reaction). After the addition was complete, the mixture was stirred at reflux 1 hr and at room temperature overnight. Work-up and tosylation as described for **3a** afforded 3.77 g (60%) of **6** as a chalky solid, mp 119–124°. Several recrystallizations from 2-propanol afforded pure **6** as white needles, mp 123–125°.

Anal. Calcd for $C_{18}H_{19}NO_2S$: C, 68.99; H, 6.11; N, 4.47; S, 10.23. Found: C, 68.74; H, 6.32; N, 4.73; S, 10.50.

Registry No.—**3a**, 30135-80-9; **3b**, 30135-81-0; **5**, 30166-89-3; **6**, 30166-90-6; **8**, 30166-91-7; **9**, 30166-92-8.

Acknowledgment.—We are grateful to Professors J. E. Baldwin (MIT) and E. Wenkert (Indiana) for helpful discussions.

trans-1-Aryl-2-(arenesulfonyl)ethenes. Copper-Catalyzed Addition of Sulfonyl Chlorides to Substituted Styrenes[1]

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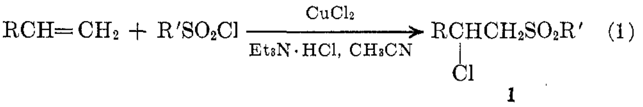
trans-1-Phenyl-2-(benzenesulfonyl)ethene (**2**, R = R′ = C_6H_5) has been prepared by (a) the condensation of benzenesulfonylacetic acid with benzaldehyde,[3] (b) the addition of benzenethiol to phenylacetylene followed by oxidation of the resulting *trans*-1-phenyl-2-(phenylmercapto)ethene with hydrogen peroxide,[4] and (c) the copper-catalyzed addition of benzenesulfonyl chloride to styrene followed by dehydrohalogenation of the resulting 1-chloro-1-phenyl-2-(benzenesulfonyl)ethane (**1**, R = R′ = C_6H_5) with triethylamine.[5] In this paper we would like to describe our studies on the synthetic utility of method c.

Arenesulfonyl chlorides can be added to styrenes to give 1-chloro-1-aryl-2-(arenesulfonyl)ethanes [**1**, R,R′ = aryl (eq 1)] in good to excellent yields (see Table I).



$$RCH{=}CH_2 + R'SO_2Cl \xrightarrow[Et_3N\cdot HCl,\ CH_3CN]{CuCl_2} \underset{\displaystyle Cl}{RCH}CH_2SO_2R' \quad (1)$$

1

The reaction appears to be little affected by substituent electronic effects or by steric effects of substituents in the 2 and 6 positions of either the sulfonyl chloride or the styrene. Treatment of the 1-chloro-1-aryl-2-(arenesulfonyl)ethanes (**1**) with triethylamine in benzene afforded the corresponding *trans*-1-aryl-2-(arenesulfonyl)ethenes [**2**, R, R′ = aryl (eq 2)] in excellent yield (see Table II).[6]

Table I.—Sulfonyl Chloride Adducts 1

Registry no.	R	R′	Mp, °C	Yield, %	Calcd, % C	H	Cl	S	Found, % C	H	Cl	S
6461-58-1	C_6H_5	C_6H_5	88–90[a]	75								
30158-41-9	C_6H_5	2,4,6-$[CH(CH_3)_2]_3C_6H_2$	119–120	89	67.87	7.68	8.71	7.88	68.02	7.86	8.90	8.13
30158-42-0	C_6H_5	2,4,6-$(CH_3)_3C_6H_2$	98–99	84	63.24	5.93	10.98	9.93	63.15	6.15	11.08	9.96
30158-43-1	C_6H_5	2-$C_{10}H_7$	124.5–125	89	65.34	4.57	10.72	9.69	65.16	4.55	10.95	9.45
30158-44-2	C_6H_5	4-FC_6H_4[b]	88–90	82	56.28	4.05	11.87	10.73	56.28	3.84	11.70	10.95
30158-45-3	C_6H_5	4-BrC_6H_4[c]	90.5–91	96	46.75	3.36	9.86	8.91	47.02	3.55	9.90	9.01
30158-46-4	C_6H_5	4-$O_2NC_6H_4$[d]	136–137	78	51.61	3.72	10.88	9.84	51.85	3.93	10.76	9.80
30158-47-5	C_6H_5	2-$O_2NC_6H_4$[e]	106–107	82	51.61	3.72	10.88	9.84	51.38	3.86	11.00	9.73
30158-48-6	C_6H_5	2-O_2N-4-ClC_6H_3[f]	135–137	82	46.69	3.05	19.69	8.90	46.85	3.26	19.44	8.97
30158-49-7	4-$CH_3C_6H_4$	C_6H_5	91–93	65	61.11	5.13	12.03	10.88	61.35	5.06	12.01	10.68
30158-50-0	4-$C_6H_5C_6H_4$	C_6H_5	130–132	46[g]	67.31	4.80	9.94	8.98	67.58	4.68	9.66	9.09
30158-51-1	2,6-$(CH_3)_2C_6H_3$	C_6H_5	75–77	78	62.24	5.51	11.49	10.37	62.35	5.57	11.69	10.49
30158-52-2	4-ClC_6H_4	C_6H_5	80.5–82	68	53.34	3.84	22.50	10.17	53.56	4.09	22.63	10.39
30158-53-3	3-$O_2NC_6H_4$[h]	C_6H_5	86–88	74	51.61	3.72	10.88	9.84	51.53	3.70	11.00	9.75
6038-47-7	C_6H_5	CH_3	70.5–72	66	49.42	5.07	16.22	14.66	49.53	5.11	15.94	14.43
30158-39-5	C_6H_5	$C_6H_5CH_2$	121–122	6[i]	61.11	5.13	12.03	10.88	61.23	5.10	11.76	10.87
30158-56-6	C_6H_5	$BrCH_2$[j]	101–102	80	36.32	3.39	11.91	10.77	36.21	3.15	11.99	10.72

[a] M. Asscher and D. Vofsi [*J. Chem. Soc.*, 4962 (1964)] report mp 89–90°. [b] *Anal.* Calcd for $C_{14}H_{12}ClFO_2S$: F, 6.36. Found: F, 6.45. [c] *Anal.* Calcd for $C_{14}H_{12}BrClO_2S$: Br, 22.22. Found: Br, 22.30. [d] *Anal.* Calcd for $C_{14}H_{12}ClNO_4S$: N, 4.30. Found: N, 4.58. [e] *Anal.* Calcd for $C_{14}H_{12}ClNO_4S$: N, 4.30. Found: N, 4.28. [f] *Anal.* Calcd for $C_{14}H_{11}Cl_2NO_4S$: N, 3.86. Found: N, 3.87. [g] A large amount of polymerization of 4-vinylbiphenyl occurred. [h] *Anal.* Calcd for $C_{14}H_{12}ClNO_4S$: N, 4.30. Found N, 4.35. [i] Most of the α-toluenesulfonyl chloride decomposed to benzyl chloride and sulfur dioxide (see text and Experimental Section) resulting in a low yield of 1:1 adduct. [j] *Anal.* Calcd for $C_9H_{10}BrClO_2S$: Br, 26.85. Found: Br, 26.70.

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[1] Unsaturated Sulfones and Suitable Precursors. III. For previous papers in this series, see W. E. Truce, C. T. Goralski, L. W. Christensen, and R. H. Bavry, *J. Org. Chem.*, **35**, 4217 (1970); W. E. Truce and C. T. Goralski, *ibid.*, **35**, 4220 (1970).

[2] Halogens Research Laboratory, The Dow Chemical Co., Midland, Mich. 48640.

[3] V. Baliah and M. Seshapathirao, *J. Org. Chem.*, **24**, 867 (1959).

[4] H. G. Klein, Ph.D. Thesis, Purdue University, 1961.

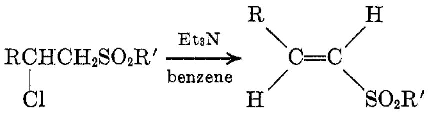
[5] M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964).

[6] The vinyl sulfones **2** were identified as the trans isomers by their nmr (J_{vinyl} = 14–16 cps) and infrared (ω_{vinyl} = 10.2–10.5 μ) spectra which are typical of trans 1,2-disubstituted olefins. We earlier described the reaction of these vinyl sulfones (Table II) with dimethylsulfonium methylide to give the corresponding *trans*-1-(arenesulfonyl)-2-arylcyclopropanes: W. E. Truce and C. T. Goralski, *J. Org. Chem.*, **34**, 3324 (1969).

TABLE II.—UNSATURATED SULFONES 2

Registry no.	R	R′	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
16212-06-9	C_6H_5	C_6H_5	75–76[a]	94						
30166-82-6	C_6H_5	2,4,6-$[CH(CH_3)_2]_3C_6H_2$	125–126	88	74.55	8.16	8.65	74.56	8.00	8.46
30166-83-7	C_6H_5	2,4,6-$(CH_3)_3C_6H_2$	89.5–90.5	96	71.30	6.33	11.20	70.90	6.20	11.06
30166-84-8	C_6H_5	2-$C_{10}H_7$	143.5–144	87	73.44	4.79	10.90	73.38	5.02	11.02
30166-85-9	C_6H_5	4-FC_6H_4[b]	83.5–84	97	64.10	4.23	12.23	64.08	4.37	12.32
30166-86-0	C_6H_5	2-$O_2NC_6H_4$[c]	123.5–124	93	58.13	3.83	11.08	58.13	4.11	11.18
30166-87-1	C_6H_5	2-O_2N-4-ClC_6H_3[d]	170–170.5	89	51.93	3.11	9.91	52.14	3.40	9.85
30166-88-2	4-$CH_3C_6H_4$	C_6H_5	137–138[e]	78						
30166-77-9	4-$C_6H_5C_6H_4$	C_6H_5	172–173	84	74.97	5.03	10.01	74.70	5.20	9.77
33166-78-0	2,6-$(CH_3)_2C_6H_3$	C_6H_5	120–121	89	70.55	5.92	11.78	70.71	5.96	11.50
30246-73-2	2-$C_{10}H_7$	C_6H_5	103–104	19[f]	73.44	4.79	10.97	73.38	5.02	11.02
20605-52-1	4-ClC_6H_4	C_6H_5	131–132[g]	80						
15436-11-0	C_6H_5	CH_3	80–81[h]	87						

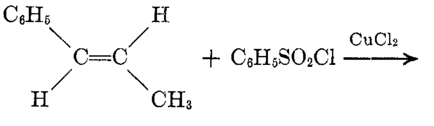
[a] M. Asscher and D. Vofsi [*J. Chem. Soc.*, 4962 (1964)] report mp 75–76°. [b] *Anal.* Calcd for $C_{14}H_{11}FO_2S$: F, 7.24. Found: F, 7.23. [c] *Anal.* Calcd for $C_{14}H_{11}NO_4S$: N, 4.84. Found: 4.55. [d] *Anal.* Calcd for $C_{14}H_{10}ClNO_4S$: Cl, 10.95; N, 4.33. Found: Cl, 10.69; N, 4.27. [e] V. Baliah and M. Seshapathirao [*J. Org. Chem.*, **24**, 867 (1959)] report mp 135.5–136.5°. [f] This represents the total overall yield from 2-vinylnaphthalene. A large amount of polymerization of the 2-vinylnaphthalene occurred, and the initial sulfonyl chloride adduct could not be isolated in pure form. [g] V. Baliah and M. Seshapathirao [*ibid.*, **24**, 867 (1959)] report mp 129–130°. [h] W. E. Parham, F. D. Blake, and D. R. Theissen [*ibid.*, **27**, 2415 (1962)] report mp 77–78°.



(2)

1 2

The reaction of *trans*-β-methylstyrene (**3**) with benzenesulfonyl chloride gave 1-chloro-1-phenyl-2-(benzenesulfonyl)propane (**4**) as a thick, viscous oil which, on treatment with triethylamine in benzene, was converted to β-(benzenesulfonyl)-*cis*-β-methylstyrene (**5**, eq 3).[7] In contrast, an attempt to react *trans*-stilbene with benzenesulfonyl chloride gave only a 95% recovery of the starting olefin.



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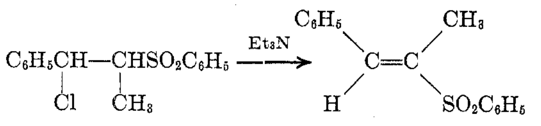
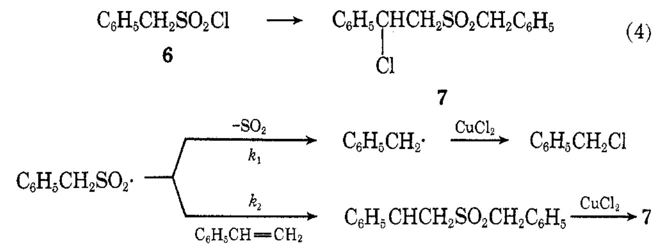


(3)

4 5

A brief study of the reaction of alkanesulfonyl chlorides with styrene was made. Methanesulfonyl chloride and bromomethanesulfonyl chloride added to styrene to give 1:1 adducts (Table I) in 66 and 80% yield, respectively, but α-toluenesulfonyl chloride (**6**) gave mainly benzyl chloride and sulfur dioxide and only a 6% yield of 1-chloro-1-phenyl-2-(α-toluenesulfonyl)ethane (**7**, eq 4). Apparently the intermediate α-toluenesulfonyl radical loses sulfur dioxide to give a benzyl radical at a faster rate than it is trapped by styrene to give a 1-phenyl-2-(α-toluenesulfonyl)ethyl radical ($k_1 > k_2$).[8]



(4)

6 7

In conclusion, the copper-catalyzed addition of sulfonyl chlorides to styrenes followed by elimination of hydrogen chloride from the resulting β-chloro sulfones represents an excellent, high-yield synthesis of *trans*-1-aryl-2-(arenesulfonyl)ethenes and other unsaturated sulfones.

Experimental Section[9]

General Procedure for the Addition of Sulfonyl Chlorides to Styrenes.—Typically, in a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet, and a reflux condenser fitted with a calcium chloride drying tube were placed 0.10 mol of the styrene, 0.10 mol of the sulfonyl chloride, 0.13 g (1.0 mmol) of anhydrous cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4.00 g of acetonitrile. The above mixture was then heated at 100–130°, with stirring, under the nitrogen for 2 hr and then cooled. Methanol (40 ml) was added to the cooled reaction mixture, and the β-chloro sulfone separated as a white, crystalline solid. The solid was filtered, washed with water, and recrystallized from 95% ethanol to give analytically pure **1**.

β-(Benzenesulfonyl)-*cis*-β-methylstyrene.—A mixture of 10.0 g (0.085 mol) of *trans*-β-methylstyrene, 15.0 g (0.085 mol) of benzenesulfonyl chloride, 0.110 g (0.85 mmol) of anhydrous cupric chloride, 0.175 g (1.27 mmol) of triethylamine hydro-

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(7) The structural assignment of **5** is based on the observation that the vinyl proton signal overlaps the ortho aromatic protons of the benzenesulfonyl group (δ 7.80) as observed for the proton geminal to the phenyl group (δ 7.67) in the nmr spectra of *trans*-1-phenyl-2-(benzenesulfonyl)ethene. In contrast, the signal for the proton geminal to the phenyl group in *cis*-1-phenyl-2-(benzenesulfonyl)ethene occurs at δ 6.90 [A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *J. Amer. Chem. Soc.*, **86**, 2877 (1964)].

(8) A similar mechanism has been proposed to explain the results of the reaction of chloromethanesulfonyl chloride with 1-octene and styrene in the presence of cupric chloride (ref 5).

(9) All reactions were carried out in a nitrogen atmosphere. Reagent grade cupric chloride was used in all addition reactions and was dried at 140° prior to use. All compounds gave nmr spectra consistent with their assigned structures (recorded on a Varian A-60A spectrometer with tetramethylsilane as an internal standard). All melting points are uncorrected. The elemental analyses were performed by Dr. C. S. Yeh and the staff of the Purdue Microanalytical Laboratory.

chloride, and 3.4 g of acetonitrile was heated with stirring at 110° for 2 hr and then cooled. Methanol (34 ml) was added to the cooled reaction mixture and the resulting solution was refrigerated. After standing under refrigeration for several days, no solid separated from the solution. The methanol was removed *in vacuo* leaving a thick, viscous, yellow oil. The oil was dissolved in a minimum amount of dry benzene and 12.87 g (0.127 mol) of triethylamine was added. The reaction mixture was stirred for 1 hr and then filtered to remove the triethylamine hydrochloride which had precipitated. 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 which crystallized on addition of a small amount of 95% ethanol. The solid was filtered, dried, and recrystallized from 95% ethanol to give 9.90 g (45% yield) of β-(benzenesulfonyl)-*cis*-β-methylstyrene: mp 94.5–95.5°; nmr δ 2.10 (d, 3), 7.33 (s, 5), 7.45–7.70 (m, 3), 7.75–8.05 (m, 3).

Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.68; H, 5.23; S, 12.53.

Attempted Reaction of Benzenesulfonyl Chloride with *trans*-Stilbene.—A mixture of 18.00 g (0.10 mol) of *trans*-stilbene, 17.67 g (0.10 mol) of benzenesulfonyl chloride, 0.130 g (1.0 mmol) of anhydrous cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4.00 g of acetonitrile was heated, with stirring, at 120° for 2 hr and then cooled. Methanol (40 ml) was added to the cooled reaction mixture and unreacted *trans*-stilbene separated as a pale yellow, crystalline solid. The recovered *trans*-stilbene was filtered, dried, and recrystallized from 95% ethanol to give 17.10 g (95% recovery), mp 125–126° (lit.[10] mp 124°).

General Procedure for the Preparation of Unsaturated Sulfones (2).—To a saturated solution of the sulfonyl chloride adduct **1** in dry benzene was added 1.5 equiv of triethylamine. The reaction mixture was allowed to stir for 45 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 an oil which crystallized on addition of a small amount of ethanol. The solid was recrystallized from 95% ethanol to give analytically pure **2**.

Reaction of α-Toluenesulfonyl Chloride (6) with Styrene.—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, and a reflux condenser with a drying tube were placed 10.41 g (0.10 mol) of styrene, 19.06 g (0.10 mol) of α-toluenesulfonyl chloride, 0.130 g (0.0010 mol) of anhydrous cupric chloride, 0.206 g (0.0015 mol) of triethylamine hydrochloride, and 4.00 g of acetonitrile. The reaction mixture was heated, with stirring, at 125° for 2 hr and then cooled. During the entire 2-hr reaction period the evolution of sulfur dioxide (SO_2) was noted. Methanol (40 ml) was added to the cooled reaction mixture, and the resulting solution was refrigerated. A small amount of a white solid separated from the cold solution. The solid was filtered, dried, and recrystallized from 95% ethanol to give 0.85 g of 1-chloro-1-phenyl-2-(α-toluenesulfonyl)ethane, mp 121–122°.

Anal. Calcd for $C_{15}H_{15}ClO_2S$: C, 61.11; H, 5.13; Cl, 12.03; S, 10.88. Found: C, 61.23; H, 5.10; Cl, 11.76; S, 10.87.

The methanol was removed from the recrystallization liquor *in vacuo* leaving a yellow oil which was distilled under reduced pressure. The distillation yielded 7.18 g of a colorless liquid which was shown by nmr to be a mixture consisting of 65% benzyl chloride and 35% styrene. A heavy, dark residue remained after distillation. The residue was dissolved in 95% ethanol and decolorized. The ethanol solution was cooled yielding an additional 1.00 g of 1-chloro-1-phenyl-2-(α-toluenesulfonyl)ethane, mp 118–119°. The total yield of 1:1 adduct was 1.85 g (6% yield).

Registry No.—**5**, 30246-74-3; **7**, 30158-39-5.

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.

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[10] "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing, Cleveland, Ohio, 1964, p C-546.

α,β-Epoxysulfonamides

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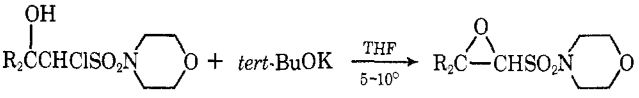
Although various electronegatively substituted epoxides are known, considerable current attention is being devoted to the synthesis of new moieties in this classification.[1] Only recently has the preparation of α,β-epoxysulfonyl and sulfinyl systems been reported.[2]

Our own interest in α-substituted sulfonic acid derivatives[3] coupled with the facile synthetic route to β-hydroxy-α-chlorosulfonamides, which we recently reported,[4] suggested the preparation of the novel α,β-epoxysulfonic acid derivatives.

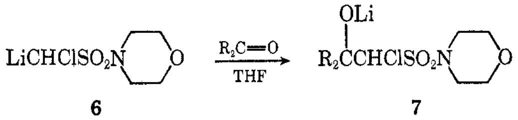
Indeed, when the precursory β-hydroxy-α-chlorosulfonamides **1** were treated with potassium *tert*-butoxide in THF, the α,β-epoxysulfonamides were formed in good to moderate yields (Table I).



1 **2**

This reaction almost certainly proceeds *via* initial formation of the β-alkoxide followed by an intramolecular displacement of the halogen atom. The ease (low temperature, short reaction time) of this displacement is noteworthy since it is in direct contrast to intermolecular S_N2 displacements α to sulfonyl groupings in both sulfones[5] and sulfonamides,[6] which occur only with difficulty. However, a parallel effect is encountered in the Ramberg–Bäcklund reaction, which also involves an intramolecular displacement α to a sulfonyl grouping and can also occur at low temperature.[7] Seemingly, when the nucleophilic center is generated in the proximity of the reaction site, the sulfonyl group exhibits either a highly diminished retarding effect or no retarding effect on α displacements.

It would be useful synthetically if the α,β-epoxide could be generated directly from the condensation of the α-chloroalkyllithium sulfonamide **6** with a ketone, thereby bypassing the isolation and subsequent ring closing of the β-hydroxy-α-chlorosulfonamide. However, allowing a solution of **6** and a ketone, *e.g.*, acetone,



6 **7**

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[1] (a) J. Cantacuzene and J.-M. Normant, *Tetrahedron Lett.*, 2947 (1970); (b) H. Newman and R. B. Angier, *Tetrahedron*, **26**, 825 (1970).

[2] (a) P. F. Vogt and D. F. Tavares, *Can. J. Chem.*, **47**, 2875 (1969); (b) F. Bohlmann and G. Haffer, *Chem. Ber.*, **102**, 4017 (1969); (c) T. Durst and K.-C. Tin, *Tetrahedron Lett.*, 2369 (1970); (d) D. F. Tavares, R. E. Estep, and M. Blezard, *ibid.*, 2373 (1970).

[3] (a) W. E. Truce and L. W. Christensen, *Tetrahedron*, **25**, 181 (1969); (b) W. E. Truce and D. J. Vrencur, *Can. J. Chem.*, **47**, 860 (1969).

[4] W. E. Truce and L. W. Christensen, *Tetrahedron Lett.*, 3075 (1969).

[5] F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, **33**, 1182 (1968).

[6] F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5184 (1951).

[7] W. E. Truce, T. C. Klingler, J. E. Parr, H. Feuer, and D. K. Wu, *J. Org. Chem.*, **34**, 3104 (1969).