropane has received considerable attention in the last 10 years, and several different synthetic approaches have been developed. Possibly the first sulfur derivatives of cyclopropane, aryl and alkyl cyclopropyl sulfones, were prepared by α,γ dehydrohalogenation of γ-chloro sulfones (eq 1).[1,2] This approach has been used by


(1)

Cristol to prepare tricyclic sulfones (1- and 2-benzenesulfonyldibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadienes) containing a cyclopropane ring[3,4] and the novel 2-quadricyclyl phenyl sulfone.[5] That such α,γ dehydrohalogenations proceed *via* intermediate carbanions (eq 2) has been established.[6]


(2)

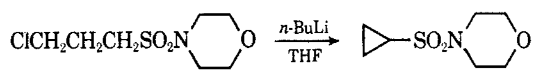
In studying the preparation of cyclopropyl sulfones by the reaction of sulfur ylides with α,β-unsaturated sulfones,[7] *trans*-1-(benzenesulfonyl)-2-phenylcyclopropane (**4**) was alternatively synthesized by α,γ dehydrohalogenation (eq 3). Reaction of 1-bromo-3-phenyl-


(3)

propane (**1**) with sodium benzenesulfinate gave 1-phenyl-3-(benzenesulfonyl)propane (**2**) which, on treatment with N-bromosuccinimide, was converted to 1-bromo-1-phenyl-3-(benzenesulfonyl)propane (**3**) in 88% yield. Treatment of **3** with n-butyllithium in tetrahydrofuran afforded **4** in 90% yield.

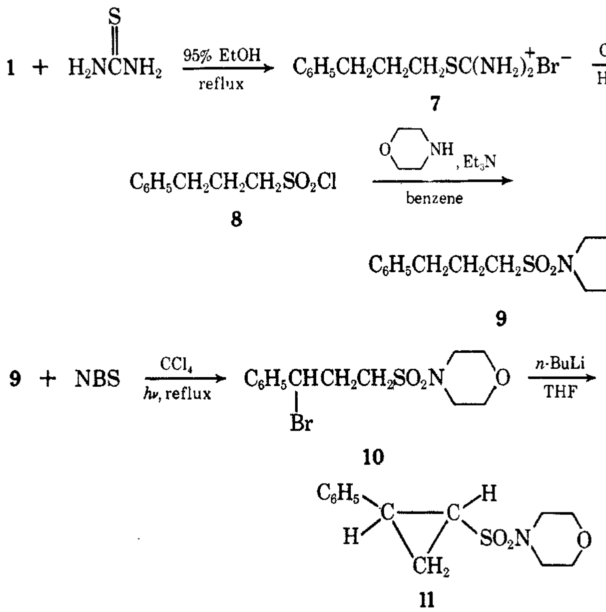
Aryl cyclopropyl sulfides have also been prepared by the α,γ-dehydrohalogenation approach.[8,9] An alternative approach to aryl cyclopropyl sulfides, involving the reaction of phenylmercaptocarbene with olefins, was developed by Schöllkopf, *et al.*[10,11] The sulfides were converted to the corresponding sulfones by oxidation with hydrogen peroxide, thus providing another route to cyclopropyl sulfones.

Also, α,γ dehydrohalogenation has been extended to the preparation of cyclopropanesulfonic acid amides and esters.[12] Treatment of 3-chloropropanesulfonmorpholide (**5**) with n-butyllithium in tetrahydrofuran gave cyclopropanesulfonmorpholide (**6**, eq 4). In a simi-


(4)

5 **6**

lar manner, *trans*-2-phenylcyclopropane-1-sulfonmorpholide[13] (**11**) was prepared (eq 5). Reaction of **1** with


(5)

(1) H. E. Zimmerman and B. S. Thyagarajan, *J. Amer. Chem. Soc.*, **82**, 2505 (1960).
(2) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961).
(3) S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, **88**, 3095 (1966).
(4) S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 401 (1967).
(5) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966).
(6) R. Bird and C. J. M. Stirling, *J. Chem. Soc., B*, 111 (1968).
(7) W. E. Truce and V. V. Badiger, *J. Org. Chem.*, **29**, 3277 (1964).
(8) W. E. Truce, K. R. Hollister, L. B. Lindy, and J. E. Parr, *ibid.*, **33**, 43 (1968).
(9) Several aryl cyclopropyl sulfides have been oxidized to the corresponding aryl cyclopropyl sulfoxides with m-chloroperbenzoic acid in chloroform (J. E. Parr, Ph.D. Thesis, Purdue University, Aug 1967). Thus, phenyl cyclopropyl sulfide afforded phenyl cyclopropyl sulfoxide [bp 110–113° (5 mm), $n^{20}D$ 1.5814] in 96% yield. p-Tolyl cyclopropyl sulfide gave p-tolyl cyclopropyl sulfoxide [bp 122–124° (5 mm), $n^{20}D$ 1.5722] in 93% yield. *Anal.* Calcd for $C_{10}H_{12}SO$: C, 66.65; H, 6.71; S, 17.76. Found: C, 66.42; H, 6.61; S, 17.54.
(10) U. Schöllkopf and G. J. Lehmann, *Tetrahedron Letters*, 165 (1962).
(11) U. Schöllkopf, G. J. Lehmann, J. Paust, and H.-D. Härtl, *Chem. Ber.*, **97**, 1527 (1964).
(12) We recently reported the preparation of cyclopropanesulfonic acid amides and esters *via* sulfur ylides: W. E. Truce and C. T. Goralski, *J. Org. Chem.*, **33**, 3849 (1968).
(13) This compound was prepared earlier[12] by the reaction of dimethylsulfonium methylide with *trans*-2-phenylethenesulfonmorpholide.

TABLE I

trans-1-(ARENESULFONYL)-2-ARYLCYCLOPROPANES (16)[a]

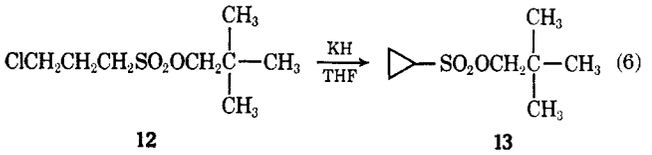
No.	R	R′	Mp, °C[c]	Yield %[b]	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
I	C_6H_5[d]	C_6H_5	95–96[e]	83						
II	C_6H_5[f]	C_6H_{11}	83–84	24	68.14	7.62	12.13	68.03	7.66	12.03
III	C_6H_5	*p*-$CH_3C_6H_4$	140.5–141.5[g]	44	70.55	5.92	11.77	70.28	5.88	11.63
IV	C_6H_5	*p*-$(CH_3)_3CC_6H_4$	100–102	55	72.57	7.05	10.20	72.61	7.13	10.25
V	C_6H_5	2,4,6-$[(CH_3)_2CH]_3C_6H_2$	87–88	72	74.95	8.39	8.34	74.64	8.09	8.24
VI	C_6H_5[h]	2-$C_{10}H_7$	118–119	84	74.00	5.23	10.40	74.06	5.10	10.31
VII[j]	C_6H_5	*p*-FC_6H_4	88.5–89.5	67	65.20	4.74	11.61	65.66	4.71	11.74
VIII[k]	C_6H_5[i]	*p*-ClC_6H_4	112–114	46	61.53	4.47	10.95	61.86	4.57	11.02
IX[l]	C_6H_5	*p*-BrC_6H_4	106–107.5	81	53.39	3.88	9.51	53.23	3.59	9.59
X[m]	C_6H_5	*o*-$O_2NC_6H_4$	91.5–92.5	21	59.39	4.32	10.57	59.29	4.41	10.55
XI	*p*-$CH_3C_6H_4$	C_6H_5	102–103.5	68	70.55	5.92	11.77	70.45	5.70	11.73
XII	4-$C_6H_5C_6H_4$	C_6H_5	133–134	63	75.42	5.42	9.59	75.33	5.35	9.44
XIII	2,6-$(CH_3)_2C_6H_3$	C_6H_5	93–95	79	71.29	6.33	11.20	71.46	6.28	11.08
XIV[n]	*p*-ClC_6H_4	C_6H_5	101–103	74	61.53	4.47	10.96	61.33	4.26	10.85
XV	*m*-$O_2NC_6H_4$	C_6H_5		0						

[a] All reactions were carried out on a 0.01 molar scale unless otherwise indicated. [b] The yields reported are based on one recrystallization. In some cases one or two additional recrystallizations were made to provide the analytical sample (see Experimental Section for details). [c] The melting points reported are those observed for the analytical sample. [d] 0.10 molar scale. [e] W. E. Truce and V. V. Badiger [*J. Org. Chem.*, **29**, 3277 (1964)] report mp 96–97°. [f] 0.0016 molar scale. [g] W. E. Truce and V. V. Badiger [*ibid.*, **29**, 3277 (1964)] report mp 146–147°. [h] 0.05 molar scale. [i] 0.0045 molar scale. [j] *Anal.* Calcd for $C_{15}H_{13}FO_2S$: F, 6.87. Found: 6.92. [k] *Anal.* Calcd for $C_{15}H_{13}ClO_2S$: Cl, 12.11. Found: Cl, 12.11. [l] *Anal.* Calcd for $C_{15}H_{13}BrO_2S$: Br, 23.70. Found: Br, 23.68. [m] *Anal.* Calcd for $C_{15}H_{13}NO_4S$: N, 4.62. Found: N, 4.81. [n] *Anal.* Calcd for $C_{15}H_{13}ClO_2S$: Cl, 12.11. Found: Cl, 12.32.

thiourea gave **7** which, on treatment with chlorine in aqueous solution, gave 3-phenylpropanesulfonyl chloride (**8**). The sulfonyl chloride **8** was not isolated but was treated, without purification, with morpholine to give 3-phenylpropanesulfonmorpholide (**9**), which was brominated with N-bromosuccinimide to give 3-bromo-3-phenylpropanesulfonmorpholide (**10**). Treatment of **10** with *n*-butyllithium in tetrahydrofuran gave **11**.

The use of *n*-butyllithium in tetrahydrofuran as the base–solvent system for the preparation of cyclopropyl sulfones and sulfonamides *via* α,γ dehydrohalogenation is a superior method in that it lowers the reaction time and increases the yield of cyclopropane, presumably because the metallation step (k_1) in the mechanism proposed by Stirling[6] is made irreversible.

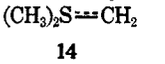
The alkylation of α-metalated sulfonate esters, and a study of the effectiveness of various base–solvent systems was recently described.[14] In the present work, it was found that treatment of neopentyl 3-chloropropanesulfonate (**12**) with potassium hydride in tetrahydrofuran gave neopentyl cyclopropanesulfonate (**13**, eq 6). However, treatment of phenyl 3-chloropropanesulfonate with *n*-butyllithium in tetrahydrofuran failed to yield the corresponding cyclopropane.



(6)

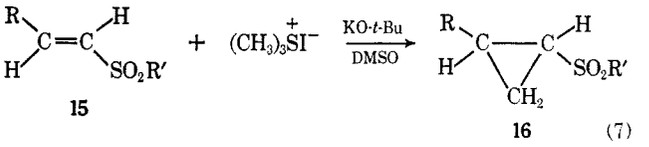
12 **13**

Aryl cyclopropyl sulfones have been prepared by the reaction of dimethylsulfonium methylide (**14**) with α,β-unsaturated sulfones.[7] We have examined this reac-



14

tion in greater detail to determine the effect of various substituents on the reaction. In this regard, a number of *trans*-1-aryl-2-(arenesulfonyl)ethenes (**15**) were converted to the corresponding *trans*-1-(arenesulfonyl)-2-arylcyclopropanes (**16**, Table I, eq 7). The yields of



15 **16** (7)

the *trans*-1-(arenesulfonyl)-2-arylcyclopropanes were in the 21–85% range, demonstrating that satisfactory to excellent yields can be obtained in the presence of a variety of substituents. The yields of purified products reported in Table I may, in some cases, only reflect different solubilities in ethanol, which was the solvent of crystallization. Where nitro substituents were present, however, the trends toward lower yields appear to be real and may be due to radical-anion formation and subsequent side reactions and polymerization.[15] The structures of the *trans*-1-(arenesulfonyl)-2-arylcyclopropanes were supported by their ir and nmr spectra (see Experimental Section).[16]

The *trans*-1-aryl-2-(arenesulfonyl)ethenes (**15**) were prepared by either the free-radical addition of the appropriate arenethiol to phenylacetylene followed by oxidation with hydrogen peroxide[7,17] or the cupric chloride catalyzed addition of arenesulfonyl chlorides[18] to the appropriate styrene followed by dehydrohalogenation of the resulting β-chloro sulfone with triethylamine in benzene.[19]

(14) W. E. Truce and D. J. Vrencur, *Can. J. Chem.*, **47**, 860 (1969).

(15) Radical anions have been detected in the reaction of dimethyl sulfoxonium methylide with aromatic nitro compounds: V. J. Traynelis and J. V. McSweeney, *J. Org. Chem.*, **31**, 243 (1966). Polymerization has been observed in the reaction of dimethylsulfoxonium methylide with α,β-unsaturated nitro compounds: C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *ibid.*, **30**, 3972 (1965); see also J. Asunskis and H. Shechter, *ibid.*, **33**, 1164 (1968).

(16) For more detailed analyses of the ir and nmr spectra of compounds of this type see ref 7 and references cited therein.

(17) L. I. Smith and H. R. Davis, Jr., *J. Org. Chem.*, **15**, 824 (1950).

(18) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964).

(19) The detailed preparations of the *trans*-1-aryl-2-(arenesulfonyl)ethenes used in this study are described in a manuscript currently in preparation.

Experimental Section[20]

1-Phenyl-3-(benzenesulfonyl)propane (2).—In a 500-ml flask equipped with a reflux condenser were placed 19.91 g (0.10 mol) of 1-bromo-3-phenylpropane (1), 16.41 g (0.10 mol) of sodium benzenesulfinate, and 200 ml of 95% ethanol. The reaction mixture was heated at reflux for 23 hr and then cooled. The ethanol was removed *in vacuo* leaving a very pale yellow oil which crystallized on standing. The crude sulfone was decolorized and recrystallized from 95% ethanol to give 14.90 g of 1-phenyl-3-(benzenesulfonyl)propane, mp 83.5–85° (lit.[21] mp 83–83.5°). The recrystallization liquor gave a second crop, 0.30 g, mp 83.5–85°, and a third crop, 1.00 g, mp 83–84°. The total yield was 16.20 g (62% yield).

1-Bromo-1-phenyl-3-(benzenesulfonyl)propane (3). Bromination of 1-Phenyl-3-(benzenesulfonyl)propane (2) with N-Bromosuccinimide.—In a 1000-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a reflux condenser, and a stopper were placed 7.80 g (0.03 mol) of 1-phenyl-3-(benzenesulfonyl)propane, 5.34 g (0.03 mol) of N-bromosuccinimide, and 500 ml of reagent grade carbon tetrachloride. The reaction mixture was heated at reflux and irradiated with a 250-W infrared heat lamp for 4 hr. After the irradiation was stopped and the reaction mixture cooled for several minutes, the reaction mixture was filtered to remove the succinimide produced (2.70 g, 92% yield, of succinimide was obtained). The carbon tetrachloride was removed from the filtrate *in vacuo* leaving a pale yellow oil. The oil was dissolved, with heating, in 95% ethanol and crystallization began. After standing under refrigeration overnight, a white, crystalline solid separated from the ethanol solution. The solid was filtered and vacuum dried to give 9.00 g (88% yield) of 1-bromo-1-phenyl-3-(benzenesulfonyl)propane, mp 70–72°.

Anal. Calcd for $C_{15}H_{15}BrO_2S$: C, 53.10; H, 4.46; Br, 23.56; S, 9.45. Found: C, 52.82; H, 4.41; Br, 23.80; S, 9.36.

***trans*-1-(Benzenesulfonyl)-2-phenylcyclopropane (4) *via* α,γ Dehydrohalogenation of 1-Bromo-1-phenyl-3-(benzenesulfonyl)-propane (3) with *n*-Butyllithium.**—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, and a rubber septum were placed 3.39 g (0.01 mol) of 1-bromo-1-phenyl-3-(benzenesulfonyl)propane and 50 ml of dry tetrahydrofuran. To this mixture 6.25 ml (0.01 mol) of a 1.6 *M* solution of *n*-butyllithium in hexane was added dropwise, with stirring, from a syringe. After the addition was complete, the reaction mixture was stirred for 3.25 hr at room temperature. The tetrahydrofuran was removed *in vacuo* leaving a yellow oil. The oil was dissolved in hot ethanol. The ethanol solution was allowed to cool, and the addition of a seed crystal of *trans*-1-(benzenesulfonyl)-2-phenylcyclopropane initiated crystallization. After standing under refrigeration overnight, the ethanol solution yielded 2.30 g (89% yield) of *trans*-1-(benzenesulfonyl)-2-phenylcyclopropane, mp 92–94°. The sulfone was recrystallized from 95% ethanol to give 2.05 g, mp 94.5–95.5°.

3-Chloropropanesulfonmorpholide (5).—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a drying tube, and a dropping funnel were placed 8.85 g (0.05 mol) of 3-chloropropanesulfonyl chloride and 25 ml of dry benzene. To this mixture a solution of 4.36 g (0.05 mol) of morpholine and 5.00 g (0.05 mol) of triethylamine in 25 ml of dry benzene was added dropwise with stirring and ice-bath cooling. After the addition was complete, the reaction was stirred for 10 min and then filtered to remove the triethylamine hydrochloride produced. The triethylamine hydrochloride was washed with several portions of dry benzene. The benzene was removed *in vacuo* from the combined filtrates leaving an orange oil which crystallized rapidly on standing. The solid was decolorized and recrystallized from 95% ethanol to give 8.50 g (75% yield) of 3-chloropropanesulfonmorpholide, mp 69–70.5°.

Anal. Calcd for $C_7H_{14}ClNO_3S$: C, 36.92; H, 6.20; Cl, 15.57; N, 6.20; S, 14.08. Found: C, 36.77; H, 6.21; Cl, 15.71; N, 5.95; S, 14.10.

Cyclopropanesulfonmorpholide (6).—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a rubber septum, and a reflux condenser with a drying tube were placed 2.28 g (0.01 mol) of 3-chloropropanesulfonmorpholide and 50 ml of dry tetrahydrofuran. To this mixture 6.25 ml (0.01 mol) of a 1.6 *M* solution of *n*-butyllithium in hexane was added dropwise, with stirring, from a syringe. The temperature of the reaction mixture rose rapidly to approximately 50°. After the addition was complete, the reaction mixture was stirred for 2.5 hr at room temperature. The tetrahydrofuran was removed *in vacuo* leaving a mixture of a heavy, clear liquid and a slightly yellow solid. A small amount of dry benzene was added to the mixture dissolving the liquid and precipitating the solid. The benzene solution was filtered to remove the solid. The solid was washed with several portions of benzene. The benzene was removed *in vacuo* from the combined benzene filtrates leaving 1.80 g of a nearly colorless liquid. The liquid was distilled at reduced pressure to give 1.45 g (76% yield) of cyclopropanesulfonmorpholide: bp 133.5–135° (1.2 mm); ir (neat) 11.2 μ; nmr δ 0.85–1.3 [m, 4, *c*-C(CH_2)$_2$], 1.8–2.58 (m, 1, SO_2CH).

Anal. Calcd for $C_7H_{13}NO_3S$: C, 43.96; H, 6.85; N, 7.32; S, 16.77. Found: C, 44.07; H, 6.95; N, 7.59; S, 16.59.

3-Phenylpropanesulfonmorpholide (9).—In a 500-ml, one-neck flask equipped with a reflux condenser were placed 29.0 g (0.145 mol) of 1-bromo-3-phenylpropane (1), 11.10 g (0.145 mol) of thiourea, and 50 ml of 95% ethanol. The mixture was heated at reflux for 48 hr and then cooled. The cooled reaction mixture was diluted with 700 ml of water and chlorine gas was bubbled through the solution, which was cooled in an ice bath, for approximately 15 min. The crude 3-phenylpropanesulfonyl chloride (8) separated as a red-orange oil. The sulfonyl chloride was extracted from the water layer with chloroform, and the chloroform solution was dried over anhydrous sodium sulfate. The chloroform was removed *in vacuo* leaving a red oil and a small amount of gelatinous red solid. The sulfonyl chloride (8) was not further purified and was used directly to prepare the amide. The crude sulfonyl chloride (8) was dissolved in 400 ml of dry benzene and a solution of 12.60 g (0.145 mol) of morpholine and 14.50 g (0.145 mol) of triethylamine in 25 ml of dry benzene was added dropwise with stirring and ice-bath cooling. After the addition was complete, the reaction mixture was stirred for 15 min and then filtered to remove the triethylamine hydrochloride produced. The benzene was removed *in vacuo* from the filtrate leaving a dark brown oil which crystallized rapidly on addition of approximately 50 ml of 95% ethanol. The crude sulfonamide was filtered, dried, decolorized, and recrystallized from 95% ethanol to give 18.90 g (48% yield) of 3-phenylpropanesulfonmorpholide, mp 96–97.5°. The sulfonamide was recrystallized from 95% ethanol to give 16.80 g, mp 97–99°.

Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20; S, 11.90. Found: C, 57.36; H, 7.11; N, 5.18; S, 11.75.

3-Bromo-3-phenylpropanesulfonmorpholide (10). Bromination of 3-Phenylpropanesulfonmorpholide (9) with N-Bromosuccinimide.—In a 1000-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a stopper, and a reflux condenser with a drying tube were placed 5.38 g (0.02 mol) of 3-phenylpropanesulfonmorpholide (9), 3.56 g (0.02 mol) of N-bromosuccinimide, and 500 ml of reagent grade carbon tetrachloride. The reaction mixture was heated at reflux and irradiated with a 250-W infrared heat lamp for 4 hr. After the irradiation was stopped and the solution cooled for several minutes, the reaction mixture was filtered to remove the succinimide produced (1.80 g, 90% yield, of succinimide was obtained). The carbon tetrachloride was removed *in vacuo* from the filtrate leaving a yellow oil which crystallized on addition of a small amount of 95% ethanol. Additional ethanol was added, and the resulting solution was heated to boiling, filtered, and refrigerated. After standing under refrigeration overnight, a white crystalline solid separated from the ethanol solution. The solid was filtered and dried to give 3.30 g (47% yield) of 3-bromo-3-phenylpropanesulfonmorpholide, mp 105–107°.

Anal. Calcd for $C_{13}H_{18}BrNO_3S$: C, 44.83; H, 5.21; Br, 22.95; N, 4.02; S, 9.20. Found: C, 45.12; H, 5.43; Br, 22.95; N, 3.95; S, 9.20.

***trans*-2-Phenylcyclopropane-1-sulfonmorpholide (11) *via* α,γ Dehydrohalogenation of 3-Bromo-3-phenylpropanesulfonmorpholide (10).**—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a drying tube, and a rubber septum were placed 2.80 g (0.008 mol) of 3-bromo-3-phenylpropanesulfonmorpholide and 50 ml of dry tetrahydrofuran. To this mixture 5.0 ml (0.008 mol) of a 1.6 *M* solution *n*-butyllithium in hexane was added dropwise, with stirring, from a syringe. After the addition was complete, the reaction mixture was stirred for 3 hr at room temperature. The tetra-

(20) All melting points and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Infracord. The nmr spectra were obtained in deuteriochloroform using a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Microanalyses were performed by Dr. C. S. Yeh and staff.

(21) P. A. S. Smith and G. E. Hein, *J. Amer. Chem. Soc.*, **82**, 5731 (1960).

hydrofuran was removed *in vacuo* leaving a pale yellow oil. The oil was dissolved in hot ethanol. The ethanol solution was allowed to cool, and addition of a seed crystal of *trans*-2-phenylcyclopropane-1-sulfonmorpholide initiated crystallization. After standing under refrigeration overnight, the ethanol solution yielded a white, crystalline solid. The solid was filtered, dried, and recrystallized twice from 95% ethanol to give 1.60 g (75% yield) of *trans*-2-phenylcyclopropane-1-sulfonmorpholide, mp 122–123°.

Phenyl 3-Chloropropanesulfonate.—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a drying tube, and a dropping funnel were placed 8.85 g (0.05 mol) of 3-chloropropanesulfonyl chloride, 4.71 g (0.05 mol) of phenol, and 25 ml of dry benzene. To this mixture, cooled in an ice bath, a solution of 5.00 g (0.05 mol) of triethylamine in 25 ml of dry benzene was added dropwise with stirring. After the addition was complete, the reaction mixture was stirred for 0.5 hr and then filtered to remove the triethylamine hydrochloride produced. The triethylamine hydrochloride was washed with several portions of dry benzene. The benzene was removed *in vacuo* from the combined benzene filtrates leaving a pale yellow oil. The yellow oil was distilled under reduced pressure (steam-jacketed condenser) to give 7.60 g (65% yield) of phenyl 3-chloropropanesulfonate as a pale yellow liquid, bp 136–138° (0.50 mm).

Anal. Calcd for $C_9H_{11}ClO_3S$: C, 46.08; H, 4.73; Cl, 15.11; S, 13.66. Found: C, 46.10; H, 4.59; Cl, 15.17; S, 13.50.

Neopentyl 3-Chloropropanesulfonate (12).—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a drying tube, and a dropping funnel were placed 4.41 g (0.05 mol) of neopentyl alcohol, 5.00 g (0.05 mol) of triethylamine, and 25 ml of dry benzene. To this mixture, cooled in an ice bath, a solution of 8.85 g of 3-chloropropanesulfonyl chloride in 25 ml of dry benzene was added dropwise with stirring. After the addition was complete, the reaction mixture was stirred for 20 min and then filtered to remove the triethylamine hydrochloride produced. The triethylamine hydrochloride was washed with several portions of dry benzene. The benzene was removed *in vacuo* from the combined benzene filtrates leaving a yellow oil. The oil was distilled at reduced pressure to give 8.10 g (78% yield) of neopentyl 3-chloropropanesulfonate, bp 107–112° (0.15 mm).

Anal. Calcd for $C_8H_{17}ClO_3S$: C, 42.00; H, 7.49; Cl, 15.50; S, 14.02. Found: C, 42.17; H, 7.46; Cl, 15.43; S, 14.13.

Neopentyl Cyclopropanesulfonate (13).—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a drying tube, and a dropping funnel were placed 1.4 g (0.015 mol) of a 50% dispersion of potassium hydride in mineral oil and 50 ml of dry tetrahydrofuran. To this mixture a solution of 3.42 g (0.015 mol) of neopentyl 3-chloropropanesulfonate (12) in 15 ml of dry tetrahydrofuran was added dropwise, with stirring, at room temperature. The reaction mixture was stirred for 5 days at room temperature. The tetrahydrofuran was removed *in vacuo* and dry benzene was added. The benzene solution was filtered, and the benzene was removed *in vacuo* leaving a colorless, oily liquid. The liquid was distilled under reduced pressure to give the following fractions: 1, bp 119–120° (5 mm); and 2, bp 128–144° (5 mm). The combined weight of the two fractions was 2.60 g. The nmr spectra of both fractions indicated that they were both mixtures of starting neopentyl 3-chloropropanesulfonate and neopentyl cyclopropanesulfonate. The cyclopropanesulfonate ester was separated from the starting material by vpc. The separation was carried out on an Aerograph Autoprep Model A-700 instrument using an SF 96 column under the following conditions: column temperature, 170°; injector temperature, 190°; detector temperature, 195°; helium flow rate, 200 ml/min. The separation yielded 0.35 g (10%) of starting neopentyl 3-chloropropanesulfonate and 0.70 g (24%) of neopentyl cyclopropanesulfonate: ir (neat) 11.2 μ; nmr δ 1.1–1.3 [m, 4, *c*-$C(CH_2)_2$], 2.2–2.8 (m, 1, SO_2CH).

Anal. Calcd for $C_8H_{16}O_3S$: C, 49.97; H, 8.39; S, 16.68. Found: C, 50.10; H, 8.41; S, 16.63.

Attempted Cyclization of Phenyl 3-Chloropropanesulfonate to Phenyl Cyclopropanesulfonate with *n*-Butyllithium.—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a rubber septum, and a reflux condenser with a drying tube were placed 2.35 g (0.01 mol) of phenyl 3-chloropropanesulfonate and 50 ml of dry tetrahydrofuran. To this mixture 6.25 ml (0.01 mol) of a 1.60 *M* solution of *n*-butyllithium in hexane was added dropwise from a syringe. The temperature of the reaction mixture rose rapidly to approximately 50°. The reaction mixture was stirred for 2 hr. The tetrahydrofuran was removed *in vacuo* leaving a mixture of a dark yellow oil and a solid. Benzene was added to the mixture and the oil dissolved leaving the solid. The benzene solution was filtered to remove the solid. The solid was washed with several portions of dry benzene. The benzene was removed *in vacuo* from the combined benzene filtrates leaving a mixture of a dark yellow oil and a white semisolid (the ir spectrum of the oil had a strong, sharp peak at 6.28 μ, indicative of an olefin). The mixture was distilled under reduced pressure to give 0.40 g (17% recovery) of starting phenyl 3-chloropropanesulfonate and a brown tar.

General Procedure for the Preparation of *trans*-1-(Arenesulfonyl)-2-arylcyclopropanes (16).—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, and an addition funnel were placed the α,β-unsaturated sulfone (0.01 mol), 2.04 g (0.01 mol) of trimethylsulfonium iodide, and 20 ml of dimethyl sulfoxide. To this mixture a solution of 1.12 g (0.01 mol) of potassium *t*-butoxide in 15 ml of dimethyl sulfoxide was added dropwise, with stirring, at room temperature. After the addition was complete, the reaction mixture was stirred for 1 hr at room temperature, and was then diluted with 250 ml of water. The diluted reaction mixture was stirred until the crude cyclopropyl sulfone separated as a solid. The crude cyclopropyl sulfone was filtered, dried, and recrystallized from 95% ethanol. These compounds show ir bands at 9.0–9.1, and 11.0–11.2 μ; nmr δ 1.3–2.08 and 2.5–3.0 (m, 4, *c*-*trans*-$CHCH_2CH_2$).

trans-1-(**Benzenesulfonyl**)-2-phenylcyclopropane (I).—*trans*-1-Phenyl-2-(benzenesulfonyl)ethene (24.40 g, 0.10 mol) gave, after one recrystallization from 95% ethanol, 21.25 g (83% yield) of *trans*-1-(benzenesulfonyl)-2-phenylcyclopropane, mp 94–95.5°. The sulfone was decolorized and recrystallized from 95% ethanol to give 19.45 g, mp 95–96°.

trans-1-(**Cyclohexanesulfonyl**)-2-phenylcyclopropane (II).—*cis*-1-Phenyl-2-(cyclohexanesulfonyl)ethene (0.4 g, 0.0016 mol) gave, after one recrystallization from 95% ethanol, 0.1 g (24% yield) of *trans*-1-(cyclohexanesulfonyl)-2-phenylcyclopropane, mp 83–84°.

trans-1-(*p*-**Toluenesulfonyl**)-2-phenylcyclopropane (III).—*trans*-1-Phenyl-2-(*p*-toluenesulfonyl)ethene (2.58 g, 0.01 mol) afforded, after one recrystallization from 95% ethanol, 1.20 g (44% yield) of *trans*-1-(*p*-toluenesulfonyl)-2-phenylcyclopropane, mp 140.5–141.5°.

trans-1-(*p*-*t*-**Butylbenzenesulfonyl**)-2-phenylcyclopropane (IV).—*trans*-1-Phenyl-2-(*p*-*t*-butylbenzenesulfonyl)ethene (3.00 g, 0.01 mol) yielded, after one recrystallization from 95% ethanol, 1.76 g (55% yield) of *trans*-1-(*p*-*t*-butylbenzenesulfonyl)-2-phenylcyclopropane, mp 100–102°.

trans-1-(**2,4,6-Triisopropylbenzenesulfonyl**)-2-phenylcyclopropane (V).—*trans*-1-Phenyl-2-(2,4,6-triisopropylbenzenesulfonyl)-ethene (3.70 g, 0.01 mol) gave 3.57 g of crude cyclopropyl sulfone. The crude sulfone was recrystallized from 95% ethanol to give 2.75 g (72% yield) of *trans*-1-(2,4,6-triisopropylbenzenesulfonyl)-2-phenylcyclopropane, mp 85–85.5°. The sulfone was recrystallized from 95% ethanol to give 2.10 g, mp 87–88°.

trans-1-(**2-Naphthalenesulfonyl**)-2-phenylcyclopropane (VI).—*trans*-1-Phenyl-2-(2-naphthalenesulfonyl)ethene (14.70 g, 0.05 mol) and trimethylsulfonium iodide (10.20 g, 0.05 mol) in 200 ml of dimethyl sulfoxide, on treatment with potassium *t*-butoxide (5.60 g, 0.05 mol) in 100 ml of dimethyl sulfoxide, gave, after one recrystallization from 95% ethanol, 12.83 g (84% yield) of *trans*-1-(2-naphthalenesulfonyl)-2-phenylcyclopropane, mp 114–115°. The sulfone was decolorized and recrystallized from 95% ethanol to give 10.00 g, mp 116–117°. The sulfone was then recrystallized from benzene–hexane to give 7.05 g, mp 118–119°.

trans-1-(*p*-**Fluorobenzenesulfonyl**)-2-phenylcyclopropane (VII).—*trans*-1-Phenyl-2-(*p*-fluorobenzenesulfonyl)ethene (2.62 g, 0.01 mol) gave 2.63 g of crude cyclopropyl sulfone. The crude sulfone was recrystallized from 95% ethanol to yield 1.85 g (67% yield) of *trans*-1-(*p*-fluorobenzenesulfonyl)-2-phenylcyclopropane, mp 86–88°. The sulfone was decolorized and recrystallized twice from 95% ethanol to give 1.10 g, mp 88.5–89.5°.

trans-1-(*p*-**Chlorobenzenesulfonyl**)-2-phenylcyclopropane (VIII).—*trans*-1-Phenyl-2-(*p*-chlorobenzenesulfonyl)ethene (1.25 g, 0.0045 mol) afforded, after one recrystallization from 95% ethanol, 0.60 g (46% yield) of *trans*-1-(*p*-chlorobenzenesulfonyl)-2-phenylcyclopropane, mp 112–114°.

trans-1-(*p*-**Bromobenzenesulfonyl**)-2-phenylcyclopropane (IX).—*trans*-1-Phenyl-2-(*p*-bromobenzenesulfonyl)ethene (3.23 g, 0.01 mol) gave, after one recrystallization from 95% ethanol, 2.72 g

(81% yield) of *trans*-1-(*p*-bromobenzenesulfonyl)-2-phenylcyclopropane, mp 106–107.5°.

***trans*-1-(*o*-Nitrobenzenesulfonyl)-2-phenylcyclopropane (X).**—*trans*-1-Phenyl-2-(*o*-nitrobenzenesulfonyl)ethene (2.89 g, 0.01 mol) gave, after dilution with 250 ml of water and stirring for 10 days, a finely divided, light tan solid. The solid was too finely divided to be filtered, so the water was carefully decanted leaving the light tan solid. The solid was dissolved in hot 95% ethanol, and the resulting solution was cooled giving 1.25 g of crude cyclopropyl sulfone. The crude sulfone was recrystallized from 95% ethanol to give 0.65 g (21% yield) of *trans*-(*o*-nitrobenzenesulfonyl)-2-phenylcyclopropane, mp 91.5–92.5°.

***trans*-1-(Benzenesulfonyl)-2-(*p*-tolyl)cyclopropane (XI).**—*trans*-1-(*p*-Tolyl)-2-(benzenesulfonyl)ethene (2.58 g, 0.01 mol) afforded, after one recrystallization from 95% ethanol, 1.85 g (68% yield) of *trans*-1-(benzenesulfonyl)-2-(*p*-tolyl)cyclopropane, mp 98.5–100°. The sulfone was yellow in color and was recrystallized five times from 95% ethanol to give 0.65 g, mp 102–103.5°.

***trans*-1-(Benzenesulfonyl)-2-(4-biphenyl)cyclopropane (XII).**—*trans*-1-(4-Biphenyl)-2-(benzenesulfonyl)ethene (3.20 g, 0.01 mol) gave 3.25 g of crude cyclopropyl sulfone. The crude sulfone was decolorized and recrystallized twice from 95% ethanol to give 2.10 g (63% yield) of *trans*-1-(benzenesulfonyl)-2-(4-biphenyl)-cyclopropane, mp 133–134°.

***trans*-1-(Benzenesulfonyl)-2-(2,6-dimethylphenyl)cyclopropane (XIII).**—*trans*-1-(2,6-Dimethylphenyl)-2-(benzenesulfonyl)ethene (2.72 g, 0.01 mol) afforded 2.40 g of crude cyclopropyl sulfone. The crude sulfone was recrystallized from 95% ethanol to give 2.25 g (79% yield) of *trans*-1-(benzenesulfonyl)-2-(2,6-dimethylphenyl)cyclopropane, mp 93–95°.

***trans*-1-(Benzenesulfonyl)-2-(*p*-chlorophenyl)cyclopropane (XIV).**—*trans*-1-(*p*-Chlorophenyl)-2-(benzenesulfonyl)ethene (2.78 g, 0.01 mol) gave 2.60 g of crude cyclopropyl sulfone. The crude sulfone was recrystallized from 95% ethanol to give 2.15 g (74% yield) of *trans*-1-(benzenesulfonyl)-2-(*p*-chlorophenyl)cyclopropane as light yellow crystals, mp 101–103°. In a similar experiment, the yellow sulfone was decolorized and recrystallized three times from 95% ethanol to give 1.00 g of *trans*-1-(benzenesulfonyl)-2-(*p*-chlorophenyl)cyclopropane as colorless crystals, mp 101–102°.

Attempted Preparation of *trans*-1-(Benzenesulfonyl)-2-(*m*-nitrophenyl)cyclopropane (XV).—*trans*-1-(*m*-Nitrophenyl)-2-(benzenesulfonyl)ethene (2.89 g, 0.01 mol) gave a small amount of brown tar and 0.16 g of a pale yellow solid. The infrared spectrum of the solid indicated that it was mainly starting vinyl sulfone.

Registry No.—Cyclopropanesulfonic acid, 21297-68-7; II, 21309-02-4; IV, 21309-03-5; V, 21309-04-6; VI, 21309-05-7; VII, 21309-06-8; VIII, 21309-07-9; IX, 21309-09-1; X, 21309-10-4; XI, 21309-11-5; XII, 21309-12-6; XIII, 21309-13-7; XIV, 21309-14-8; **3**, 21297-81-4; **4** (*trans*), 21309-15-9; **5**, 21297-82-5; **6**, 21297-83-6; **9**, 21297-84-7; **10**, 21297-80-3; **11** (*trans*), 17299-25-1; **12**, 21297-85-8; **13**, 21297-86-9; phenyl 3-chloropropanesulfonate, 21297-87-0.

Acknowledgment.—The authors wish to express their appreciation for financial support of this work by the Purdue Research Foundation and the Public Health Service Research Grant No. CA-04536-09 from the National Cancer Institute.

Liquid Crystals. II.[1] Cholesteric Properties of Some 9,19-Cyclopropane Triterpene Fatty Acid Esters[2]

FURN F. KNAPP,[3] HAROLD J. NICHOLAS,

Institute of Medical Education and Research and Department of Biochemistry, St. Louis University School of Medicine, St. Louis, Missouri 63104

AND JOSEPH P. SCHROEDER

Department of Chemistry, University of North Carolina, Greensboro, North Carolina 27412

Received April 18, 1969

In an attempt to relate structure and the ability of certain steryl esters to form a cholesteric mesophase, nine even-chain esters of 24-methylene cycloartanol were synthesized. The esters varied in chain length from acetate to stearate. None of these esters was cholesteric, while four exhibited a smectic mesophase. This substantiates an earlier observation that the C-24 (31) double bond in esters of this triterpene interferes with formation of a cholesteric mesophase. Each of the esters was reduced by catalytic hydrogenation. Four of the dihydro esters were smectic, while three were cholesteric. To investigate the effect of modifications of the steroid nucleus, the palmitate ester of cycloeucalenol was prepared and found not to be mesomorphic, while the dihydro ester exhibited a cholesteric transition state, again demonstrating the influence of the 24-methylene group. The effect of double-bond position in the side chain was further explored by the synthesis of cycloartenol palmitate. In this case, the unsaturated ester exhibited a cholesteric mesophase. With this type of nucleus, therefore, a C-24 (25) double bond is compatible with the formation of a cholesteric transition state, at least when there is no substitution at C-24. These data strongly suggest a very critical steric requirement for cholesteric mesomorphism, and are discussed in detail.

Liquid crystals are compounds which do not pass directly from the crystalline to the isotropic liquid state when melted. The intermediate phase has properties generally associated with crystalline substances even though the material is a liquid. The seemingly contradictory term "liquid crystal" is thus used to describe these interesting substances.[4] Such compounds are anisotropic and transmit light with varying velocity in different directions.[5] They are thus birefringent (doubly refractive). The reason for this crystal-like behavior of mesomorphic liquids is the parallel alignment of the relatively rigid, rod-shaped molecules, due in part to mutual attractive forces. Liquid crystals are subdivided into three categories—nematic,

(1) For the first paper in this series, see F. F. Knapp and H. J. Nicholas, *J. Org. Chem.*, **33**, 3995 (1968).

(2) F. F. Knapp and H. J. Nicholas, presented in part at the 6th International Symposium on the Chemistry of Natural Products (Steroids and Terpenes), Mexico City, April 1969.

(3) NASA Predoctoral Fellow. This work represents part of the research partially fulfilling the requirements for the degree of Doctor of Philosophy at St. Louis University.

(4) O. Lehmann, *Z. Phys. Chem.*, **4**, 468 (1889).

(5) G. H. Brown, *Chemistry*, **40**, 10 (1967).