TABLE III
IR SPECTRA OF 1,5-BISANILINO-1,4-NAPHTHOQUINONE[a]

^{14}N	^{15}N
1608	1606.5
1592	1592
1553	1554
1537 (s)[b]	1525
1491	1491
1423.5	1423.5
1289 (b)[c]	1284
1147	1147
949.5	949.5

[a] $CDCl_3$ solution. [b] s, shoulder. [c] b, broad.

nitrogen could be identified. In Table III it can be seen that the strong band at 1537 cm^{-1} and the one at 1289 cm^{-1} shift appreciably upon isotopic substitution and these are the only absorptions observed with appreciable shifts.

Experimental Section

Spectra were taken as previously described.[1]

Compound 1.—To 54 mg (0.3 mmol) of 1,5-diamino-4,8-naphthoquinone was added 166 mg, 1.2 mmol, of aniline and 1 ml of acetic acid. The solution was gently refluxed for 4 hr and then the solvent was removed. The residue was crystallized from toluene–hexane, wt 86 mg, mp 220–221°.[9]

The ^{15}N compound was synthesized in the same manner, employing 99.5% aniline-^{15}N.

Compound 3.—This compound was synthesized as 1. The material was crystallized from xylene, mp 220–222°. *Anal.* Calcd for $C_{26}H_{24}O_4N_2$: C, 72.88; H, 5.69; N, 6.54. Found: C, 72.77; H, 7.53; N, 6.43.

Registry No.—**1**, 26823-92-7; **3**, 26823-93-8.

(9) C. Neudecker, Thesis, Würzburg, Germany, 1930.

The Reaction of α-Sulfonyl Carbanions with Carbon Disulfide

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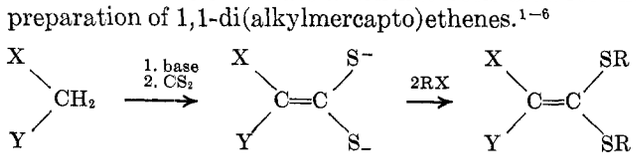
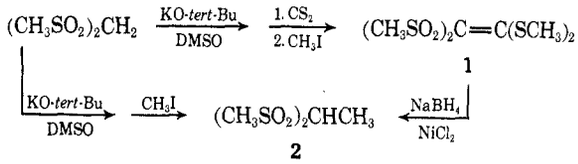
The base-induced reaction of activated methylene groups with carbon disulfide followed by alkylation of the intermediate dithiolate anion has been used for the preparation of 1,1-di(alkylmercapto)ethenes.[1-6]



This reaction has now been investigated as a synthetic route to structures of the type $RSO_2(R')C{=}C(SR'')_2$ and $(RSO_2)_2C{=}C(SR')_2$, starting with the appropriate sulfone or disulfone.

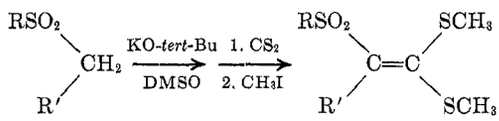
(1) R. Gompper and W. Topfl, *Chem. Ber.*, **95**, 2861 (1962).
(2) E. Soderback, *Acta Chem. Scand.*, **17**, 362 (1963).
(3) R. Gompper, E. Kutter, and W. Topfl, *Justus Liebigs Ann. Chem.*, **659**, 90 (1962).
(4) A. Thuillier and J. Vialle, *Bull. Soc. Chim. Fr.*, 2182, 2194 (1962).
(5) D. C. Dittmer, H. E. Simmons, and R. D. Vest, *J. Org. Chem.*, **29**, 497 (1964).
(6) K. A. Jensen and L. Henriksen, *Acta Chem. Scand.*, **22**, 1107 (1968).

The expected product, 1,1-di(methylsulfonyl)-2,2-di(methylmercapto)ethene (**1**), was isolated in 11.5% yield when di(methylsulfonyl)methane was treated with carbon disulfide in dimethyl sulfoxide in the presence of potassium *tert*-butoxide, followed by methylation. The structure of **1** was demonstrated by reduc-



tion of the double bond with simultaneous desulfurization of the mercaptal unit by treatment with the sodium borohydride–nickelous chloride system.[7] The resulting 1,1-di(methylsulfonyl)ethane (**2**)[8] was identical with an authentic sample prepared by methylation of di(methylsulfonyl)methane. An attempt to extend this sequence to di(*p*-tolylsulfonyl)methane led only to methylated starting material, 1,1-di(*p*-tolylsulfonyl)ethane.

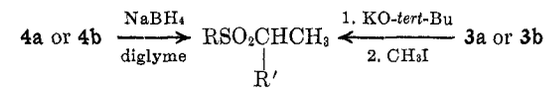
Treatment of the monosulfones benzyl phenyl sulfone (**3a**), benzyl *p*-tolyl sulfone (**3b**), and methyl *p*-tolyl sulfone (**3c**) in a like manner afforded products **4a–c** in 30, 50, and 2.5% yields, respectively.



3a, R = Ph; R′ = Ph
b, R = *p*-$CH_3C_6H_4$; R′ = Ph
c, R = *p*-$CH_3C_6H_4$; R′ = H

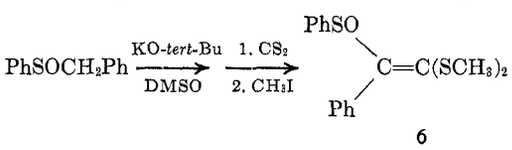
4a, R = Ph; R′ = Ph
b, R = *p*-$CH_3C_6H_4$; R′ = Ph
c, R = *p*-$CH_3C_6H_4$; R′ = H

Reduction of **4a** and **4b** with sodium borohydride in diglyme produced the α-methyl benzyl sulfones, **5a** and **5b**, which were prepared independently by methylation of the benzyl sulfones.



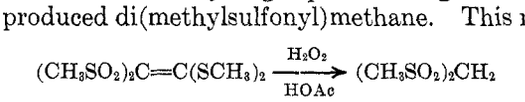
5a, R = Ph; R′ = Ph
b, R = *p*-$CH_3C_6H_4$; R′ = Ph

Application of the reaction sequence to benzyl phenyl sulfoxide gave a material whose spectral characteristics were in accord with 1-phenyl-1-(phenylsulfinyl)-2,2-di(methylmercapto)ethene (**6**). The initial product **6**



decomposed to a pungent black oil which was not further investigated.

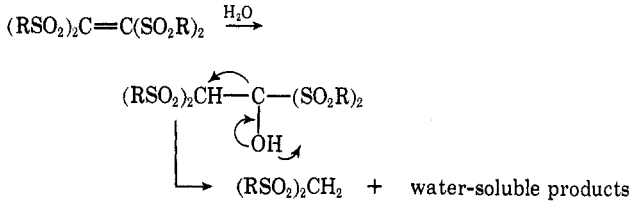
Oxidation of **1** with hydrogen peroxide in glacial acetic acid produced di(methylsulfonyl)methane. This result



is analogous to that of oxidation of 1,1,2,2-tetra(*p*-tolylmercapto)ethene[9] and 1-nitro-2,2-di(methylmercapto)-ethene.[10] The products of the oxidation reactions

(7) W. E. Truce and F. M. Perry, *J. Org. Chem.*, **30**, 1316 (1965).
(8) D. T. Gibson, *J. Chem. Soc.*, 2640 (1931).
(9) W. E. Truce and B. Groten, *J. Org. Chem.*, **27**, 128 (1962).
(10) K. A. Jensen, O. Buchardt, and C. Lohse, *Acta Chem. Scand.*, **21**, 2797 (1967).

are believed to arise by hydration of an initially formed intermediate tri- or tetra(alkylsulfonyl)ethene, followed by cleavage of the hydrate to the observed product and to water-soluble products which were not recovered.



Experimental Section[11]

Starting Materials.—Di(methylsulfonyl)methane,[12] di(*p*-tolylsulfonyl)methane,[13] benzyl phenyl sulfone,[14] benzyl *p*-tolyl sulfone,[15] and benzyl phenyl sulfoxide[14] were prepared by known methods. Methyl *p*-tolyl sulfone, potassium *tert*-butoxide, and methyl iodide were commercially available and used without further purification. Commercial grade carbon disulfide was distilled before use.

General Procedure for Dimercaptomethylation.—To a stirred solution of potassium *tert*-butoxide in dimethyl sulfoxide, under nitrogen, was added a solution of the sulfone in dimethyl sulfoxide. After the solution was stirred for 10 min, carbon disulfide was added, after which the solution became dark red to purple. Methyl iodide was added dropwise to the solution, whereupon the color changed to yellow. The resulting solution was stirred from 1.5 to 3 hr, poured into water, and extracted with methylene chloride, and the extracts were washed with water. After drying ($MgSO_4$), the solvent was removed *in vacuo* and the red oil remaining was dissolved in hot methanol, decolorized, and cooled. Recrystallization afforded the pure product.

1,1-Di(methylsulfonyl)-2,2-di(methylmercapto)ethene (1).—This was prepared from 11.2 g (0.10 mol) of potassium *tert*-butoxide, 8.6 g (0.05 mol) of di(methylsulfonyl)methane, 3.2 ml (0.05 mol) of carbon disulfide, and 6.2 ml (0.10 mol) of methyl iodide, according to the above procedure. Work-up gave 1.8 g of solid which was recrystallized from toluene to afford 1.6 g (11.5%) of **1**: mp 153–154°; nmr ($CDCl_3$) δ 2.69 (s, 6 H, CH_3S), 3.33 ppm (s, 6 H, CH_3SO_2).

Anal. Calcd for $C_6H_{12}O_4S_4$: C, 26.08; H, 4.35; S, 46.38. Found: C, 26.24; H, 4.66; S, 46.01.

1-Phenyl-1-(phenylsulfonyl)-2,2-di(methylmercapto)ethene (4a).—This was prepared, as above, from 11.6 g (0.05 mol) of benzyl phenyl sulfone. Work-up and recrystallization from methanol gave 5.10 g (30%) of product: mp 120–121°; nmr ($CDCl_3$) δ 2.20 (s, 6 H, CH_3S),[16] 7.1–8.0 ppm (m, 10 H, aromatic protons).

Anal. Calcd for $C_{16}H_{16}O_2S_3$: C, 57.15; H, 4.76; S, 28.57. Found: C, 57.32; H, 5.03; S, 28.43.

1-Phenyl-1-(*p*-tolylsulfonyl)-2,2-di(methylmercapto)ethene (4b).—Treatment of 12.3 g (0.05 mol) of benzyl *p*-tolyl sulfone as described above afforded 7.1 g (50%) of product: mp 104–106°; nmr ($CDCl_3$) δ 2.15 (s, 3 H, CH_3S), 2.21 (s, 3 H, CH_3S), 2.39 (s, 3 H, $CH_3C_6H_5$), 7.15–7.81 ppm (m, 9 H, aromatic protons).

Anal. Calcd for $C_{17}H_{18}O_2S_3$: C, 58.35; H, 5.14; S, 27.42. Found: C, 58.73; H, 5.31; S, 27.27.

1-(*p*-Tolylsulfonyl-2,2-di(methylmercapto)ethene (4c).—This was prepared as described above from 8.5 g (0.05 mol) of methyl *p*-tolyl sulfone. Work-up and recrystallization from methanol afforded 0.35 g (2.5%) of light yellow crystals: mp 137–138°; nmr ($CDCl_3$) δ 2.32 (s, 6 H, CH_3S),[16] 2.39 (s, 3 H, $CH_3C_6H_4$), 6.00 (s, 1 H, vinyl proton), 7.21–7.95 ppm (m, 4 H, aromatic protons).

Anal. Calcd for $C_{11}H_{14}O_2S_3$: C, 48.18; H, 5.15; S, 35.00. Found: C, 48.28; H, 5.27; S, 35.30.

1-Phenyl-1-(phenylsulfinyl)-2,2-di(methylmercapto)ethene (6).—This was prepared in 10% yield from 10.80 g (0.05 mol) of benzyl phenyl sulfoxide, using the procedure given above. The crude oil isolated after work-up was dissolved in boiling benzene, and hexane was added until cloudiness persisted. Cooling gave light yellow crystals which were recrystallized several times from hexane to afford **6**: mp 89–90°; nmr ($CDCl_3$) δ 2.15 (s, 3 H, CH_3S), 2.55 (s, 3 H, CH_3S), 6.90–7.60 (m, 10 H, aromatic protons). This material decomposed to a pungent black oil over a period of 4 days.

Anal. Calcd for $C_{16}H_{16}OS_3$: C, 59.97; H, 4.99; S, 30.00. Found: C, 59.36; H, 4.59; S, 29.51.

Reduction of 1,1-Di(methylsulfonyl)2,2-di(methylmercapto)-ethene.—To a stirred slurry of 6.15 g of pulverized nickelous chloride hexahydrate and 0.35 g (0.0013 mol) of **1** in 30 ml of absolute ethanol was slowly added a solution of 3.0 g (0.08 mol) of sodium borohydride in water (stabilized by adding a few drops of 10% sodium hydroxide). A vigorous reaction ensued as the borohydride solution was added. The black reaction mixture was allowed to reflux for 20.5 hr and was filtered. The precipitate was washed with acetone. A white solid (mp >300°) precipitated from the filtrate. It was removed by filtration and the filtrate was evaporated *in vacuo* to give 0.8 g of a white solid which was extracted with boiling acetone. Evaporation of the acetone extracts afforded 0.2 g of **2**: mp 119.5–122.5° (lit.[8] mp 122°); nmr ($CDCl_3$) δ 1.87 (d, 3 H, J = 7.2 cps, CH_3CH), 3.20 (s, 6 H, CH_3SO_2), 4.19 (q, 1 H, J = 7.2 cps, CH_3CH).

Reduction of 1-Phenyl-1-(*p*-tolylsulfonyl)-2,2-di(methylmercapto)ethene.—To a solution of 0.25 g (0.0066 mol) of sodium borohydride in 60 ml of rigorously dried diglyme was added a solution of 2.0 g (0.006 mol) of **4b** in 45 ml of diglyme, and the resulting solution heated at 50° for 17 hr. The cloudy mixture was poured into 600 ml of ice water to which a few drops of sulfuric acid had been added. The precipitate which formed was filtered, dissolved in hot methanol, and filtered while hot to remove a small amount of insoluble material. Cooling the methanol solution produced **5b**: mp 131–133.5° [lit.[17] mp 133–135° (*dl* mixture)]; nmr ($CDCl_3$) δ 1.73 (d, 3 H, J = 7.5 cps, CH_3CH), 2.39 (s, 3 H, $CH_3C_6H_4$), 4.18 (q, 1 H, J = 7.5 cps, CH_3CH), 7.04–7.42 ppm (m, 9 H, aromatic protons).

Reduction of 1-Phenyl-1-(phenylsulfonyl)-2,2-di(methylmercapto)ethene.—The above procedure was followed using 1.92 g (0.0057 mol) of **4a**, 0.25 g (0.0066 mol) of sodium borohydride, and 100 ml of diglyme. The mixture was heated to 64° for 17 hr, and work-up as above gave 0.90 g (75%) of **5a**: mp 113–115° (lit.[18] mp 114–115°); nmr ($CDCl_3$) δ 1.80 (d, 3 H, J = 7.5 cps, CH_3CH), 4.25 (q, 1 H, J = 7.5 cps, CH_3CH), 7.30 ppm (m, 10 H, aromatic protons).

1,1-Di(methylsulfonyl)ethane (2).—To a stirred solution of 2.80 g (0.025 mol) of potassium *tert*-butoxide in 25 ml of dimethyl sulfoxide, under nitrogen, was added a solution of 4.3 g (0.025 mol) of di(methylsulfonyl)methane in 20 ml of dimethyl sulfoxide. After the solution was stirred at room temperature for 20 min, 1.6 ml (0.025 mol) of methyl iodide was added. The solution was stirred for 1.75 hr, poured into 100 ml of water, and extracted with methylene chloride. The extracts were washed with water and dried ($MgSO_4$), and the solvent was removed *in vacuo*. The resulting solid was recrystallized twice from methanol to afford 1.8 g (42%) of **2**, mp 121–123° (lit.[8] mp 122°). In a similar manner, α-methylbenzyl phenyl sulfone (**5a**), mp 113–114°, and α-methylbenzyl *p*-tolyl sulfone (**5b**), mp 132–133°, were prepared.

Oxidation of 1,1-Di(methylsulfonyl)-2,2-di(methylmercapto)-ethene.—To a suspension of 0.5 g (0.0018 mol) of **1** in 4 ml of glacial acetic acid was added 1.5 ml of 30% hydrogen peroxide. The stirred mixture was heated at reflux for 2 hr during which time the suspension changed to a clear yellow solution and finally to a clear colorless solution. On pouring the reaction mixture

(11) All melting points and boiling points are uncorrected. Microanalyses were performed by Dr. C. S. Yeh and staff. The nmr spectra were obtained using a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

(12) H. Bohme and R. Marx, *Chem. Ber.*, **74**, 1667 (1941).

(13) E. Fromm, A. Forster, and B. V. Scherschewitzki, *Justus Liebigs Ann. Chem.*, **394**, 343 (1912).

(14) R. L. Shriner, H. C. Struck, and W. J. Joreson, *J. Amer. Chem. Soc.*, **52**, 2060 (1930).

(15) R. Otto, *Chem. Ber.*, **13**, 1272 (1880).

(16) Apparently, the barriers to rotation about the double bonds in **4a** and **4c** are sufficiently low to allow rotation and subsequent equivalence of these protons. When the nmr spectrum of **4a** was taken at −25°, the methylmercapto signals appeared at δ 2.03 (s, 3 H) and 2.18 ppm (s, 3 H). For a discussion of similar behavior of other 1,1-dimethylmercaptoethenes, see G. Isakson, J. Sandstrom, and I. Wennerbeck, *Tetrahedron Lett.*, 2233 (1967).

(17) C. L. Arcus, M. P. Balfe, and J. Kenyon, *J. Chem. Soc.*, 485 (1938).

(18) F. Ashworth and G. N. Burkhardt, *ibid.*, 1797 (1928).

into ice, no precipitate was produced. Evaporation of the solution to near dryness produced white crystals which were diluted with water and filtered producing 0.2 g (67%) of product, mp 142–146°. The infrared spectrum was identical with that of di(methylsulfonyl)methane.

Registry No.—Carbon disulfide, 75-15-0; **1**, 26958-44-1; **4a**, 26958-45-2; **4b**, 26958-46-3; **4c**, 26958-47-4; **6**, 26958-48-5.

Acknowledgment.—This investigation was supported by the U. S. Army Research Office under Grant No. DA-31-124-ARO-D-211, and by Public Health Service Research Grant No. CA-04536-07 from the National Cancer Institute.

Solvent Effects on the Energy of the Principal Electronic Transition of *p*-Nitrotoluene-α-d_3 and *p*-Methylanisole-α-d_3

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In recent years it has been postulated that the experimental finding that is called the Baker–Nathan effect owes its origin to direct solvent influences rather than to an inherent predominance of C–H hyperconjugation, other modes of electronic stabilization such as C–C hyperconjugation, and the inductive effect. One group has attributed the Baker–Nathan effect to steric hindrance to solvation near bulkier alkyl groups.[1,2] Another has attributed it to solvent enhancement of C–H over C–C hyperconjugation, through incipient hydrogen bonding of the α hydrogens of the alkyl substituent with the solvent.[3] The observation that the inductive order of principal electronic transition energies found for *p*-alkyl nitrobenzenes and acetophenones in the gas phase and in inert solvents tends to be inverted in basic solvents is qualitatively consistent with either viewpoint.[2,4] It therefore appeared desirable to try to find direct evidence for solvent enhancement of C–H hyperconjugation in the effect of a number of solvents on the relative principal electronic transition energies of *p*-nitrotoluene and *p*-nitrotoluene-α-d_3. The principal electronic transition of the nitrobenzenes is highly electronic demanding on the para substituent, the electron migration being in the long axis of the molecule and away from the substituent.[5] Also included here are solvent studies on the energy of the principal electron transition of *p*-methylanisole and *p*-methylanisole-α-d_3, in which the electron migration is toward the substituent.[5]

An increase in excitation energy spread between *p*-nitrotoluene and *p*-nitrotoluene-α-d_3 in basic solvents could be considered as direct evidence for solvent enhancement of C–H hyperconjugation. On the other hand, the absence of such a finding does not prove that solvent enhancement of C–H hyperconjugation is absent in other systems, *e.g.*, in chemical transitions. That is, in the present system, in contrast to chemical systems, the upper (electronic) state that originally arises is not an "equilibrium state." In the short time of the electronic excitation of a molecule (*ca.* 10^{-16} sec), nuclear relaxation (*ca.* 10^{-13} sec) is minimal (Franck–Condon principle). Thus, orientation of basic portions of solvent molecules to the α hydrogens of the polar excited state species may be minimal, since such orientation is essentially that pertaining in ground state species.

The only trend discernible is a slight increase in $\nu_{CD_3} - \nu_{CH_3}$ in highly acidic solvents, a trend that accompanies a large increase in $\nu_H - \nu_{CH_3}$, the excitation energy difference between nitrobenzene and *p*-nitrotoluene (Table I). In fact, a plot of $\nu_H - \nu_{CD_3}$ against $\nu_H - \nu_{CH_3}$ is linear to a high degree of precision. This indicates that in the transition to the nonequilibrium Franck–Condon excited state, differential solvent perturbation of the CH_3 and CD_3 groups is negligible. The slope of the line is 1.036 with a standard deviation of ± 0.002 and a correlation coefficient of 0.999+. In terms of the Hammett relationship, the slope is the substituent constant ratio, $\sigma_{CH_3}/\sigma_{CD_3}$,[6] and the value of the slope can be taken as meaning that the methyl group has a greater absolute σ value than the CD_3 group.[8]

TABLE I

VALUES OF ν_H, $\nu_H - \nu_{CH_3}$, AND $\nu_{CD_3} - \nu_{CH_3}$ IN CM^{-1} FOR *p*-$RC_6H_4NO_2$ IN VARIOUS SOLVENTS[a-c]

Solvent	ν_H	$\nu_H - \nu_{CH_3}$	$\nu_{CD_3} - \nu_{CH_3}$
Gas phase	41,820	1850	80[d]
Heptane	39,700	1810	50
n-$BuNH_2$	38,200	1920	40
tert-BuOH	38,790	1960	40
Dioxane	38,650	2090	30
EtOH	38,530	2090	30
H_2O	37,440	2280	50
52% $HClO_4$	36,810	2480	60
70% $HClO_4$	35,720	2750	70
96% H_2SO_4	34,580	2710	70

[a] Values of ν_{max}, determined as previously described,[5] are averages of three determinations, duplicable to ±15 cm^{-1} or better except where noted. [b] Compound preparation and purification also previously described.[5] [c] The isotopic composition of the sample of *p*-nitrotoluene-α-d_3 was: d_3, 85.4%; d_2, 13.9%; d_1, 0.7%; d_0, 0%.[5] [d] Value of ref 5, duplicable to ±20–30 cm^{-1}.

The effect of a few solvents on the excitation energy of *p*-methylanisole-α-d_3 is shown in Table II. Within

* To whom correspondence should be addressed.

(1) W. M. Schubert and D. F. Gurka, *J. Amer. Chem. Soc.*, **91**, 1443 (1969), and preceding papers.

(2) W. M. Schubert, J. Robins, and J. Haun, *ibid.*, **79**, 910 (1957).

(3) V. J. Shiner, Jr., and C. J. Verbanic, *ibid.*, **79**, 373 (1957); V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

(4) A quantitative treatment of the data in twelve widely varying solvents, dealing with the relative linearity of plots of $\nu_H - \nu_R$ against ν_H was considered to favor the steric hindrance to solvation argument.[2]

(5) W. M. Schubert, R. B. Murphy, and J. Robins, *J. Org. Chem.*, **35**, 951 (1970), and references therein.

(6) Since ν is proportional to energy, the Hammett relationship for electronic transitions can be written $\nu_H - \nu_{CH_3} = \sigma_{CH_3}\rho'$, where ρ' is dependent on the solvent and the units of energy used.[7] By combining this equation with the corresponding one for CD_3 one obtains $\nu_H - \nu_{CH_3} = (\sigma_{CH_3}/\sigma_{CD_3})(\nu_H - \nu_{CD_3})$, which is the equation of the line.

(7) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(8) It is to be noted that the various kinds of σ values that have been assigned to alkyl substituents, all negative, have the wrong sign for the principal electron transition of anisoles, phenols, and anilines.[5,9]

(9) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962).