Free-Radical Addition of Organic Disulfides to Acetylenes

E. I. HEIBA AND R. M. DESSAU

Mobil Oil Corporation, Central Research Division Laboratory, Princeton, New Jersey 08540

Received June 5, 1967

The free-radical addition of organic disulfides to acetylenes gives high yields of the corresponding 1:1 adducts and thus provides a synthetic route to 1,2-dialkylmercaptoethenes. The high yields of adduct obtained with acetylenes, unlike the corresponding reactions with olefins, is attributed to the limited reversibility of the initial thiyl radical addition and the greater reactivity of the vinyl radical intermediate.

The free-radical addition of thiols to unsaturated compounds has been studied extensively.[1] However, very little is known about the free-radical addition of organic disulfides to olefinic or acetylenic hydrocarbons.

We have found that organic disulfides can be readily added to acetylenic compounds by a free-radical mechanism, resulting in high yields of the 1:1 adducts. The corresponding addition to olefins results in poor yields of the 1:1 adducts.

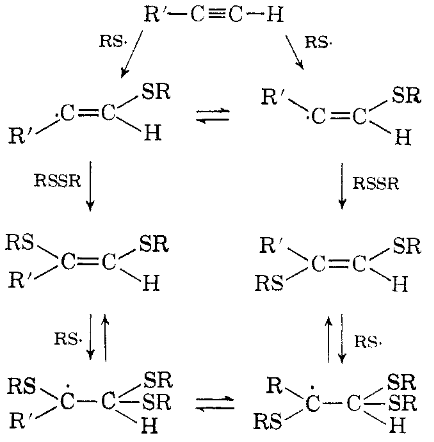
Results and Discussion

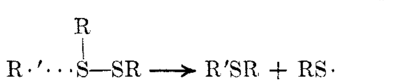
Product Analysis of the Radical Addition of Disulfides to Monosubstituted Acetylenes.—The free-radical addition of methyl or *n*-butyl disulfide to methylacetylene was carried out in sealed quartz ampoules and initiated by ultraviolet light from a 200-w Hanovia lamp at room temperature. The radical addition of disulfides to 1-heptyne was initiated by ultraviolet light at room temperature or by *t*-butyl peroxide at 120°. In general, the reaction proceeded smoothly and gave the disulfide–acetylene 1:1 adduct in over 80% yield, based on the acetylenic compound consumed. In all cases, the main components of the adduct mixture were the *cis*- and *trans*-1,2-dialkylmercapto-1-ethenes (*cis* or *trans* refer to the configurational relationship of the two alkylmercapto substituents). The *cis* and *trans* 1:1 adducts were separated by vpc and it was shown that no isomerization took place under the method of separation. Some of the physical data and elemental analyses are listed in Tables I and II. The configurations of the *cis* and *trans* isomeric 1:1 adducts were established by their characteristic infrared, ultraviolet, and nmr spectra. The *cis* 1:1 adducts exhibited a strong infrared absorption band at 1580 cm^{-1} compared with a low-intensity band for the *trans* 1:1 adduct isomer.[2] The ultraviolet absorption spectrum of the *trans* isomer contained a maximum at 268 mμ (ϵ_{max} 12,400), while the *cis* isomer displayed a maximum at 254 mμ (ϵ_{max} 7300). The nmr spectrum of the *cis* 1:1 adduct showed the vinylic hydrogen peak at lower field than the *trans* adduct.[3] The *cis* isomer also had a larger allylic coupling constant than the *trans* compound.[4]

The ratio of *trans/cis* isomers was independent of the chain length of the disulfide or the monosubstituted acetylene used. The *trans/cis* ratio was also found to be constant at various degrees of conversion (Table III).

Mechanism of the Radical Addition of Disulfides to Acetylenes.—The –SS– bond of disulfides undergoes homolytic cleavage upon irradiation with ultraviolet light.[5,6] The first propagation step of the radical chain addition of disulfides is the terminal addition of a thiyl radical to the monosubstituted acetylene (Scheme I). The vinyl radical intermediates[7] continue the chain by displacing a thiyl radical from the disulfide probably through a backside displacement sequence.[8]

SCHEME I





$$R\cdot' \cdots \overset{R}{\overset{|}{S}}—SR \longrightarrow R'SR + RS\cdot$$

The *trans–cis* ratio was found to be constant at various degrees of conversion (Table III). This may be due to thermodynamic rather than kinetic control since either isomer could be readily isomerized to the equilibrium mixture (Table IV) under the reaction condition. The rapid isomerization, as well as the failure to detect any appreciable amounts of further addition of disulfide, can be attributed to the facile reversibility of the thiyl radical addition to the 1:1 adduct.

The Relative Reactivity of Methylacetylene and Propylene toward Radical Addition of Methyl Disulfide.—Although the radical addition of disulfides to monosubstituted acetylenes proceeds readily, the analogous

---

(1) J. A. Kampmeier and G. Chen, *J. Am. Chem. Soc.*, **87**, 2608 (1965); A. A. Oswald, K. Greisbaum, B. E. Hudson, Jr., and J. M. Bregman, *ibid.*, **86**, 2877 (1964), and references therein.

(2) The intensity of the C=C stretching band in the 1600-cm^{-1} region was utilized for characterizing *cis*- and *trans*-1,2-dichloropropene: H. T. Bernstein and T. Powling, *ibid.*, **73**, 1843 (1951).

(3) The vinylic hydrogen in *cis*-1,2-dichloroethene shows a nmr signal at lower field than the *trans* isomer: NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1963.

(4) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, 108.

(5) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 4435 (1955).

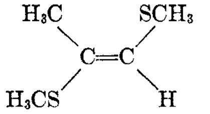
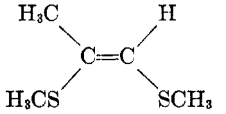
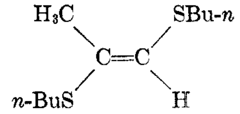
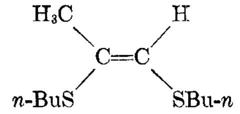
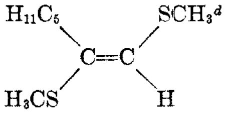
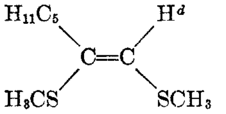
(6) C. Walling and R. Rabinowitz, *ibid.*, **81**, 1137 (1959).

(7) R. W. Fessenden and R. H. Schuler [*J. Chem. Phys.*, **39**, 2147 (1963)] have shown that methyl vinyl radicals exist in two distinct isomeric forms with little barrier for interconversion. It is not unexpected, therefore, that the mercaptovinyl radical intermediate equilibrates prior to transfer of a second thiyl group.

(8) W. A. Pryor and H. Guard, *J. Am. Chem. Soc.*, **86**, 1150 (1964).

TABLE I

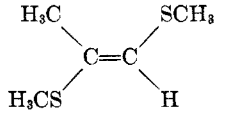
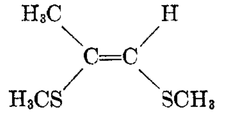
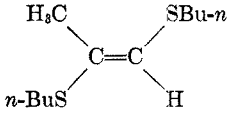
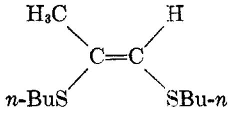
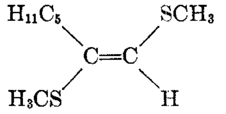
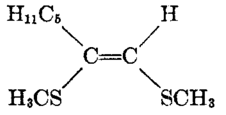
SOME PHYSICAL AND ANALYTICAL DATA OF DISULFIDE–MONOSUBSTITUTED ACETYLENE 1:1 ADDUCTS[a]

Product	Bp (mm), °C (Registry No.)	Isomer,[b] %	Calcd, %				Found, %				Formula[c]
			C	H	S	Mol wt[c]	C	H	S	Mol wt[c]	
	193–195 (14255-30-2)	81	44.71	7.51	47.78	134	44.62	7.45	47.81	134	$C_5H_{10}S_2$
	193–195 (14255-31-3)	19	44.71	7.51	47.78	134	44.62	7.45	47.81	134	$C_5H_{10}S_2$
	130–132 (4.7) (14255-32-4)	80	60.55	10.1	29.35	218	60.47	10.15	29.42	218	$C_{11}H_{22}S_2$
	130–132 (4.7) (14255-33-5)	20	60.55	10.1	29.35	218	60.47	10.15	29.42	218	$C_{11}H_{22}S_2$
	91–95 (0.08) (14255-34-6)	77	56.76	9.54		190	56.77	9.61		190	$C_9H_{18}S_2$
	(14255-35-7)	23	56.76	9.54		190	56.91	9.43		190	$C_9H_{18}S_2$

[a] Addition reactions initiated with ultraviolet light at 20°. [b] Analysis of the 1:1 adduct isomers were carried out by vpc and also nmr. [c] Empirical formula and molecular weights were determined by mass spectroscopy. [d] Initiated with ultraviolet light at 20° or *t*-butyl peroxide at 120°.

TABLE II

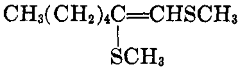
NMR, INFRARED, AND ULTRAVIOLET SPECTRA OF DISULFIDE–MONOSUBSTITUTED ACETYLENES 1:1 ADDUCTS

Product	Infrared spectra,[a] cm^{-1}	Ultraviolet spectra[b]		Nmr group signal, chemical shift in τ[c]	
		λ_{max}, mμ	ϵ_{max}	Vinyl H	Methyl
	1580 (w), 1100, 985, 955, 915, 815	268	11,000	4.2 (q) ($J \sim 1.0$)	8.1 (d) ($J \sim 1.0$)
	1580 (s), 1100, 985, 915, 825	255	7,300	4.0 (q) ($J \sim 1.4$)	8.0 (d) ($J \sim 1.4$)
	1580 (w), 1100, 985, 915, 825	267	12,500	4.0 (q) ($J \sim 1.0$)	8.0 (d) ($J \sim 1.0$)
	1580 (s), 1100, 1015, 915, 835	254	7,300	3.9 (q) ($J \sim 1.4$)	7.9 (d) ($J \sim 1.4$)
	1580 (w)	269	10,400	4.4 (s)	
	1580 (s)	255	6,900	4.0 (triplet)	

[a] The spectra were carried out neat using KBr optics. [b] The ultraviolet absorption spectra were carried out in 95% EtOH using Beckman spectrophotometer, Model DK-2. [c] The nmr spectra were recorded with a Varian Model A-60 proton resonance spectrophotometer. In all cases tetramethylsilane (TMS) was used as an internal standard and chemical shifts are given in τ, J in cycles per second.

TABLE III
ADDITION OF METHYL DISULFIDE TO 1-HEPTYNE INITIATED WITH ULTRAVIOLET LIGHT AT 20°

	Mole % of 1:1 adduct	
Time of irradiation, hr	*trans*	*cis*
2	77.0	23.0
4	77.4	22.1
6	74.1	25.9
24	74.7	25.3
48	73.4	26.6



$CH_3(CH_2)_4\underset{SCH_3}{C}{=}CHSCH_3$

TABLE IV
THE ISOMERIZATION OF $CH_3(CH_2)_4\underset{SCH_3}{C}{=}CHSCH_3$ UPON IRRADIATION IN THE PRESENCE OF CH_3SSCH_3

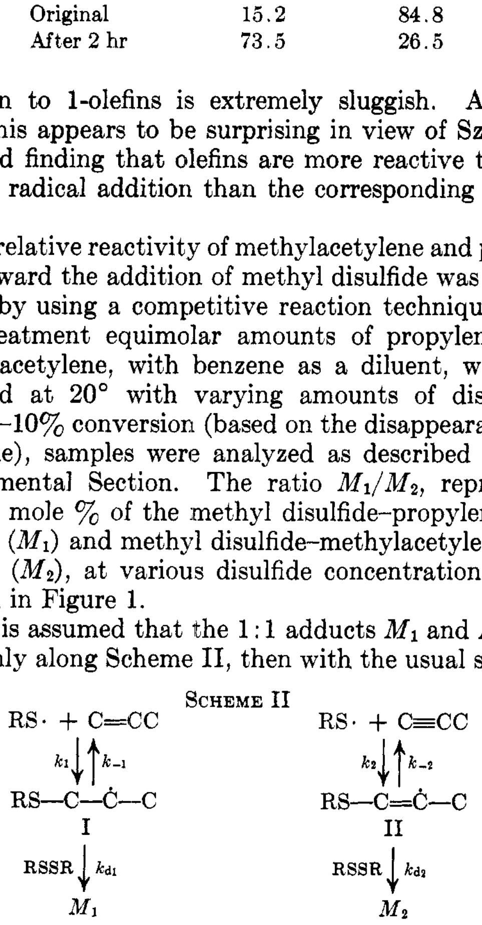
	Mole %	
	trans	*cis*
Original	98.4	1.6
After 2 hr	75.8	24.2
Original	15.2	84.8
After 2 hr	73.5	26.5

addition to 1-olefins is extremely sluggish. At first hand this appears to be surprising in view of Szwarc's reported finding that olefins are more reactive toward methyl radical addition than the corresponding acetylenes.[9]

The relative reactivity of methylacetylene and propylene toward the addition of methyl disulfide was determined by using a competitive reaction technique. In this treatment equimolar amounts of propylene and methylacetylene, with benzene as a diluent, were irradiated at 20° with varying amounts of disulfide. After 5–10% conversion (based on the disappearance of disulfide), samples were analyzed as described in the Experimental Section. The ratio M_1/M_2, representing the mole % of the methyl disulfide–propylene 1:1 adduct (M_1) and methyl disulfide–methylacetylene 1:1 adduct (M_2), at various disulfide concentrations were plotted in Figure 1.

If it is assumed that the 1:1 adducts M_1 and M_2 appear only along Scheme II, then with the usual steady-state approximation for the radical intermediates I and II, the rate expressions are given in eq 1 and 2. At the same molar concentrations of propylene and methylacetylene, one obtains eq 3. The reactivity ratio M_1/M_2 depends not only on the reactivities of propylene and methylacetylene toward RS· addition, but also on the rates of elimination of RS· from I and II and on the rates of reaction of I and II with RSSR.

SCHEME II



$$\frac{dM_1}{dt} = \frac{k_1k_{d_1}(C{=}CC)(RS\cdot)(RSSR)}{k_{-1} + k_{d_1}(RSSR)} \qquad (1)$$

$$\frac{dM_2}{dt} = \frac{k_2k_{d_2}(C{\equiv}CC)(RS\cdot)(RSSR)}{k_{-2} + k_{d_2}(RSSR)} \qquad (2)$$

$$\frac{dM_1}{dM_2} = \frac{k_1k_{d_1}(k_{-2} + k_{d_2}[RSSR])}{k_2k_{d_2}(k_{-1} + k_{d_1}[RSSR])} \qquad (3)$$

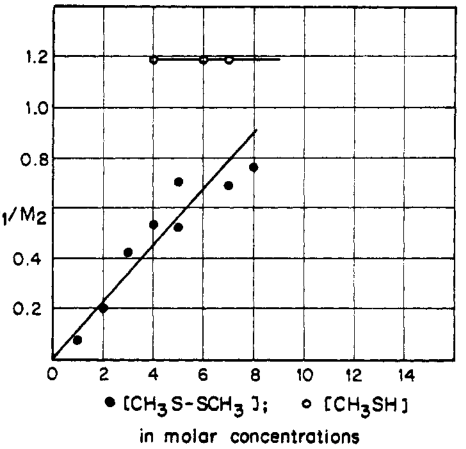


Figure 1.—Relative reactivity of propylene and methylacetylene. Dependence of M_1/M_2 on the disulfide or thiol concentrations.

There are two limiting cases (a and b).

(1) At high and constant disulfide concentration where $k_{-1} \ll k_{d_1}$ (RSSR) and $k_{-2} \ll k_{d_2}$ (RSSR), eq 3 is reduced to eq 4. Owing to the relatively low transfer constants of the disulfide[10] to radicals I and II, the conditions for eq 4 were not achieved with methyl disulfide. The conditions for irreversibility were satisfied, however, for CH_3SH addition at high molar concentrations, from which a value for k_1/k_2 was obtained. Figure 1 yields a value for $k_1/k_2 = 1.2$, which indicates that the rate constant for addition of $CH_3S\cdot$ to propylene is slightly higher than for addition of methylacetylene. This agrees with Szwarc's observation for methyl radical addition, although his value is somewhat higher than that reported here. This is not unexpected in view of the relatively high activation energy for the addition of methyl radicals compared with thiyl radicals.

$$M_1/M_2 = k_1/k_2 \qquad (4)$$

(b) At low disulfide concentrations where $k_{-1} \gg k_{d_1}$ (RSSR) and $k_{-2} \gg k_{d_2}$ (RSST), there are two extreme possibilities. (1) Where $k_{-1} \cong k_{-2}$, eq 3 is reduced to eq 5 and M_1/M_2 is independent of (RSSR).

$$M_1/M_2 = \frac{k_1k_{-2}k_{d_1}}{k_2k_{-1}k_{d_2}} \qquad (5)$$

This situation was not verified by the results in Figure 1. (2) Where $k_{-2} = 0$ and k_{-1} is finite, eq 6 holds

$$M_1/M_2 = \frac{k_1k_{d_1}}{k_2k_{-1}}(RSSR) \qquad (6)$$

and M_1/M_2 is a linear function of (RSSR). This was indeed verified in Figure 1. Even though it cannot be assumed that $k_{-2} = 0$, it should be expected that $k_{-1} > k_{-2}$. The addition of $CH_3S\cdot$ to methylacetylene is more exothermic than the corresponding addition to propylene.[11] Since the activation energy for $CH_3S\cdot$

---

[9] M. Gazith and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 3339 (1957).

[10] R. M. Pierson, A. J. Costanza, and A. H. Winstein, *J. Polymer Sci.*, **17**, 221 (1955).

[11] The heat of hydrogenation of propylene and methylacetylene is 30.1 and 69.1 kcal/mole, respectively: C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press Inc., New York, N. Y., 1962, p 55. The calculated π-bond energies for C═C in propylene and C≡C in methylacetylene are 60 and 64 kcal/mole, respectively. On the basis of available bond-dissociation energies data, D(═$CSCH_3$) in radical II is estimated to be about 7 kcal/mole greater than D(—$CSCH_3$) in radical I. Considering these values, the addition of $CH_3S\cdot$ to methylacetylene is about 3 kcal/mole more exothermic than the corresponding addition to propylene.

addition to methylacetylene is slightly higher than that for addition to propylene, the activation energy for the dissociation of radical II ($E_{k_{-2}}$) should be at least 3 kcal/mole greater than the corresponding $E_{k_{-1}}$. Furthermore, radical II, being a vinylic radical, is more reactive than the secondary radical I and thus it is expected that $k_{d_2} > k_{d_1}$. Both conditions require that the rato M_1/M_2 would increase with the increase of the disulfide concentration. This was indeed observed.

In conclusion, the synthetic utility of the free radical addition of disulfides to acetylenes does not derive from any greater reactivity of acetylenes, but rather from the limited reversibility of the initial addition step and the greater reactivity of the vinyl radical intermediate.

Experimental Section

General Procedure for the Addition of Disulfides to Acetylenes.—In a typical experimental run, a mixture of disulfide (0.3 mole) and acetylene (0.1 mole) was transferred into a quartz ampoule fitted with a ground joint. The mixture was flushed with nitrogen then connected to a vacuum line, cooled to −78°, evacuated to remove traces of oxygen, and the sealed while on the vacuum line. When methylacetylene was used, the exact volume was condensed while the ampoule was connected to the vacuum line. Each ampoule was placed in a constant-temperature water bath (20 ± 2°) and irradiated with ultraviolet light from a Hanovia ultraviolet 200-w lamp. When *t*-butyl peroxide was used as initiator, the reaction mixture was sealed in a thick-walled Pyrex ampoule and heated in a constant-temperature oil bath at 120 ± 2°. In most runs the reaction was carried out for 24 hr. The reaction mixture was distilled and the different fractions were analyzed by gas chromatography using a 10-ft column of 10% Carbowax (20M) on Chromosorb P. Helium was used as a carrier gas and a temperature increase of 11°/min was programmed over the range of 80–225°. In all the runs side reactions were negligible. Products corresponding to thiol–acetylene 1:1 adduct were less than 2% and the undistillable residues were less than 10% (by weight) of all the reaction products. The per cent yield of the *cis* and *trans* 1:1 adducts was determined by vpc and the value obtained was found to be consistent with that obtained by nmr analysis of the crude reaction mixture prior to distillation.

Determination of the Relative Reactivity of Propylene and Methylacetylene toward the Addition of Methyl Disulfide.—Each of several solutions of various concentrations of methyl disulfide (1–8 *M*) in benzene was transferred into a quartz ampoule, flushed with nitrogen, cooled at −78°, and evacuated on a vacuum system. Equimolar quantities of propylene and methylacetylene (0.5 *M* each) were condensed and the ampoule was sealed under vacuum. The ampoules were placed in a constant-temperature water bath at 20 ± 2° and irradiated with a 200-w ultraviolet lamp. The runs at each methyl disulfide concentration were carried out in triplicate. The irradiation was continued until about 10% conversion took place (based on the disappearance of methyl disulfide). The radiation time varied from about 4 hr at the higher disulfide concentrations to about 18 hr at the lower concentrations. Each reaction mixture was analyzed by vpc (10-ft Carbowax column) and the ratios of the 1:1 adducts from the addition of methyl disulfide to propylene (M_1) and to methylacetylene (M_2) at various methyl disulfide concentrations were plotted in Figure 1.

Determination of the Reactivity of Propylene and Methylacetylene toward the Addition of Methyl Thiyl Radicals.—Equimolar amounts of propylene and methylacetylene (0.5 *M* each) were mixed with various concentrations of methanethiol in benzene (4, 6, and 7 *M*) applying the above-described technique. The runs at each methanethiol concentration were carried out in duplicate and irradiated with ultraviolet light until the reaction proceeded to about 10% conversion (based on the appearance of the products). The irradiation time varied from 10 to 30 min depending on the concentration of the methanethiol used. The major reaction products were 1-methylthiopropane, 1-methylthiopropene, and small amounts of 1,2-bismethylthiopropane resulting from the addition of two molecules of methanethiol to methylacetylene. The ratio of M_1/M_2 in Figure 1 represents the mole % of methanethiol–propylene 1:1 adduct relative to methanethiol–methylacetylene 1:1 adduct correcting for the fraction of the 1:1 adduct in the 2:1 adduct.

The Effect of Structure on the Rates of Thermal Decomposition of Solid Benzyldimethylsulfonium Salts[1a]

W. DICKINSON BURROWS[1b] AND JOHN H. CORNELL

Clothing and Organic Materials Laboratory, U. S. Army Natick Laboratories, Natick, Massachusetts 01760

Received May 19, 1967

The rates of thermal decomposition of 22 different benzyldimethylsulfonium salts have been measured. Counterion, substituent, particle size, and temperature effects have been studied. It is concluded that particle size and crystal lattice energy may be as important as chemical structure in determining reaction rates for these salts.

The rates of decomposition of neutral sulfonium salts in solution have been widely studied. In particular it is known that trimethylsulfonium salts undergo a second-order displacement reaction when the anion is a good nucleophile such as halide ion[2] (eq 1),

$$(CH_3)_3SX \dashrightarrow (CH_3)_2S + CH_3X \qquad (1)$$

but that the competing, pseudo-first-order solvolysis (eq 2) dominates when the anion is a poor nucleophile, such as arenesulfonate.[3] With benzyldimethylsulfonium compounds the benzyl group is preferentially displaced (eq 3), permitting a systematic study of

$$(CH_3)_3S^+ + H_2O \dashrightarrow (CH_3)_2S + CH_3OH + H^+ \qquad (2)$$

$$C_6H_5CH_2S(CH_3)_2X \dashrightarrow (CH_3)_2S + C_6H_5CH_2X \qquad (3)$$

substituent effects. These reactions give curved Hammett plots and where hydroxide is the anion the Hammett plot displays a minimum, indicative of a change in mechanism from a process involving bond making to one involving bond breaking.[4] In the interest of learning whether the thermal decomposition of solid sulfonium salts shows the same dependence on the counterion and substituents, we have prepared 22 different benzyldimethylsulfonium salts and have

---

[1] (a) Presented in part before the Division of Organic Chemistry of the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967; (b) National Academy of Sciences–National Research Council Senior Visiting Scientist, 1966–1967.

[2] C. G. Swain and L. E. Kaiser, *J. Am. Chem. Soc.*, **80**, 4089 (1958).

[3] (a) E. D. Hughes, C. K. Ingold, and Y. Pocker, *Chem. Ind.* (London), 1282 (1959); (b) C. G. Swain and W. D. Burrows, unpublished results.

[4] (a) C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961); (b) C. G. Swain, T. Rees, and L. J. Taylor, *ibid.*, **28**, 2903 (1963); (c) K. B. J. Schowen, Ph.D. Thesis, Massachusetts Institute of Technology, April, 1964.