odically, quenched as in the preceding experiment, and analyzed. The solvolysis of the acidified K salt suspension was complete in less than 1 hr (Figure 3).

B. Solvolysis at High Temperature (in Glass Vessels).—I (50 mg), 6 ml of dioxane, and 18 μl of H_2O were mixed in a 10-ml Bantam ware flask fitted with a condenser. The mixture desulfated before it had reached maximum temperature on top of a steam bath. In many such experiments solvolysis occurred within 2–4 min. The solvolysis in glass could be prevented for many hours by 10–20 μl of KOH (8–1 M), but only if the reaction mixture was not disturbed (*vide supra*). The aqueous alkali does not dissolve in the dioxane, but merely coats the walls of the flask.

C. Stability at High Temperature in Teflon. 1.—A reaction mixture of 50 mg of I, 5 ml of dioxane, and 20 μl of 8×10^{-3} M KOH (<0.001 mol/mol sulfate ester) was heated in a Teflon bottle for intermittent brief periods until the sulfate had dissolved, and thence continuously in a steam cone (96°). This concentration of KOH did not prevent desulfation in glass. After 2 hr, the solution was chilled, sampled, and found not acidic to methyl red; nor was octanol-2 detectable by glc. The solution was transferred to a clean, glass round-bottom flask with condenser and heated on the steam bath. Desulfation occurred in about 3 min.

2.—Experiment C-1 was repeated except that 18 μl of deionized water was substituted for the alkali. The mixture was heated at full steam bath temperature for 1 hr, carefully removed, and allowed to cool and crystallize. The crystalline material was recovered by filtration and washing with cold ethanol, 43 mg, sinters at 165°, begins to foam and melt at 174°, and is complete at 182°, *i.e.*, essentially identical with the starting 2-octanol (potassium sulfate). The mother liquor was neutral.

3.—II (40 mg) in 5 ml of dioxane plus 10 μl of H_2O in a Teflon bottle was heated as above. At 21 min the flask was removed, cooled, and sampled. The material had not dissolved completely and the suspension was not acidic to methyl red. It was reheated for an additional 40 min and now was completely desulfated. The insoluble material was identified as $KHSO_4$ (mp 206–208°); cholestan-3-β-ol (mp 143°) was recovered from the organic phase.

4.—The previous experiment was repeated with 51 mg of II. After 20 min, the flask was removed from the steam bath and chilled. A small sample was tested and found to be not acidic. Water (15 ml) was added to the reaction mixture along with a drop of methyl red. A 30-μl portion of 0.01 N H_2SO_4 was more than enough to give an intense red color. Accordingly, solvolysis could not have progressed to even 0.3% of the sulfatide charged. In glass the sulfatide solvolyzed completely in the interval between 6.5 and 7.5 min.

From the preceding experiments (1–4) it is evident that the solvolysis occurs only suddenly—there is no evidence of a slow progression.

D. Initiation of Solvolysis by Trace Materials.—In these experiments stable solutions of 2-octanol (potassium sulfate) (50 mg) in 5–6 ml of dioxane plus 10–20 μl of H_2O were maintained in Teflon in a boiling water bath, usually for 20–30 min, at which time minute amounts of test solids or aqueous solutions were dropped in. Quantities of solids were ordinarily those left on the very tip of a microspatula or a needle-pointed capillary tube after insertion into a bottle of reagent and tapping off excess. Liquids were judged to be about 0.5 μl (*cf.* Results and Discussion).

Registry No.—I, 41209-93-2; II, 41209-94-3.

Substituent Effects in Sulfone Carbanions[1a]

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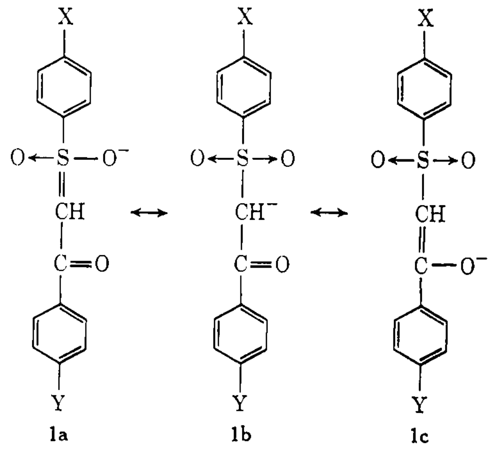
The pK_a's of a series of substituted phenyl phenacyl sulfones (2) were determined. With variation of the phenylsulfonyl substituents, the sulfone acidities followed a linear correlation with σ. The ρ value for this correlation was +2.01, indicating that electron-withdrawing substituents increase sulfone acidity and that this system is very responsive to substituent changes. Since correlation of acidity with σ^+ was not obtained, there is no enhanced resonance interaction between the substituent and the electron-deficient sulfone group. Variation of the phenacyl substituents gave linear correlation of acidity with σ and a ρ value of +2.35. Acidifying effects in the sulfones are considered to be identical with the factors stabilizing the corresponding sulfone carbanions. The large positive ρ indicates that the carbanion is stabilized substantially by pπ–dπ overlap with the sulfur. The magnitude of this stabilization depends upon the electronegativity of the sulfur which, in turn, is determined by the electronic effects of the substituents. The interaction of the substituents through the phenyl ring with the sulfur is principally inductive in nature.

It is well established that the sulfone group can stabilize an adjacent carbanion.[2] Sulfone carbanions have been utilized in numerous syntheses, but there has been no quantitative systematic study of their electronic effects. This study was undertaken to determine the nature and magnitude of such carbanion stabilization. Several resonance structures which can be envisioned for β-carbonyl sulfone carbanions are **1a**, utilizing sulfur d orbitals; **1b**, the carbanion structure; and **1c**, the enolate structure. The magnitude of carbanion stabilization afforded through resonance structures **1a** and **1c** was determined by measuring the acidity of the sulfone precursors. Schwarzenbach and Felder[3] determined the pK_a's (in water) of several sulfones [*i.e.*, $CH_3SO_2CH_2COCH_3$, 10; $(CH_3SO_2)_2CH_2$,



1a **1b** **1c**

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[1] (a) This work was presented in part at the Twenty-third Annual Undergraduate Chemistry Symposium of the Chicago Section of the American Chemical Society, Chicago, Ill., May 1972. (b) Author to whom inquiries should be addressed at Department of Chemistry, Viterbo College, LaCrosse, Wis. 54601. (c) Undergraduate Research Participant.

[2] A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 351–352.

[3] G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1701 (1944).

TABLE I

PROPERTIES OF β-CARBONYL SULFONES[a]

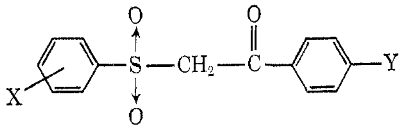
Compd	X[b]	Y	Mp, °C	pK_a	Nmr ($CDCl_3$ solvent), δ, multiplicity[c] Methylene	Aromatic	X or Y
2a	NO_2	H	169–171	9.42	s, 5.90[d]	m, 7.64–8.82	
2b	m-NO_2	H	132–134	9.54	s, 5.36	m, 7.80–9.34	
2c	Br	H	122–123	10.33	s, 5.28	m, 7.80–8.56	
2d	Cl	H	131.5–132.5	10.52	s, 5.28	m, 7.80–8.54	
2e	F	H	148–150	10.80	s, 5.26	m, 7.60–8.64	
2f	H	H	89–90	10.97	s, 5.20	m, 7.74–8.44	
2g	CH_3	H	105–107	11.25	s, 5.20	m, 7.64–8.44	s, 2.78
2h	OCH_3	H	105–106	11.42	s, 5.24	m, 7.40–8.54	s, 4.36
2i	H	Br	138.5–139.5	10.44	s, 5.24	m, 7.80–8.50	
2j	H	Cl	129–131	10.53	s, 5.26	m, 7.80–8.50	
2k	H	C_6H_5	147–149	10.85	s, 5.26	m, 7.76–8.64	
2l	H	F	116–117.5	10.90	s, 5.24	m, 7.48–8.60	
2m	H	OCH_3	112–114	11.70	s, 5.20	m, 7.32–8.50	s, 4.34

[a] Satisfactory analytical data were reported for all new compounds listed in the table: Ed. [b] The substituent is in the para position unless indicated otherwise. [c] s, singlet; m, multiplet; all integrations were in accord with theory. [d] Solvent was $(CD_3)_2SO$.

~14; and $(CH_3SO_2)_3CH$, ~0], which indicated the acidifying effect attained by successively adding sulfone groups to a carbon. Bordwell, *et al.*,[4] determined the pK_a's (in DMSO) of several sulfones which were capable of affording little stabilization to the conjugate base [pK_a's ranging from $C_6H_5SO_2C_2H_5$, 29, to $(C_6H_5CH_2)_2SO_2$, 22]. This work showed that when benzyl groups were substituted for methyl groups the pK_a decreased 6.5 units [compare $(C_6H_5CH_2)_2SO_2$, 22, with $CH_3SO_2CH_3$, 28.5] indicating that the phenyl ring was electron withdrawing relative to methyl. When an ethyl group was substituted for a methyl group the pK_a increased 2.0 units [compare $C_6H_5SO_2CH_3$, 27, with $C_6H_5SO_2C_2H_5$, 29], showing that a methyl group provided electron release relative to hydrogen. Bordwell further reported that replacing methyl with phenyl decreased the pK_a 1.5 units [compare $C_6H_5SO_2CH_3$, 27, with $CH_3SO_2CH_3$, 28.5]. The magnitude of this lowering was consistent with the lowering reported by Johnson and Amel[5] for similar sulfonium and phosphonium systems. This paper will describe the linear correlation of sulfone acidities with substituent constants and elaborate the electronic effects involved in the stabilization of phenyl phenacyl sulfone carbanions.

Results

A series of substituted phenyl phenacyl sulfones (**2**) was prepared. The properties of these sulfones are listed in Table I. The pK_a's of the sulfones were determined potentiometrically in 95% ethanol solution using the method of Speziale and Ratts.[6] The average deviation was ±0.04 pK_a unit.



2a–m

For sulfones substituted on the phenylsulfonyl end, linear correlation was achieved when log K/K_0 (K_0 is the dissociation constant of the unsubstituted sulfone, **2f**) was plotted against σ but not when σ^+ or σ^0 were used (Figure 1). A ρ of +2.01 was calculated using a least-squares treatment of the data. For sulfones substituted on the phenacyl end, linear correlation again was possible with σ and a ρ of +2.35 was calculated (Figure 2).

Discussion

Our research was designed to determine the nature and magnitude of the carbanion stabilization provided by the sulfonyl moiety as well as that provided by the substituted benzoyl group. In order to obtain this information, the relative acidities of a series of sulfones were determined. In this study, the factors determining sulfone acidity were considered to be identical with the factors affording stabilization to the corresponding sulfone carbanion. Only meta- and para-substituted phenyl groups were used so that stabilization differences could be ascribed to electronic effects without intervention of steric effects.

Variation of the Sulfonyl Moiety.—Figure 1 demonstrates that the acidities of phenyl phenacyl sulfones substituted on the sulfonyl moiety could be correlated with σ. The ρ value for this correlation was positive, indicating that electron-withdrawing substituents increased the acidity of the sulfone or decreased the basicity of the sulfone carbanion. For example, the unsubstituted sulfone **2f** had a pK_a of 10.97, while with X = NO_2 the acidity was increased to a pK_a of 9.42 and with X = CH_3O the pK_a was 11.42. Craig and Magnusson[7] have proposed that increasing the electronegativity of sulfur, by attaching electron-withdrawing substituents, will contract the sulfur d orbitals, allowing more efficient overlap with the filled 2p orbital of an adjacent carbanion. Employing this idea in our system, the differences in carbanion stabilization as a result of changing substituent X can be explained as differences in the amount of d orbital overlap possible with the sulfonyl group. Consequently, the degree of carbanion stabilization afforded by the sulfonyl moiety is interpreted to be a measure of pπ–dπ overlap, as depicted in the double-bonded structure **1a**. Robinson and Gillespie[8] have reported correlation of sulfur electronegativity variation with the amount of pπ–dπ

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(4) F. G. Bordwell, R. H. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, **89**, 3905 (1967).

(5) A. W. Johnson and R. T. Amel, *Can. J. Chem.*, **46**, 461 (1968).

(6) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **85**, 2790 (1963).

(7) D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

(8) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961); R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1965).

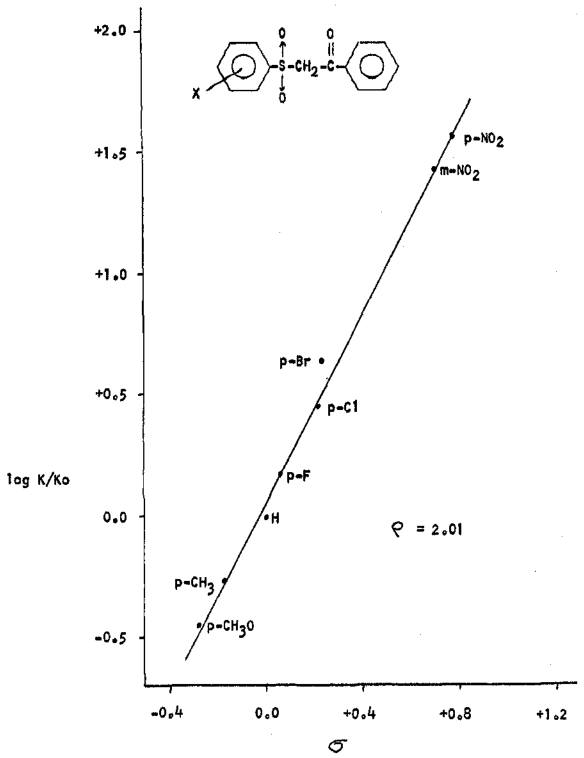

Figure 1.—Acidities of X-phenyl phenacyl sulfones *vs.* σ.

bonding. In their work with sulfones and sulfoxides, they found that increasing the electronegativity or electron-withdrawing capability of groups attached to the sulfur caused stronger S–O bonds, as evidenced by higher vibrational absorption frequencies.

Bordwell and Cooper[9] reported that an enhanced σ constant was required to express the acidifying effect of the 4-methylsulfonyl group on phenol. This indicated an increased stabilization of the phenolate anion by the sulfonyl group. In this case the d orbitals in the electron-deficient sulfur were utilized in conjugatively delocalizing the charge on the phenolate anion. In our system, however, sulfone acidity did not correlate with σ^+, indicating no such enhanced electron donation from the phenyl substituents to the sulfur. In addition, Johnson, *et al.*,[10] reported finding no enhanced interaction between phenyl substituents and the electron-deficient phosphorus in the 9-fluorenyltri(*p*-X-phenyl)-phosphonium bromide system. Johnson explained his results on the basis of steric considerations. With the crowded quaternary phosphorus atom it is understandable that steric requirements would not allow the orbitals of the three phenyl rings to line up properly with the phosphorus 3d orbitals. With our sulfone system, however, steric problems should not be the factor. Wheatly[11] and Speziale and Ratts[12] reported in the molecular structure analysis of $CH_3C_6H_4SO_2CH{=}P(C_6H_5)_3$ that the tolyl ring was nearly perpendicular to a plane containing the tetrahedral sulfur, the carbanion, and the phosphorus. This situation would not appear to preclude, on steric grounds, d orbital overlap with either the phenyl ring or the carbanion.

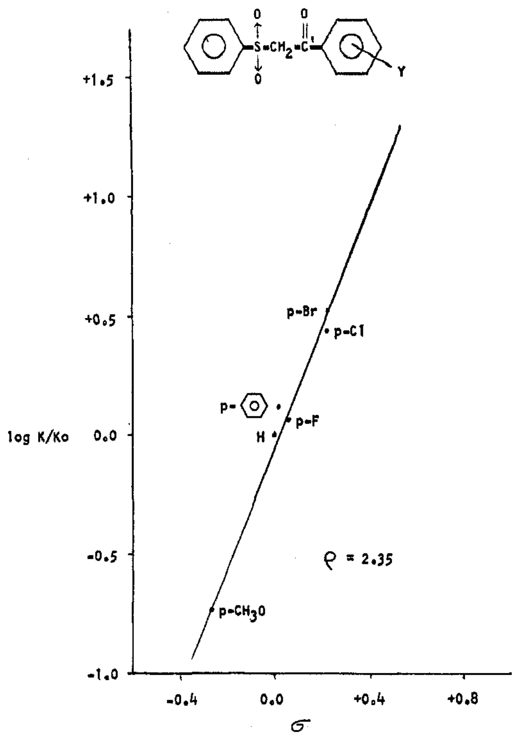

Figure 2.—Acidities of phenyl (Y-phenacyl) sulfones *vs.* σ.

However, since linear correlation was accomplished with σ rather than σ^+, the degree of conjugative electron donation by the substituted phenyl ring to the sulfur in our system must be considerably less than that observed by Bordwell. Johnson and Jones[13] have concluded that in phosphorus systems involving strong pπ–dπ interaction with one substituent (*i.e.*, a carbanion) there is relatively little such interaction possible with any other substituents. This conclusion is applicable to sulfone systems as well. Consequently, the substituent effects causing electronegativity changes in the sulfonyl sulfur must be principally inductive in nature. The magnitude of these electronegativity changes is significant because it determines the degree of participation of the sulfur d orbitals in bonding with the carbanion.

Figure 1 shows $\rho = +2.01$, indicating that electron-withdrawing groups increased the acidity of the sulfones. The magnitude of ρ shows that the sulfone carbanion required considerable electron delocalization into the sulfur d orbitals. Ratts[14] determined a ρ of $+1.23$ for the corresponding methylphenylsulfonium ylide system. Johnson, *et al.*,[10] have reported a triphenylphosphonium ylide system with a ρ of $+4.8$ (for three substituted phenyls attached to phosphorus), which can be broken down into a ρ of $+1.7$ for each substituted phenyl group. The magnitude of ρ in the sulfone system was higher than the values for the phosphonium and sulfonium systems. Perhaps this is because the sulfone system has a considerably smaller net positive charge on the heteroatom, resulting in diminished coulombic stabilization of the carbanion. This situation may require more stabilization from pπ–dπ overlap with the sulfur. Because the magnitude of such stabilization is dependent upon the electronegativity of the sulfone groups, the sulfone system is more

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[9] F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **74**, 1058 (1952).

[10] A. W. Johnson, S. Y. Lee, R. A. Swor, and L. D. Royer, *J. Amer. Chem. Soc.*, **88**, 1953 (1966).

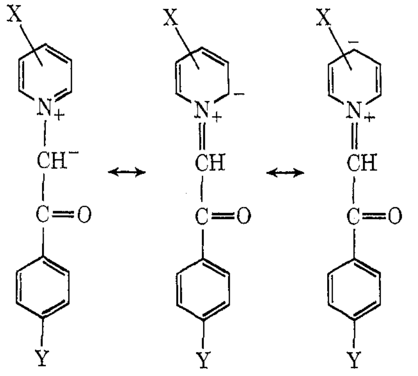
[11] P. J. Wheatley, *J. Chem. Soc.*, 5785 (1965).

[12] A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **87**, 5603 (1965).

[13] A. W. Johnson and H. L. Jones, *J. Amer. Chem. Soc.*, **90**, 5232 (1968).

[14] K. W. Ratts, *J. Org. Chem.*, **37**, 848 (1972).

dependent upon substituent effects for increasing the positive charge on sulfur than are the corresponding onium systems. Ratts and Phillips[15] studied the basicity of substituted pyridinium phenacylides, obtaining a ρ of $+2.5$. The higher ρ was attributed to the additional carbanion delocalization possible through resonance structures such as **3b** and **3c**.



3a **3b** **3c**

Variation of the Benzoyl Moiety.—In considering the substituted benzoyl portion of the molecule (Figure 2), a ρ of $+2.35$ was calculated, again indicating that electron withdrawal stabilized the carbanionic charge and $\log K/K_0$ correlated with σ. This ρ value is similar to values reported by Ratts[14,15] and Fliszar[16] for corresponding pyridium, sulfonium, and phosphonium systems. It should be noted that in this case there can be no direct conjugation between Y and the carbanion. It is perhaps surprising that the ρ values for these four systems should be so similar, since the pK_a's of the analogous ylides vary considerably as a result of the wide differences in acidifying power (or carbanion stabilizing ability) of the heteroatom groups. The order of heteroatom group stabilizing ability can now be extended to include the sulfone system, *i.e.*, $(C_6H_5)_2S^+$ (pK_a = 5.36)[5] > $(C_6H_5)_3P^+$ (pK_a = 5.60)[5] > $(C_6H_5)_3As^+$ (pK_a = 8.25)[5] > $C_5H_5N^+$ (pK_a = 9.7)[15] > $C_6H_5SO_2$ (pK_a = 10.97).

Even though the sulfone group provided less carbanion stabilization than the other heteroatom groups mentioned, enough stabilization was afforded so that we were able to isolate several sulfone carbanions. Treatment of the precursor sulfones **2a**, **2c**, **2f**, **2g**, **2h**, and **2i** with sodium hydride produced the corresponding carbanions, which could be stored in closed containers for reasonable periods without significant decomposition. They were solids that could be reprotonated to form again the parent sulfone. These ylides showed the typical infrared carbonyl shift of 50–100 cm^{-1} to lower frequencies, indicating the strong contribution of resonance from **1c**. Shifts of the SO_2 vibrational frequencies also were observed. Further characterization of these isolable sulfone carbanions is in progress.

In summary, the same factors that have been suggested for the carbanion stabilization in onium systems appear to apply to the stabilization of sulfone carbanions. Two chief differences in magnitude are observed: (a) less carbanion stabilization is afforded by the sulfone system, as evidenced by the higher pK_a's; (b) the sulfone system has a higher sensitivity to substituent effects than do comparable onium systems, as evidenced by the higher ρ value.

Experimental Section

General.—Analyses were by Galbraith Laboratories, Knoxville, Tenn. Potentiometric measurements were carried out on a Corning Digital 112 research pH meter equipped with glass, saturated calomel, and automatic temperature control electrodes which were standardized with standard pH 4.008 and pH 7.00 buffers in aqueous solutions at 25°. Melting points are uncorrected. Nmr spectra were recorded in $CDCl_3$ on a Varian A-60 spectrometer using TMS as an internal standard with chemical shifts reported as parts per million downfield from TMS. Ir spectra were recorded as KBr pellets on a Beckman IR-10 spectrophotometer.

Preparation of Phenyl Phenacyl Sulfones 2. Method 1.—In this synthesis, reported by Becker and Russell,[17] the appropriate substituted phenyl methyl sulfone in twofold excess was treated with sodium hydride in dry dimethyl sulfoxide under nitrogen. To this was added the substituted methyl benzoate in tetrahydrofuran. Upon quenching with water and acidification with hydrochloric acid, the reaction mixture yielded the sulfone product as crystals. The products were recrystallized from 95% ethanol.

Method 2.—The appropriately substituted sodium benzenesulfinate[18] was treated with the appropriate phenacyl bromide in 95% ethanol and refluxed from 12 to 24 hr to yield the sulfone. The sulfones were recrystallized from 95% ethanol or ethanol–water mixtures.

pK_a Determinations.—Approximately 0.5 mmol of the desired sulfone was dissolved in 100 ml of 95% ethanol and titrated potentiometrically with 0.100 N KOH in 95% ethanol prepared by dissolving 6.61 g of potassium hydroxide in 95% ethanol and diluting to 1 l. with more 95% ethanol. The pK_a is taken as the pH at the half-equivalence point. A reverse titration was run using 0.100 N HCl prepared by mixing 9.3 ml of concentrated (12%) hydrochloric acid with 40.7 ml of water and 950 ml of absolute ethanol.

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Registry No.—**2a**, 41024-48-0; **2b**, 41024-49-1; **2c**, 41024-50-4; **2d**, 36603-45-9; **2e**, 432-99-5; **2f**, 3406-03-9; **2g**, 31378-03-7; **2h**, 41024-54-8; **2i**, 41024-55-9; **2j**, 38488-19-6; **2k**, 41024-57-1; **2l**, 41024-58-2; **2m**, 27918-37-2.

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[15] W. G. Phillips and K. W. Ratts, *J. Org. Chem.*, **35**, 3144 (1970).

[16] S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).

[17] H. D. Becker and G. H. Russell, *J. Org. Chem.*, **28**, 1896 (1963).

[18] S. Smiles and C. M. Bere, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 7; C. W. Ferry, J. S. Buck, and R. Baltzly, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 239.