Cyclopropanesulfonic Acid Esters and Amides

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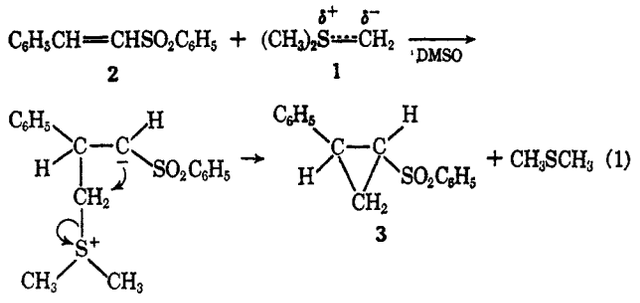
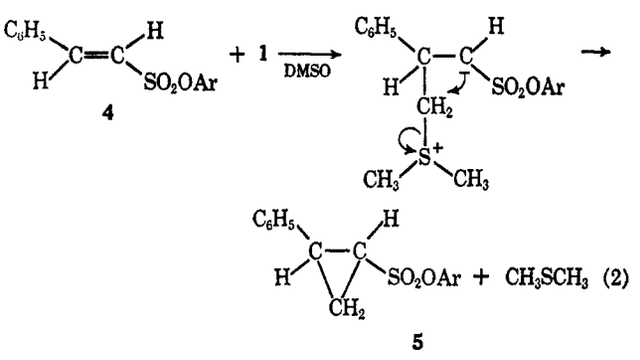
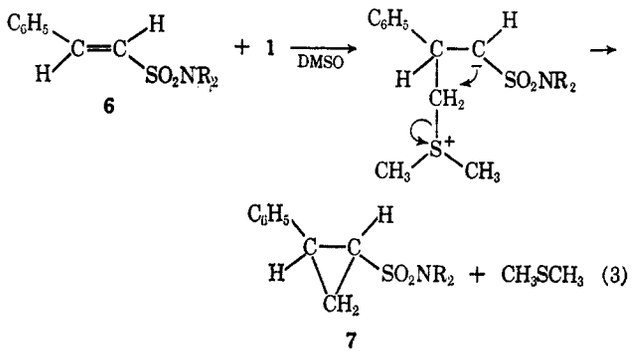
The formation of cyclopropanesulfonic acid esters and amides by the reaction of dimethylsulfonium methylide with *trans*-2-phenylethenesulfonic acid esters and amides, respectively, is described.

In a previous paper[1] we described the synthesis of *trans*-1-(benzenesulfonyl)-2-phenylcyclopropane (**3**) by the reaction of either *cis*- or *trans*-1-phenyl-2-(benzenesulfonyl)ethene (**2**) with dimethylsulfonium methylide **1** (eq 1). In this paper we wish to report the extension of this approach to the synthesis of cyclopropanesulfonic acid esters and amides.[2]

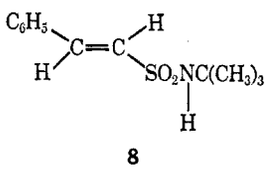


Treatment of aryl *trans*-2-phenylethenesulfonates (**4**) with trimethylsulfonium iodide[3] in the presence of potassium *t*-butoxide in dimethyl sulfoxide at room temperature afforded aryl *trans*-2-phenyl-1-cyclopropanesulfonates (**5**, eq 2 and Table I). In a similar manner, treatment of N,N-disubstituted *trans*-2-phenylethenesulfonamides (**6**) with trimethylsulfonium iodide in the presence of potassium *t*-butoxide in dimethyl sulfoxide at room temperature produced N,N-disubstituted *trans*-2-phenyl-1-cyclopropanesulfonamides (**7**, eq 3 and Table II).





An attempt to prepare a cyclopropane from an N-substituted *trans*-2-phenylethenesulfonamide, N-*t*-butyl *trans*-2-phenylethenesulfonamide (**8**), gave nearly quantitative recovery of starting material. Apparently the acid–base reaction between the sulfonamide proton and the potassium *t*-butoxide competes very well with ylide formation.



The assignment of the *trans* configuration to structures **5** and **7** is based on infrared (ir) and nuclear magnetic resonance (nmr) spectral data. The sulfonate esters and sulfonamides both gave nmr spectra containing complex multiplets at δ 1.3–2.0 and 2.5–3.0 (four protons) corresponding to the cyclopropane ring protons.[4] The ir spectra contained absorption bands at 9.0–9.1 and 11.0–11.2 μ characteristic of *trans*-cyclopropane derivatives. Furthermore, the ir spectra do not display a strong band at 12.0 μ, the characteristic absorption of *cis*-cyclopropane derivatives.[5]

The *trans*-2-phenylethenesulfonic acid esters (**4**, Table III) and amides (**6**, Table IV) were prepared by room temperature treatment of *trans*-2-phenylethenesulfonyl chloride (**9**) with the appropriate phenol (in a benzene solution of triethylamine) or secondary

(1) W. E. Truce and V. V. Badiger, *J. Org. Chem.*, **29**, 3277 (1964).

(2) (a) Sulfur ylides also react with α,β-unsaturated ketones,[2b-e] carboxylic acid esters[2f] and amides,[2f-k] nitriles,[2f,l] and nitro compounds[2m] to give the corresponding cyclopropane derivatives. (b) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965). (c) C. Agami, *Bull. Soc. Chim. Fr.*, 1391 (1967). (d) C. Agami and C. Prevost, *ibid.*, 2299 (1967). (e) E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967). (f) C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *J. Org. Chem.*, **30**, 3972 (1965). (g) H. Metzger and K. Seelert, *Angew. Chem.*, **75**, 919 (1963). (h) H. Metzger and K. Seelert, *Angew. Chem. Intern. Ed. Engl.*, **2**, 624 (1963). (i) H. Konig, H. Metzger, and K. Seelert, *Chem. Ber.*, **98**, 3712 (1965). (j) P. T. Izzo, *J. Org. Chem.*, **28**, 1713 (1963). (k) B. Loev, M. F. Kormendy, and K. M. Snader, *Chem. Ind.* (London), 1710 (1964). (l) H. Konig and H. Metzger, *Z. Naturforsch.*, **18**, 976 (1963). (m) J. Ansunskis and H. Shechter, *J. Org. Chem.*, **33**, 1164 (1968).

(3) In our previous work with α,β-unsaturated sulfones[1] the ylide **1** was generated from trimethylsulfonium bromide. Trimethylsulfonium iodide was used in the present work because of its greater ease of preparation.

(4) The nmr spectra obtained for the compounds prepared in this study are similar to that obtained for *trans*-1-(benzenesulfonyl)-2-phenylcyclopropane (**3**) which we studied earlier.[1] In addition, it was shown earlier that under the reaction conditions employed in this study *cis*-1-(benzenesulfonyl)-2-phenylcyclopropane isomerizes to the *trans* isomer, lending further support to the assignment of the *trans* configuration to **5** and **7**.

(5) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

TABLE I

ARYL *trans*-2-PHENYL-1-CYCLOPROPANESULFONATES (5)

Ar	Mp, °C	Yield, %	Molecular formula[c]	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
C_6H_5	82–84	79	$C_{15}H_{14}O_3S$	65.67	5.14	11.69	65.79	5.42	11.46
p-$CH_3C_6H_4$	51–52	70	$C_{16}H_{16}O_3S$	66.66	5.55	11.11	66.58	5.65	11.09
p-BrC_6H_4[a]	83–84	60	$C_{15}H_{13}BrO_3S$	51.00	3.71	9.08	50.82	3.66	9.09
p-$C_6H_5C_6H_4$	93–95	72	$C_{21}H_{18}O_3S$	71.98	5.17	9.15	71.54	5.23	9.32
4-Cl-2-[$(CH_3)_2CH$]-5-$CH_3C_6H_2$[b]	62–64	45	$C_{19}H_{21}ClO_3S$	62.54	5.80	8.79	62.30	5.51	8.64

[a] Bromine analysis. Calcd for $C_{15}H_{13}BrO_3S$: Br, 22.62. Found: Br, 22.64. [b] Chlorine analysis. Calcd for $C_{19}H_{21}ClO_3S$: Cl, 9.7.2 Found: Cl, 9.94. [c] Respective registry numbers follow: 17299-18-2; 17299-19-3; 17299-20-6; 17299-21-7; 17299-22-8.

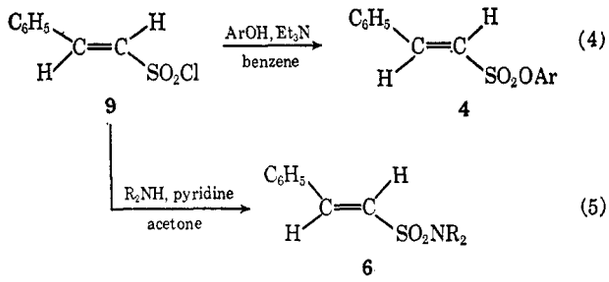
TABLE II

trans-2-PHENYL-1-CYCLOPROPANESULFONAMIDES (7)

R	Mp, °C	Yield, %	Molecular formula[a]	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % S	Found, % C	Found, % H	Found, % N	Found, % S
C_6H_5	121.5–122.5	88	$C_{21}H_{19}NO_2S$	72.17	5.48	4.01	9.18	72.43	5.46	3.89	9.10
	82–83	75	$C_{18}H_{19}NO_2S$	68.98	6.11	4.47	10.23	69.10	6.25	4.45	10.31
$CH_2CH_2OCH_2CH_2$	124–125	68	$C_{13}H_{17}NO_3S$	58.40	6.14	5.24	11.99	58.31	6.50	5.06	11.94

[a] Respective registry numbers follows: 17299-23-9; 17299-24-0; 17299-25-1.

amine (in an acetone solution of pyridine), respectively (eq 4 and 5).



(4)

(5)

Experimental Section[6]

Reagents and General Procedures.—*trans*-2-Phenylethenesulfonyl chloride was prepared according to a known procedure[7] or purchased from Research Organic/Inorganic Chemical Co. The diphenylamine, 1,2,3,4-tetrahydroquinoline, phenol, p-cresol, p-bromophenol, 4-hydroxybiphenyl, and 6-chlorothymol were Eastman White Label grade. The dimethyl sulfoxide was Baker Analyzed Reagent grade and the potassium t-butoxide was purchased from MSA Corp.

In the following part of the Experimental Section, general procedures for the syntheses summarized in Tables I–IV are described.

General Procedure for the Preparation of Cyclopropanesulfonic Acid Esters and Amides.—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a drying tube, and an addition funnel were placed the α,β-unsaturated sulfur compound (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 at room temperature. After the addition was complete, the reaction mixture was stirred for 1 hr and then diluted with 250 ml of water. The diluted reaction mixture was stirred until the cyclopropyl sulfur compound separated as a solid. The crude cyclopropyl sulfur compound was filtered, dried, and recrystallized from 95% ethanol.

Phenyl *trans*-2-Phenyl-1-cyclopropanesulfonate.—Phenyl *trans*-2-phenylethylenesulfonate (2.60 g, 0.01 mol) gave 2.40 g of crude phenyl *trans*-2-phenyl-1-cyclopropanesulfonate, mp 77–79°. The crude sulfonate ester was recrystallized from 95% ethanol to give 2.15 g (Table I).

p-Tolyl *trans*-2-Phenyl-1-cyclopropanesulfonate.—p-Toly *trans*-2-phenylethenesulfonate (2.74 g, 0.01 mol) afforded 2.00 g (70% yield) of p-tolyl *trans*-2-phenyl-1-cyclopropanesulfonate, mp 47–50°. The sulfonate ester was recrystallized from 95% ethanol to give 1.70 g (Table I). The recrystallization liquor yielded an additional 0.20 g, mp 50–51°.

p-Bromophenyl *trans*-2-Phenyl-1-cyclopropanesulfonate.—p-Bromophenyl *trans*-2-phenylethenesulfonate (3.39 g, 0.01 mol) gave a yellow oil which solidified on standing for 5 days. The solid was recrystallized from 95% ethanol to give 2.10 g (60% yield) of p-bromophenyl *trans*-2-phenyl-1-cyclopropanesulfonate, mp 81–82°. The sulfonate ester was recrystallized from 95% ethanol to give 1.75 g (Table I).

4-Biphenyl *trans*-2-Phenyl-1-cyclopropanesulfonate.—4-Biphenyl *trans*-2-phenylethenesulfonate (3.36 g, 0.01 mol) gave, after two recrystallizations from 95% ethanol, 2.50 g of 4-biphenyl *trans*-2-phenyl-1-cyclopropanesulfonate (Table I).

4-Chloro-2-isopropyl-5-methylphenyl *trans*-2-Phenyl-1-cyclopropanesulfonate.—4-Chloro-2-isopropyl-5-methylphenyl *trans*-2-phenylethenesulfonate (3.50 g, 0.01 mol) yielded 1.65 g of 4-chloro-2-isopropyl-5-methylphenyl *trans*-2-phenyl-1-cyclopropanesulfonate (Table I).

N,N-Diphenyl *trans*-2-Phenylcyclopropane-1-sulfonamide.—N,N-Diphenyl *trans*-2-phenylethenesulfonamide (3.35 g, 0.01 mol) afforded 3.48 g of crude cyclopropyl sulfonamide. The crude sulfonamide was recrystallized from 95% ethanol to give 3.06 g of N,N-diphenyl *trans*-2-phenylcyclopropane-1-sulfonamide (Table II).

***trans*-2-Phenylcyclopropane-1-sulfon-1′,2′,3′,4′-tetrahydroquinolide.**—*trans*-2-Phenylethenesulfon-1′,2′,3′,4′-tetrahydroquinolide (2.99 g, 0.01 mol) gave 2.35 g (75% yield) of *trans*-2-phenylcyclopropane-1-sulfon-1′,2′,3′,4′-tetrahydroquinolide, mp 80.5–82°. The sulfonamide was recrystallized from 95% ethanol to give 2.20 g (Table II).

***trans*-2-Phenylcyclopropane-1-sulfonmorpholide.**—*trans*-2-Phenylethenesulfonmorpholide (2.53 g, 0.01 mol) afforded 1.80 g of *trans*-2-phenylcyclopropane-1-sulfonmorpholide (Table II).

Attempted Reaction of N-t-Butyl *trans*-2-Phenylethenesulfonamide with Dimethylsulfonium Methylide.—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, and an addition funnel were placed 2.39 g (0.01 mol) of N-t-butyl *trans*-2-phenylethenesulfonamide, 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 then diluted with 250 ml of water. The diluted reaction mixture was stirred until a white solid separated. The solid was filtered and dried to give 2.30 g (96% recovery) of the starting N-t-butyl *trans*-2-phenylethenesulfonamide, mp 109–110°. The recovered sulfonamide was recrystallized from 95% ethanol to give 2.05 g, mp 110–111°.

(6) All melting points are uncorrected. The ir 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.

(7) C. S. Rondestvedt and F. G. Bordwell, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1964, p 846.

TABLE III

ARYL *trans*-2-PHENYLETHENESULFONATES (4)

Ar	Mp, °C	Yield, %	Molecular formula[d]	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
C_6H_5	123–124[a]	84	$C_{14}H_{12}O_3S$	64.59	4.65	12.32	64.46	4.67	12.14
p-$CH_3C_6H_4$	74–75	75	$C_{15}H_{14}O_3S$	65.67	5.14	11.69	65.85	5.19	11.48
p-BrC_6H_4[b]	61.5–63	60	$C_{14}H_{11}BrO_3S$	49.57	3.27	9.45	49.34	2.99	9.33
p-$C_6H_5C_6H_4$	144–145	80	$C_{20}H_{16}O_3S$	71.40	4.80	9.53	71.24	4.98	9.57
4-Cl-2-[$(CH_3)_2CH$]-5-$CH_3C_6H_2$[c]	91–92	73	$C_{18}H_{19}ClO_3S$	61.62	5.46	9.14	61.52	5.28	9.08

[a] A. P. Terent'ev and R. A. Gracheva [*Zh. Obshchei. Khim.*, **30**, 3663 (1960)] report mp 123°. [b] Bromine analysis. Calcd for $C_{14}H_{11}BrO_3S$: Br, 23.56. Found: Br, 23.48. [c] Chlorine analysis. Calcd for $C_{18}H_{19}ClO_3S$: Cl, 10.10. Found: Cl, 9.97. [d] Respective registry numbers follow: 17299-26-2; 17299-27-3; 17299-28-4; 17299-29-5; 17299-30-8.

TABLE IV

trans-2-PHENYLETHENESULFONAMIDES (6)

R	Mp, °C	Yield, %	Molecular formula[a]	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % S	Found, % C	Found, % H	Found, % N	Found, % S
C_6H_5	157–158	56	$C_{20}H_{17}NO_2S$	71.61	5.11	4.18	9.56	71.41	5.11	4.05	9.38
	103–104.5	70	$C_{17}H_{17}NO_2S$	68.20	5.72	4.68	10.71	68.16	5.91	4.64	10.83
$CH_2CH_2OCH_2CH_2$	113.5–115	82	$C_{12}H_{15}NO_3S$	56.89	5.97	5.53	12.66	56.93	5.79	5.24	12.68

[a] Respective registry numbers follows: 17299-31-9; 17326-51-1; 17299-32-0.

General Procedure for the Preparation of Aryl *trans*-2-Phenylethenesulfonates.—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a reflux condenser, and a drying tube were placed 5.00 g (0.025 mol) of *trans*-2-phenylethenesulfonyl chloride, 0.025 mol of the desired phenol, and 25 ml of dry benzene. To this mixture was added 2.50 g (0.025 mol) of triethylamine and the reaction mixture was stirred for 45 min to 1 hr at room temperature. The reaction mixture was filtered to remove the triethylamine hydrochloride which had precipitated, and the triethylamine hydrochloride was washed with several portions of dry benzene. The combined benzene filtrates were evaporated leaving a pale yellow oil which generally crystallized upon addition of a small amount of 95% ethanol. The sulfonate esters were purified by recrystallization from 95% ethanol.

Phenyl *trans*-2-Phenylethenesulfonate.—Phenol (4.62 g, 0.05 mol), *trans*-2-phenylethenesulfonyl chloride (10.00 g, 0.05 mol), and triethylamine (5.00 g, 0.05 mol) in 50 ml of dry benzene afforded 10.70 g (84% yield) of phenyl *trans*-2-phenylethenesulfonate, mp 122–123.5°. The sulfonate ester was decolorized and recrystallized from 95% ethanol to give 7.50 g (Table III).

***p*-Tolyl *trans*-2-Phenylethenesulfonate.**—*p*-Cresol (2.67 g, 0.025 mol) gave, after two recrystallizations from 95% ethanol, 5.10 g (75% yield) of *p*-tolyl *trans*-2-phenylethenesulfonate, mp 73.5–74°. The sulfonate ester was decolorized and recrystallized from 95% ethanol to give 3.60 g (Table III).

***p*-Bromophenyl *trans*-2-Phenylethenesulfonate.**—*p*-Bromophenol (4.27 g, 0.025 mol) afforded 5.00 g (60% yield) of *p*-bromophenyl *trans*-2-phenylethenesulfonate, mp 60.5–61.5°. The sulfonate ester was decolorized and recrystallized from 95% ethanol to give 4.00 g (Table III).

4-Biphenyl *trans*-2-Phenylethenesulfonate.—4-Hydroxybiphenyl (8.51 g, 0.05 mol), *trans*-2-phenylethenesulfonyl chloride (10.10 g, 0.05 mol), and triethylamine (5.00 g, 0.05 mol) in a mixture of 400 ml of dry benzene and 100 ml of chloroform gave, after one recrystallization from 95% ethanol, 13.40 g of 4-biphenyl *trans*-2-phenylethenesulfonate (Table III).

4-Chloro-2-isopropyl-5-methylphenyl *trans*-2-Phenylethenesulfonate.—4-Chloro-2-isopropyl-5-methylphenol (9.23 g, 0.05 mol), *trans*-2-phenylethenesulfonyl chloride (10.10 g, 0.05 mol), and triethylamine (5.00 g, 0.05 mol) afforded 12.65 g of 4-chloro-2-isopropyl-5-methylphenyl *trans*-2-phenylethenesulfonate (Table III).

General Procedure for the Preparation of *trans*-2-Phenylethenesulfonamides.[8]—In a 300-ml, three-neck flask equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel were placed 10.00 g (0.05 mol) of *trans*-2-phenylethenesulfonyl chloride and 100 ml of acetone. To this mixture a solution of the appropriate amine (0.20 mol) in 25 ml of pyridine was added dropwise, with stirring, at room temperature. After the addition was complete, the reaction mixture was stirred for 1.5 hr at room temperature and then poured into a mixture of crushed ice and water. The diluted reaction mixture was stirred until the sulfonamide separated as a solid. The solid was filtered, dried, decolorized, and recrystallized from 95% ethanol.

N,N-Diphenyl *trans*-2-Phenylethenesulfonamide.—Diphenylamine (4.17 g, 0.025 mol) in 12.5 ml of pyridine and *trans*-2-phenylethenesulfonyl chloride (5.00 g, 0.025 mol) in 50 ml of acetone gave the crude sulfonamide as a purple, hydrated solid. The solid was filtered, dried, decolorized, and recrystallized from 95% ethanol to afford 4.65 g of N,N-diphenyl *trans*-2-phenylethenesulfonamide (Table IV).

***trans*-2-Phenylethenesulfon-1′,2′,3′,4′-tetrahydroquinolide.**—1,2,3,4-Tetrahydroquinoline (6.66 g, 0.05 mol) in 12.5 ml of pyridine and *trans*-2-phenylethenesulfonyl chloride (5.00 g, 0.025 mol) in 50 ml of acetone gave, after decolorization and three recrystallizations from 95% ethanol, 5.20 g of *trans*-2-phenylethenesulfon-1′,2′,3′,4′-tetrahydroquinolide (Table IV).

***trans*-2-Phenylethenesulfonmorpholide.**—Morpholine (17.42 g, 0.20 mol) in 25 ml of pyridine and *trans*-2-phenylethenesulfonyl chloride (10.00 g, 0.049 mol) in 100 ml of acetone gave 10.10 g (82% yield) of crude sulfonamide, mp 110–113°. The crude sulfonamide was recrystallized from 95% ethanol to give 9.90 g of tan crystals, mp 113–114°. The tan crystals were decolorized and recrystallized from 95% ethanol to give 8.40 g of *trans*-2-phenylethenesulfonmorpholide as colorless needles (Table IV).

N-*t*-Butyl *trans*-2-Phenylethenesulfonamide.—*t*-Butylamine (7.3 g, 0.10 mol) in 12.5 ml of pyridine and *trans*-2-phenylethenesulfonyl chloride (5.00 g, 0.025 mol) in 50 ml of acetone gave 5.90 g of crude sulfonamide, mp 105–107°. The sulfonamide was decolorized and recrystallized three times from 95% ethanol to give 3.45 g (59% yield) of N-*t*-butyl *trans*-2-phenylethenesulfonamide, mp 110–111°.

Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85; S, 13.40. Found: C, 60.17; H, 7.32; N, 5.76; S, 13.40.

Registry No.—8, 17299-33-1.

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(8) This procedure is an adaptation of that reported by C. S. Rondestvedt and J. C. Wygant [*J. Amer. Chem. Soc.*, **73**, 5785 (1951)] for the preparation of N,N-diethyl *trans*-2-phenylethenesulfonamide.