acids) since this compound is mesomorphic and possesses high smectic thermal stability.

Although the cyano group in **7** has a strong dipole operating along the long axis of the molecule, the compound exhibits nematic behavior because enough residual lateral attractive forces are present. However, when these lateral cohesions are considerably reduced by substitution of the alkoxy group with CH_3 (**15**), H (**16**), Cl (**18**), $N(CH_3)_2$ (**19**), and NO_2 (**20**), which all have dipoles acting along the long axis of the molecule, mesomorphism is completely destroyed. Thus, a critical balance of lateral and terminal intermolecular attractive forces must be attained in order for mesomorphism to occur in these anils. The mesomorphic behavior of **17** is undoubtedly due to the increased length and stronger lateral attractions as a result of dimer formation. Similar results have been reported[5] for the series of *para*-substituted compounds derived from *p*-cyanobenzylideneaniline.

The substitution of the strongly dipolar ester group of the alkylbenzoate or cinnamate type generally confers smectic properties upon a mesomorphic compound and **1** and **2** are no exception. The nematic (monotropic) behavior of **5** is probably due to a low ratio of lateral to terminal interactions resulting from the presence of short alkyl chains in the terminal portion of the molecule. When the alcohol portion of the ester function is phenolic, however, nematic mesomorphism occurs (compounds **3** and **10**). The terminal attractions in the latter compounds are high because electron density is localized at the carbonyl groups. In compounds **1** and **2** on the other hand, the delocalization of electrons as a result of conjugation of the carbonyl group with the aromatic system produces a higher ratio of lateral to terminal cohesions. It is also noteworthy that reversal of the substituent groups in **3** results in a decrease (30°) in the crystal–nematic transition temperature (see Table I, compound **10**). The small change in direction of the dipole moment as a result of inversion of the atoms in the central group causes rearrangement of molecules in the crystal lattice. This is not the case, however, for compounds **8** and **21** which are not nematic at all because of the strong terminal interactions in their crystal lattices.

Our previous studies[1] have shown that substitution of fluorine for hydrogen in the alkoxy group of benzylideneanils results in increased lateral interactions and smectic mesomorphism. Replacement of the alkoxy group by the alkylthio group on the other hand might be expected to result in the disappearance of mesomorphism since the latter group is slightly less polar than the former. A comparison between the nematic compound **3** and its sulfur analog **22** bears this out. A similar result is obtained when the atoms in the azomethine group are reversed as in **23**; however, this compound does exhibit monotropic mesomorphism (compare with **10**). The smectic (monotropic) behavior of **26** compared with that of **24** and **25** (not mesomorphic) may be due to the longer alkyl chain, which would be expected to produce greater lateral attractions. It is possible, however, that melts of **24** and **25** would also exhibit mesomorphism if they could be supercooled below about 90°.

(5) M. E. Huth, Doctoral Dissertation, University of Halle, 1909.

The Reaction of α-Halo Ketones with Triphenylphosphine. Effect of Base on the Formation of α-Ketophosphonium Salts

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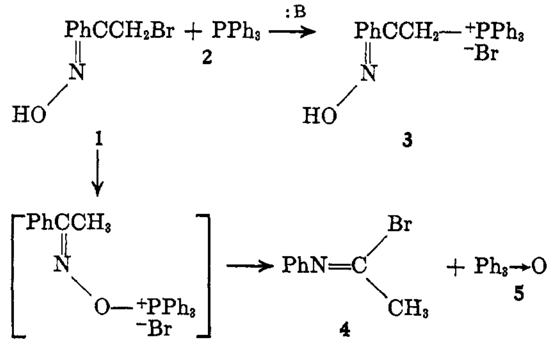
In the reaction of 2-bromoacetophenone with triphenylphosphine, the presence of a catalytic amount of base was remarkably effective for the formation of the α-ketophosphonium salt. The catalytic effect of the base was also observed in the reaction of triphenylphosphine with *para*-substituted 2-bromoacetophenone or 2-bromopropiophenone, but the reaction with 2-chloroacetophenone was not affected by the base. The yields of α-ketophosphonium salts were directly proportional to the Hammett σ value of the substituent in the *para* position of 2-bromoacetophenone. In the base-catalyzed reaction, the most probable reaction course is through initial nucleophilic attack on the carbonyl carbon atom of the ketone by the base giving a tetrahedral intermediate which is susceptible to substitution on the α-carbon atom by phosphine.

The previous paper[1] described the catalytic effect of base in the reaction of 2-bromoacetophenone oxime **1** with triphenylphosphine **2**. Under ordinary conditions the reaction of **1** with **2** gave no oximinophosphonium salt **3** but gave imidoyl bromide **4** and triphenylphosphine oxide **5** *via* a Beckmann rearrangement of the initially formed quasi-phosphonium salt. However, in the presence of a catalytic amount of base, the same reaction led to the exclusive formation of oximinophosphonium salt **3**. These reactions were rationalized to proceed through an initial nucleophilic attack of phosphine or base on the oximino carbon atom.



Naturally, it was of interest to examine whether base has an analogous catalytic effect in the reaction of

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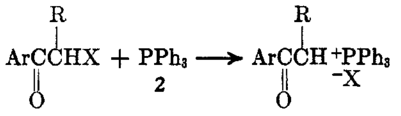
[1] M. Masaki, K. Fukui, and M. Ohta, *J. Org. Chem.*, **32**, 3564 (1967).

α-halo ketones with triphenylphosphine **2**. This paper describes the positive catalytic effect of base in such reactions and deals with the reaction mechanism.

Results

Reaction of 2-bromoacetophenone **6a** with triphenylphosphine **2** in acetonitrile at room temperature afforded 2-oxo-2-phenylethyltriphenylphosphonium bromide **7a** in 22% yield after 2 hr.[2,3] The yield was almost unchanged after 24 hr. In contrast, when the same reaction was carried out in the presence of a catalytic amount of triethylamine,[4] the α-ketophosphonium salt **7a** was formed in 93% yield after 2 hr. In reaction in dry benzene solution the addition of a catalytic amount of triethylamine increased remarkably the yield of α-ketophosphonium salt **7a**. A similar catalytic effect for the formation of **7a** was also observed by using other bases, such as pyridine or an aqueous solution of potassium cyanide or potassium hydroxide.

Treatment of 2-bromoacetophenone **6a** with triphenylphosphine **2** in a protolytic solvent is known to result in the formation of acetophenone and triphenylphosphine oxide.[3b] When **6a** was treated with **2** in benzene–methanol in the presence of a catalytic amount of triethylamine or pyridine at room temperature, an exclusive formation of α-ketophosphonium salt **7a** resulted, whereas the reaction in the same solvent without base afforded only 3% yield of α-ketophosphonium salt **7a** even at refluxing temperature. These results are summarized in Table I.



$$\mathrm{ArC(=O)CH(R)X} + \underset{\mathbf{2}}{\mathrm{PPh_3}} \longrightarrow \mathrm{ArC(=O)CH(R)\overset{+}{P}Ph_3}\ \mathrm{^{-}X}$$

6 **7**

6a, Ar = C_6H_5; R = H; X = Br
b, Ar = p-$NO_2C_6H_4$; R = H; X = Br
c, Ar = p-BrC_6H_4; R = H; X = Br
d, Ar = p-$CH_3C_6H_4$; R = H, X = Br
7e, Ar = p-$CH_3OC_6H_4$; R = H; X = Br
f, Ar = C_6H_5; R = CH_3; X = Br
g, Ar = C_6H_5; R = H; X = Cl

The effect of base was also examined in the reaction of triphenylphosphine **2** with 2-bromoacetophenones (**6b–e**) possessing nitro-, bromo-, methyl-, and methoxy substituents in the *para* position. The results are shown in Table II. The yields of the corresponding α-ketophosphonium salts (**7b–e**) were increased in proportion to augmentation of the Hammett σ value by the substituents ($NO_2 > Br > H > CH_3 > CH_3O$).

When 2-bromopropiophenone (**6f**), an example of a secondary α-bromo ketone, was treated with triphenylphosphine **2** in acetonitrile at room temperature, no α-ketophosphonium salt was isolated after 2 hr. However, the same reaction system in the presence of a catalytic amount of triethylamine afforded a 56% yield of 1-methyl-2-oxo-2-phenylethyltriphenylphosphonium bromide (**7f**) after 2 hr. In all of these reactions a catalytic amount of base was remarkably effective for the formation of α-ketophosphonium salts. However, no catalytic effect was observed in the reaction of 2-chloroacetophenone (**6g**) with triphenylphosphine **2**.

Table I

Reaction of 2-Bromoacetophenone with Triphenylphosphine

Solvent	Catalyst	Time, hr	Yields, %		
			Ketophosphonium bromide	Acetophenone[e]	Triphenylphosphine oxide[f]
Acetonitrile[a]	—	2[c]	22	58	53
	—	24[c]	20	57	50
	—	2[d]	19	57	56
Acetonitrile[b]	—	2[c]	43	37	39
	—	2[d]	73	17	22
Acetonitrile[a]	NEt_3	2[c]	93		
	KCN	2[c]	94		
	KOH	2[c]	91		
Acetonitrile[b]	NEt_3	2[c]	94		
Benzene	—	2[c]	34	35	41
	—	24[c]	46	28	39
	—	2[d]	75	10	7
	NEt_3	2[c]	94		
Benzene–methanol	—	2[d]	3	87	71
	NEt_3	2[c]	92		
	Pyridine	2[c]	94		
	Pyridinium salt	2[c]	8	46	70

[a] Distilled from phosphorus pentoxide and redistilled from potassium carbonate. [b] Dried over calcium hydride after the redistillation. [c] Reaction at room temperature. [d] Reaction in refluxing solvent. [e] The yield was based on conversion into the 2,4-dinitrophenylhydrazone. [f] The yield was based on conversion into the complex with zinc chloride.

Table II

Reaction of α-Halo Ketones with Triphenylphosphine in Aceonitrile[a]

α-Halo ketone	Catalyst	Time, hr	Ketophosphonium salt	Dehalogenated ketone	Triphenylphosphine oxide[b]
6b	—	2[c]	69[d]	12	15
	—	24[c]	66	8	28
	—	2[e]	68	15	17
	NEt_3	2[c]	100		
6c	—	2[c]	46	42[f]	31
	—	24[c]	43	24	34
	—	2[e]	41	38	37
	NEt_3	2[c]	93		
6d	—	2[c]	11	38[f]	62
	NEt_3	2[c]	91		
6e	—	2[c]	0	75[f]	72
	NEt_3	2[c]	91		
6f	—	2[c]	0	64[g]	69
	NEt_3	2[c]	56	13	29
6g	—	2[c]	26		
	NEt_3	2[c]	26		

[a] See footnote *a* in Table I. [b] The yield was based on conversion into the complex with zinc chloride. [c] Reaction at room temperature. [d] Recrystallization from ethanol afforded yellowish needles, which decomposed with effervescence at 105° and melted at 220–221°. S. Fliszar, R. F. Hudson, and G. Salvadori [*Helv. Chim. Acta*, **46**, 1580 (1963)] report mp 125.7°. *Anal.* Calcd for $C_{26}H_{21}BrNO_3P$: C, 61.66; H, 4.15; N, 2.77. Found: C, 61.36; H, 4.40; N, 2.96. [e] Reaction in refluxing solvent. [f] The yield was based on conversion into the phenylhydrazone. [g] The yield was based on conversion into the 2,4-dinitrophenylhydrazone.

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[2] Although the reactions of **6a** with **2** have been reported,[3] reactions under these conditions were reinvestigated by us as control experiments for the base-catalyzed reactions. In anhydrous acetonitrile dried over calcium hydride, **7a** was obtained in 43% yield under the same conditions.

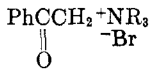
[3] (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957); (b) I. J. Borowitz and R. Virkhaus, *J. Amer. Chem. Soc.*, **85**, 2183 (1963).

[4] In each 10-mmol-scale reaction, 5 drops (*ca.* 0.5 mmol) of triethylamine were used.

Discussion

A number of possibilities have been discussed mechanistically for the reaction of α-halocarbonyl compounds with tertiary phosphines.[5,6] Recently, Borowitz and Parnes investigated the kinetics of the reaction of α-haloacetophenones with triphenylphosphine and revealed that α-ketophosphonium salts are formed by an SN2-type displacement of halide ion by the nucleophile in aprotic solvents.[6b] In the reaction in protolytic solvent to give the debrominated ketone, the debromination has been postulated to proceed *via* attack on bromine by triphenylphosphine in a concerted reaction involving prior to concurrent protonation on an incipient enolate ion by the prototropic species present.[6a] However, the catalytic effect of base was observed both in aprotic and protolytic runs, as shown in Table I. It could not be interpreted by these reaction mechanisms that the promotion of the formation of the α-ketophosphonium salt and the inhibition of the debromination were effected with base.

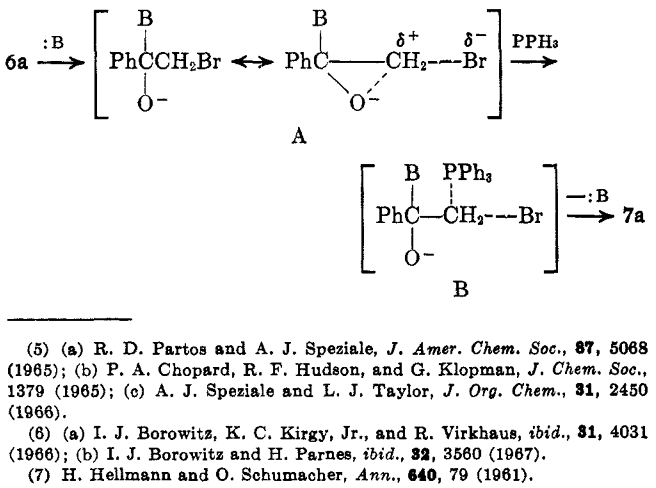
For the base-catalyzed reaction two possible mechanistic rationalizations might be envisaged. Although it is known that a quaternary ammonium salt can be exchanged by tertiary phosphine to yield the corresponding phosphonium salt,[7] a reaction course involving intermediacy of the quaternary ammonium salt **8** can be safely ruled out by the following control experiments. If the reaction proceeds through such a process, the reaction of 2-chloroacetophenone (**6g**) with triphenylphosphine (**2**) should also be catalyzed by base, and (2-oxo-2-phenylethyl)pyridinium bromide (**9**) should catalyze the reaction of **6a** with **2**, since pyridine itself was effective. However, these assumptions were not realized as mentioned above.



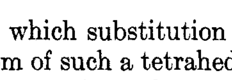
$$\underset{\displaystyle O}{\overset{}{PhC\!\!\!\!\!\parallel}}CH_2{}^{+}NR_3 \quad {}^{-}Br$$

8, $NR_3 = NEt_3$
9, $NR_3 = NC_5H_5$

A more credible mechanism involves an initial attack of base at the carbonyl carbon atom to give a tetrahedral intermediate A, which would be susceptible to substitution on the α-carbon atom by phosphine, since the bromine–carbon bond would be loosened. The transition state B in the substitution step of the intermediate would have somewhat of an SN1 character (borderline SN2) and be stabilized by mesomeric electron release from the negatively charged oxygen atom.[8]



The ease with which substitution reactions occur on the α-carbon atom of such a tetrahedral intermediate is supported by our previous observation.[1] In the oximination of 2-bromo-acetophenone **6a** with hydroxylamine hydrochroride in methanol, a considerable amount of 2-chloroacetophenone oxime was formed together with the oxime of **6a**. This halogen exchange reaction is rationalized by taking a tetrahedral intermediate C into consideration.[9–11]



C

Through this mechanistic process it is reasonable that the addition of methanol caused no effect on the yield of α-ketophosphonium salt **7a** in the base-catalyzed reaction, since the tetrahedral intermediate A would be inert to a hydroxylic solvent such as methanol or water.

In the case of 2-chloroacetophenone (**6g**), the corresponding tetrahedral intermediate formed reversibly would not be so effective as in the bromo analog, since the carbon–chlorine bond energy is generally larger than the carbon–bromine bond energy. The electron density of α-methylene carbon atom of **6g** is less than that of **6a** owing to the difference of electronegativity of the halogen atoms. Thus, the reaction of **6g** with **2** would proceed through SN2-type displacement[3b,6] preferably to the course involving the tetrahedral intermediate.

Experimental Section

Acetonitrile used in the general reactions was distilled from phosphorus pentoxide and redistilled from potassium carbonate. Absolute acetonitrile was prepared by being dried over calcium hydride after redistillation. Benzene was dried over sodium. All concentrations and evaporations were carried out under reduced pressure. All melting points were determined in a liquid bath and are uncorrected.

Reaction of 2-Bromoacetophenone 6a with Triphenylphosphine 2.—The following experiments are general procedures for the reaction of α-halo ketones with **2**.

In the Absence of Catalyst. A. Reaction in Acetonitrile.—A solution of **6a** (1.99 g, 10 mmol) in acetonitrile (30 ml) was added to a solution of **2** (2.62 g, 10 mmol) in acetonitrile (60 ml) and the resultant solution was stirred at room temperature or refluxed. After the appropriate hours, given in Table I, water (5 ml) was added to the mixture. The mixture was concentrated by rotary evaporation and the residue was treated with tetrahydrofuran (20 ml). The crystalline (2-oxo-2-phenylethyl)triphenylphosphonium bromide (**7a**) was collected by filtration. Recrystallization from water afforded colorless prisms, mp 264.5° (lit.[3a] 269–271°). The filtrate separated from the phosphonium bromide was concentrated, and the residue was treated with zinc chloride in ethanol to give the complex of triphenylphosphine oxide, mp 231° (lit.[12] 229–230°). After removal of the complex, the filtrate was evaporated and the residual oil was heated in a mixture of benzene and water. From the organic layer acetophenone was isolated as the 2,4-dinitrophenylhydrazone, mp 235–236°.

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[5] (a) R. D. Partos and A. J. Speziale, *J. Amer. Chem. Soc.*, **87**, 5068 (1965); (b) P. A. Chopard, R. F. Hudson, and G. Klopman, *J. Chem. Soc.*, 1379 (1965); (c) A. J. Speziale and L. J. Taylor, *J. Org. Chem.*, **31**, 2450 (1966).

[6] (a) I. J. Borowitz, K. C. Kirgy, Jr., and R. Virkhaus, *ibid.*, **31**, 4031 (1966); (b) I. J. Borowitz and H. Parnes, *ibid.*, **32**, 3560 (1967).

[7] H. Hellmann and O. Schumacher, *Ann.*, **640**, 79 (1961).

[8] A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," A. Weissberger, Ed., Interscience Publishers Inc., New York, N. Y., 1964, p 270.

[9] Analogous substitution reactions on an α-carbon atom in a tetrahedral intermediate of an α-halo ketone have been observed in many cases such as the Favorskii rearrangement[10] and epoxide formations,[11] although these are intermolecular reactions.

[10] H. Krauch and W. Kunz, "Organic Name Reactions," John Wiley and Sons, Inc., New York, N. Y., 1964, p 154; see also references cited therein.

[11] Reference 8, pp 137–146.

[12] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **89**, 262 (1906).

B. Reactions in benzene were performed analogously. After the appropriate hours shown (Table I), methanol (10 ml) was added to the reaction mixture, and the mixture was treated in the same manner as the reaction in acetonitrile for the isolation of the products.

C. Reaction in Benzene–Methanol.—A solution of **6a** (1.99 g, 10 mmol) in benzene–methanol (8.4:1, 30 ml) was added to a boiling solution of **2** (2.62 g, 10 mmol) in benzene–methanol (8.4:1, 40 ml) and the resultant solution was refluxed for 2 hr. The mixture was concentrated by rotary evaporation, and the residue was treated in the same manner as the reaction in acetonitrile for the isolation of the products.

In the Presence of Catalyst. A. Reaction in Acetonitrile.—To a solution of **2** (2.62 g, 10 mmol) in acetonitrile (50 ml) were added, with stirring, 5 drops of triethylamine[4] and then a solution of **6a** (1.99 g, 10 mmol) in acetonitrile (30 ml). After 2 hr, methanol (10 ml) was added to the mixture. The mixture was concentrated by rotary evaporation, and the residue was treated with tetrahydrofuran (20 ml). The crystalline **7a** was collected by filtration (4.2 g, 91%). In place of triethylamine as the catalyst, aqueous potassium cyanide (5 drops of a 33% solution) was effecively used in each 10-mmol-scale reaction.

B. Reaction in Benzene.—To a solution of **2** (2.62 g, 10 mmol) in benzene (40 ml) were added, with stirring at room temperature, 5 drops of triethylamine and then a solution of **6a** (1.99 g, 10 mmol) in benzene (30 ml). After 2 hr, methanol (10 ml) was added to the mixture. The mixture was concentrated by rotary evaporation and the residue was treated with tetrahydrofuran (20 ml). The crystalline **7a** was collected by filtration (4.35 g, 94%).

C. Reaction in Benzene–Methanol.—To a solution of **2** (2.62 g, 10 mmol) in benzene–methanol (8.4:1, 40 ml) were added, with stirring at room temperature, 5 drops of triethylamine and then a solution of **6a** (1.99 g, 10 mmol) in benzene–methanol (8.4:1, 30 ml). After 2 hr, the resultant mixture was concentrated by rotary evaporation and the residue was treated with tetrahydrofuran (20 ml). The crystalline **7a** was collected by filtration (4.25 g, 92%). In place of triethylamine as catalyst, pyridine (5 drops) was effectively used in a 10-mmol-scale reaction.

Reaction in the Presence of (2-Oxo-2-phenylethyl)pyridinium Bromide (9).—To a solution of **2** (2.62 g, 10 mmol) in benzene–methanol (8.4:1, 40 ml) were added, with stirring at room temperature, 0.3 g (1 mmol) of (2-oxo-2-phenylethyl)pyridinium bromide (**9**), mp 191.5–192° (lit.[13] 199–200°), and then a solution of **6a** (1.99 g, 10 mmol) in the mixed solvent (30 ml). After 2 hr, the mixture was concentrated by rotary evaporation and the residue was treated in a same manner as in the reaction in acetonitrile for the isolation of the products.

Registry No.—**2**, 603-35-0; **6a**, 70-11-1; **6b**, 99-81-0; **6c**, 99-73-0; **6d**, 619-41-0; **6e**, 2632-13-5; **6f**, 2114-00-3; **6g**, 532-27-4; **7b**, 17730-93-7.

[13] J. W. Baker, *J. Chem. Soc.*, 1148 (1932).

The Thermal Decomposition of Solid Benzyldimethylsulfonium Salts. Significance of the Kinetic Behavior

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The kinetics of thermal decomposition of solid benzyldimethylsulfonium salts are compared with predictions derived from a theoretical model, construction of which assumes that each reacting particle approximates a sphere or regular polyhedron, that reaction takes place at the surface only, and that the distribution of particle sizes is accurately expressed by a simple exponential equation. Kinetic orders based on the "log normal" distribution law (eq 5) are constant through at least 95% reaction and best fit the experimental values.

In an earlier paper[2] it was suggested that a cubic or spherical particle or a uniform aggregate of such particles decomposing at the surface to give volatile products should obey two-thirds-order kinetics (eq 1). The

$$\frac{dw}{dt} = -kw^{2/3} \qquad (1)$$

kinetics of thermal decomposition of solid benzyldimethylsulfonium salts vary from less than two-thirds order to greater than first order for pulverized and unpulverized samples (Table I). Decomposition of a pulverized sample incorporating a wide range of particle sizes might not be expected to follow eq 1, and evidence presented here argues that orders higher than two-thirds are to be anticipated.

TABLE I

REACTION ORDERS FOR THERMAL DECOMPOSITION OF SOLID $RC_6H_4CH_2S(CH_3)_2X^a$

1–6a, X = Cl
b, X = Br
c, X = I

Compd	R	X: Cl[b]	X: Br	X: I
1	H	0.7–0.9	0.7–0.9	0.6–0.7
2	p-CH_3	0.7–0.8	0.9–1.1	1.2–1.3
3	p-Cl	0.6–0.7	1.0–1.2	1.3–1.5
4	p-NO_2	0.8	0.67	1.0 (88°) 0.9 (93°) 0.7 (98°)
5	m-NO_2	0.7	0.8–1.2	0.9–1.0
6	p-CH_3O	0.9 (78°) 0.6 (83°)	0.8 (78°) 0.5 (83°) 0.4 (88°)	0.6 (60°) 0.5 (65°) 0.5 (70°)

[a] Reaction orders are evaluated by fitting to eq 6 the kinetic data obtained as described in ref 2. [b] Chloride samples were not pulverized.

A number of equations have been proposed to describe the particle size distribution of milled solids. One of the earliest was suggested by Heywood,[3] who assumed that the number of particles of diameter x would obey eq 2, and that the particle weight distribution would therefore follow eq 3. Later, Rosin and Rammler developed a modified form of eq 3 which could be applied to mill products of a wide variety of

$$\frac{dN}{dx} = be^{-bx} \qquad (2)$$

$$\frac{dG}{dx} = kx^3e^{-bx} \qquad (3)$$

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[2] W. D. Burrows and J. H. Cornell, *J. Org. Chem.*, **32**, 3840 (1967).

[3] H. Heywood, *J. Inst. Fuel*, **6**, 241 (1933).