primary importance, these considerations being opposite to those previously reported[8] for I.

Experimental Section

Materials.—The 3-substituted 4-nitroanilines which were commercially unavailable were prepared as indicated by footnotes to Table III.

TABLE III

MELTING POINTS OF 3-SUBSTITUTED 4-NITROANILINES

3 substituent	Mp, °C[a]	Lit, mp, °C
H	146–147.5	145–147[b]
CF_3	127–128.5	129[c]
Cl	156–157	156–157[d]
CH_3CO	148–150	148–149,[e] 150[f]
NO_2	153–155[g]	154[h]
$CO_2C_2H_5$	105–107	107.5[i,j]
CH_3	134.5–135.5	135[k,l]

[a] Corrected. [b] F. K. Beilstein, "Handbuch der organischen Chemie," Vol. XII, 4th ed, J. Springer, Berlin, 1929, p 711. F. K. Beilstein, "Handbuch der organischen Chemie," Vol. XII, 1950, p 477 (2nd supplement). [d] H. H. Hodgson and A. Kershaw, *J. Chem. Soc.*, 2919 (1929). [e] J. C. E. Simpson, C. M. Atkinson, K. Schofield, and O. Stephenson, *ibid.*, 654 (1945). [f] W. A. Waters, *ibid.*, 629 (1945). [g] A benzene solution of the substance melting between 153 and 155° was chromatographed on alumina according to K. Pausaika and J. Scroggie, *ibid.*, 1897 (1955). Only one band was observed. [h] O. N. Witt and E. Witte, *Ber.*, **41**, 3091 (1908). [i] L. Kalb and O. Gross, *ibid.*, **59**, 736 (1926). [j] *Chem. Zentr.*, II, 951 (1899). [k] J. W. Cook and O. L. Brady, *J. Chem. Soc.*, **117**, 752 (1920). [l] J. P. Wibaut, *Rec. Trav. Chim.*, **32**, 287 (1913).

Analytical grade hydrochloric acid was used in the spectral studies. All water used was deionized by passing distilled water through an "Ilco-Way" universal deionizing column.[25]

Ultraviolet Spectra and Measurement of pK_a's.—Stock solutions (0.0003 M) were prepared as described previously.[8] The absorption spectra were measured as described previously,[8] except that hydrochloric acid solutions of various concentrations, rather than buffered solutions, were used. The pK_a's were calculated from eq 8.[12b] In eq 8, A is the absorbance of the

$$\mathrm{p}K_a = H_0 - \log \frac{A - A_a}{A_b - A} \tag{8}$$

solution containing various concentrations of aqueous hydrochloric acid, A_a is the absorbance of the solution in concentrated hydrochloric acid, A_b is the absorbance of the solution in 0.2 M sodium hydroxide, and H_0 is the acidity function for hydrochloric acid.[26]

The medium shift was minimal in all cases and the absorbance of all solutions was measured at the wavelength at which A_b was measured.

Calculation of the Excited-State pK_a*'s.—The pK_a*'s were calculated using eq 9.[10,19] In eq 9, ν_b and ν_a represent the frequencies of corresponding transitions in wavenumbers of a base and its conjugate acid, N is Avogadro's constant, h is Planck's constant, c is the velocity of light, and R is the gas constant. The uncertainty involved in the calculation of pK_a^+ has been treated elsewhere.[10]

$$\mathrm{p}K_a{}^* = \frac{(\nu_b - \nu_a)Nhc}{2.303RT} + \mathrm{p}K_a \tag{9}$$

Registry No.—IIb (R = H), 100-01-6; IIb (R = CF_3), 393-11-3; IIb (R = Cl), 825-41-2; IIb (R = $COCH_3$), 16994-13-1; IIb (R = NO_2), 610-41-3; IIb (R = $CO_2C_2H_5$), 16994-15-3; IIb (R = CH_3), 611-05-2.

Acknowledgments.—This study was supported in part by a research grant from The Robert A. Welch Foundation. The statistical calculations were performed by the Data Processing Center, Texas Engineering Experiment Station, College Station, Texas, on an IBM-7094 computer.

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[25] Illinois Water Treatment Co., Rockford, Ill.

[26] E. M. Arnett and George W. Mach, *J. Amer. Chem. Soc.*, **88**, 1177 (1966).

Liquid Crystals. II.[1] Effects of Terminal Group Substitution on the Mesomorphic Behavior of Some Benzylideneanilines

JOSEPH A. CASTELLANO, JOEL E. GOLDMACHER, LUCIAN A. BARTON, AND JEAN S. KANE

David Sarnoff Research Center, RCA Laboratories, Princeton, New Jersey 08540

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In an effort to prepare nematic compounds with crystal–nematic transition temperatures below 100°, benzylideneaniline was substituted with a variety of functional groups in the *para* positions of both rings. Of the 21 new compounds that were prepared by the acid-catalyzed condensation of appropriate *para*-substituted benzaldehydes with *para*-substituted anilines only nine exhibited nematic behavior. Trends in the mesomorphic behavior of a homologous series, namely, *p*-*n*-alkoxybenzylidene-*p*′-aminoacetophenones, are discussed in detail. The profound effect of changes in the nature of terminal groups on the probability of mesomorphism in benzylideneanils is demonstrated by comparison with *para*-substituted benzylidene-*p*′-aminobiphenyl derivatives. That some residual lateral intermolecular attractions are necessary in order to maintain nematic order is demonstrated by the fact that substitution of groups with dipoles acting along the long axis of the molecule destroys mesomorphic behavior. Replacement of oxygen by sulfur in the alkoxy group of benzyldeneanils results in loss of mesomorphic (enantiotropic) behavior.

Liquid crystallinity or mesomorphism[2] is a unique state of matter intermediate between a crystalline solid and a normal isotropic liquid. The phenomenon is usually exhibited by long, rod-shaped molecules which contain dipolar groups. This permits the molecules to orient themselves with their long axes parallel. Since rotation can occur only about the long axis of the molecule, compounds of this type behave as anisotropic liquids and are birefringent. Three main types of mesomorphic states have been recognized:[3] nematic mesophases, in which the molecules can rotate only about their long axes; smectic mesophases, in which the

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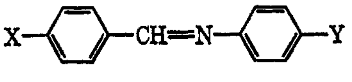
[1] For the first paper in this series, see J. Goldmacher and L. Barton, *J. Org. Chem.*, **32**, 476 (1967).

[2] G. Friedel, *Ann. Phys.* (Paris), **18**, 273 (1922).

[3] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962, Chapters I, VIII, and IX.

Table I

Substituted Benzylideneanilines Prepared for This Study



Compd	Registry no.	X	Y	Smectic range, °C	Nematic range, °C	Anal, %					
						Calcd			Found		
						C	H	N	C	H	N
1		CH_3O	$CH{:}CHCO_2C_4H_9$	71–95	95–113[a]	74.75	6.87	4.15	74.78	6.90	4.27
2	17224-11-2	$C_7H_{15}O$	$CH{:}CHCO_2C_4H_9$	102–138	...	76.92	8.37	3.32	76.88	8.42	3.52
3		CH_3CO_2	OCH_3	...	112–117[b]	71.37	5.61	5.20	71.80	5.65	5.32
4	17224-12-3	CH_3CONH	OCH_3	...	188[c,d]	71.62	6.01	10.44	71.75	6.03	10.36
5	17224-13-4	C_2H_5O	$CO_2C_2H_5$	...	94[e] (87)[f,g]	72.71	6.44	4.71	72.75	6.44	4.77
6	17224-14-5	CH_3O	$CONH_2$	176–95	...	70.86	5.51	11.02	70.60	5.68	11.20
7		CH_3O	CN	...	105–118[h]	76.25	5.12	11.86	76.51	5.61	11.93
8	17224-15-6	CH_3CO_2	CN	...	157–158[c]	72.69	4.58	10.60	72.65	4.54	10.50
9	17224-16-7	Ph	$OCOCH_3$	...	155–182	79.95	5.39	4.45	80.18	5.44	4.58
10		CH_3O	$OCOCH_3$	...	83–110[i]	71.36	5.62	5.20	71.42	5.57	5.17
11		CH_3O	$COCH_3$	...	124.5[c,j]	75.87	5.97	5.53	75.82	5.53	5.50
12	17224-17-8	C_2H_5O	$COCH_3$	...	123[e] (118)[f]	76.38	6.41	5.24	76.20	6.49	5.22
13	17224-18-9	n-C_4H_9O	$COCH_3$	85–97	98–111	77.26	7.17	4.74	77.66	7.13	4.66
14	17224-19-0	n-$C_8H_{17}O$	$COCH_3$	73–116	117–119	78.59	8.32	3.99	78.88	8.61	4.06
15	17224-20-3	CH_3	CN	...	130[c]	81.77	5.49	12.72	81.97	5.69	12.40
16	17224-21-4	H	CN	...	71.5–2[c]	81.55	4.85	13.59	81.52	4.86	13.67
17	17224-22-5	HO_2C	CN	259–305	306–18[k]	71.99	4.04	11.19	72.12	4.10	11.05
18	17224-23-6	Cl	CN	...	169–70[c,k]	69.86	3.77	11.64	69.79	3.93	11.40
19	17224-24-7	$(CH_3)_2N$	CN	...	183[c]	77.08	6.05	16.86	77.34	6.29	16.51
20	17224-25-8	O_2N	CN	...	190[c]	66.92	3.61	16.73	66.84	3.78	16.80
21	17224-26-9	NC	$OCOCH_3$	...	164–165[c]	72.69	4.58	10.60	73.05	4.74	10.78
22	17224-27-0	CH_3CO_2	SCH_3	...	116–117[c]	67.60	5.28	4.92	67.91	5.38	4.95
23	17224-28-1	CH_3S	$OCOCH_3$	...	100[e] (82)[f]	67.60	5.28	4.92	67.84	4.98	5.00
24	17224-29-2	CH_3S	SCH_3	...	143–145[c]	66.20	5.54	5.18	66.43	5.73	5.24
25		CH_3O	OCH_3	...	142[c,l]	...	...	...	...	...	...
26	17224-30-5	n-C_4H_9O	SCH_3	(83.5)[m]	99[e] (94)[f]	72.20	7.03	4.67	72.53	6.88	4.79
27	17224-31-6	n-C_4H_9O	OCH_3	...	111[e] (106)[f]	76.60	7.43	4.95	76.80	7.30	5.15

[a] D. Vorlander [*Ber.*, **41**, 2033 (1908)] reports a mesomorphic range of 58–76°. [b] P. Hansen [*Diss. Halle* (1907)] reports a nematic range of 112–118°. [c] Not mesomorphic. [d] Recrystallized from benzene. [e] Melts to isotropic liquid at this temperature. [f] Monotropic (isotropic liquid → nematic) transition temperature. [g] H. Sackmann and D. Demus, *Z. Phys. Chem.* (Leipzig), **224**, 177 (1963). No transition temperatures are given. Although we only observed one mesophase, these workers report the presence of a smectic phase. [h] A. Frohlich [*Diss. Halle* (1910)] reports a nematic range of 103–113.5°. [i] P. Hansen [*Diss. Halle* (1907)] reports a nematic range of 81.5–108°. [j] M. Guia and E. Bagiella, *Gazz. Chem. Ital.*, **51**, II, 116 (1921). [k] Recrystallized from ethanol. [l] A. Hantzsh, *et al.*, *Ber.*, **34**, 832 (1901). [m] Monotropic (nematic → smectic) transition temperature.

molecules are further constrained to move in layers; and cholesteric mesophases, in which the direction of the long axis of the molecules in a chosen layer is slightly displaced from those in adjacent layers to produce a helical structure.

Although a large number of nematic materials have previously been prepared, very few known compounds exhibit crystal-nematic transition temperatures below 100°. In the past most workers were concerned with the synthesis of compounds with high nematic stability (a high nematic–isotropic transition temperature) and, as a result of the relatively high molecular weight of the compounds which they prepared, high crystal–nematic transition temperatures were obtained. Our efforts on the other hand have been directed toward the preparation of comparatively low molecular weight Schiff bases, specifically, benzylideneanilines containing various substituent groups in the *para* positions of both rings.

Experimental Section

General.—Transition temperatures were measured in open capillary tubes with an Arthur H. Thomas Model No. 6406-K melting point apparatus and are all corrected. Reagent grade chemicals were used throughout but purification by distillation or recrystallization was carried out whenever necessary to achieve the physical constants reported in the literature. *p*-Alkoxybenzaldehydes were prepared from *p*-hydroxybenzaldehyde and various alkyl iodides in methanolic KOH by the method of Weygand and Gabler[4] to give 50–60% yields of the known compounds. Combustion analyses were performed by B. L. Goydish and M. Ippolito of these laboratories.

Substituted Benzylideneanilines.—In the general procedure a mixture of 0.010 mol each of the appropriate *para*-substituted benzaldehyde and *para*-substituted aniline in 150 ml of benzene containing 0.1 g of benzenesulfonic acid was refluxed for 2–4 hr. The water was removed azeotropically and was collected and measured in a Dean–Stark trap. After the calculated amount of water was collected, the solvent was removed *in vacuo* and the residue recrystallized from hexane unless otherwise noted (Table I). Yields of product obtained after one recrystallization ranged from 47 to 95%. All of the nonmesomorphic compounds were recrystallized to constant melting point while the nematic materials were recrystallized until the nematic–isotropic transition temperatures were constant and reversible.

Results

The preparation of 21 new anils was carried out by the acid-catalyzed condensation of appropriate aromatic aldehydes with substituted anilines, but only nine of the compounds exhibited nematic mesomorphism. The properties of these compounds are presented in Table I along with the analytical data. Compounds **1**, **3**, **7**, **10**, **11**, and **25** are included in the table for comparative purposes.

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(4) C. Weygand and R. Gabler, *J. Prakt. Chem.*, **155**, 338 (1940).

Discussion

Molecules which exhibit nematic mesomorphism are generally cylindrically shaped and possess polar and/or polarizable groups in addition to aromatic rings. They do not have very strong dipole moments operating along the long axis of the molecule nor do they have very long alkyl chains. The latter feature tends to enhance the formation of smectic mesormorphism. The thermal stability of a smectic mesophase is largely determined by the low ratio of terminal to lateral intermolecular cohesive forces while a high ratio of these forces is important in determining nematic isotropic transition temperatures. Comparison between the mesomorphic properties of **1** and **2** serves to illustrate this point. Since the dipolar (alkoxy) and polarizable (azomethine) centers of the molecule have become further separated from one another as a result of the lengthened alkyl chain, the terminal intermolecular attractions have decreased while the residual lateral attractions are essentially unchanged. This increase in the ratio of lateral to terminal cohesive forces makes the probability greater that the layer arrangement, which is characteristic of the smectic mesophase, will persist after melting occurs. Changes in this ratio are therefore quite important in determining the type of mesomorphism being exhibited by certain molecules in a series of liquid crystalline compounds as well as the temperatures at which mesomorphic transitions occur.

It is well known that, when the mesomorphic transition temperatures for a homologous series of compounds, *e.g.*, in a series of *n*-alkyl ethers or esters, are plotted against the number of carbon atoms in the alkyl chain, smooth curve relationships between even or odd members of the series are found to exist. This regular alternation of transition points has been explained by assuming that the alkyl chains adopt the "cog wheel" rather than the "zig-zag" conformation in the mesomorphic state.[3]

An example of this trend is provided by the homologous series derived from *p*-anisylidene-*p*′-aminoacetophenone (**11**). Although this compound appears to possess all the necessary requirements for mesomorphic behavior, it is in fact nonmesomorphic. As the length of the alkyl chain in the ether portion of the molecule is increased, however, mesomorphic behavior appears (Figure 1). An unusual feature of the phase transition plot for this series is the increased nematic as well as smectic thermal stability as the chain length is increased from four to eight carbon atoms. This behavior has only been observed[3] with the series of 2- and 2′-substituted 4-*p*-*n*-alkoxybenzylidene-*p*′-aminobiphenyls in which the alkoxy chain had from seven to 18 carbon atoms. The trend of nematic–isotropic transition temperatures for these compounds, which contain lateral substituents, was postulated to occur as a result of very weak lateral cohesions brought about by the increased side spacing of the molecules. Since no lateral substituents are present in the series **11–14**, one must assume that the acetyl group produces such strong terminal intermolecular attractive forces that the ratio of lateral to terminal cohesions is very low. The molecules of **11** may, therefore, be firmly linked together by molecular attraction of their ends as previously postulated by Gray.[3] In the absence of adequate lateral interactions, however, chains of these molecules may be disrupted and will quickly break up into individual molecules as a result of thermal vibrations. As the lateral interactions are increased by lengthening the chain from four to eight carbon atoms, disruption is prevented and nematic thermal stability rises. That these lateral interactions are indeed increased is illustrated by the higher smectic thermal stability.

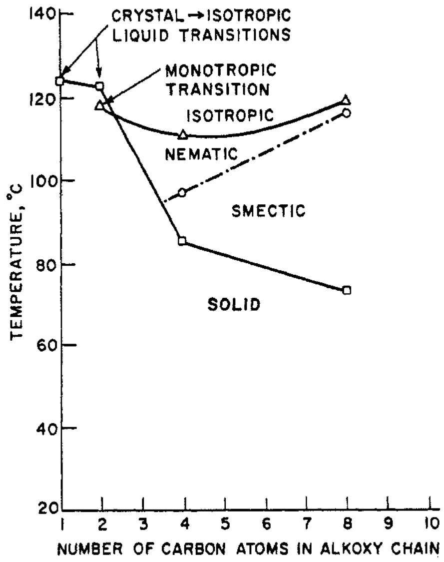
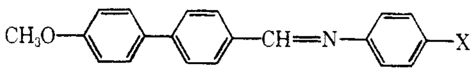
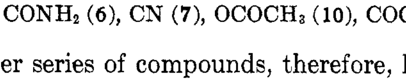


Figure 1.—Phase transition temperatures for the series p,p'-$C_nH_{2n+1}OC_6H_4CHNC_6H_4COCH_3$: △ (nematic → isotropic liquid); □ (crystal → mesophase); ○ (smectic → nematic).

The importance of molecular length in determining the probability for nematic mesomorphism is dramatically illustrated by a comparison of the behavior of several of the compounds reported here with the series of type I Schiff bases which are all reported[3] to be nematic. Obviously the nature of the terminal group at one end of this type of molecule plays only a minor role in determining mesomorphic behavior. This is also illustrated by the nematic behavior of **9**. This is not the case, however, for type II benzylideneanils where Y is a small group. Thus, **6** is a purely smectic compound, **7** and **10** are purely nematic, and **11** is nonmesomorphic. The nature of the dipolar end groups in the latter series of compounds, therefore, has a profound effect on the melting characteristics of these compounds. Introduction of the acetamido group into the terminal position of a Schiff base as in **4** produces such strong intermolecular interactions in the crystal lattice as a result of hydrogen bonding that no residual cohesions are present at 188° and the compound is nonmesomorphic. On the other hand, intermolecular hydrogen bonding through the primary amido group in **6** results in dimer formation (as is the case for carboxylic



I, X = H, CH_3, CH_3O, n-C_3H_7O, n-$C_5H_{11}O$, i-C_3H_7O, F, Cl, Br, NO_2, $N(CH_3)_2$, $NHCOCH_3$



II, Y = $CONH_2$ (**6**), CN (**7**), $OCOCH_3$ (**10**), $COCH_3$ (**11**) 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°.

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[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

Kiyoshi Fukui, Rokuro Sudo, Mitsuo Masaki, and Masaki Ohta

Laboratory of Organic Chemistry, Tokyo Institute of Technology, Okayama, Meguro-ku, Tokyo, Japan

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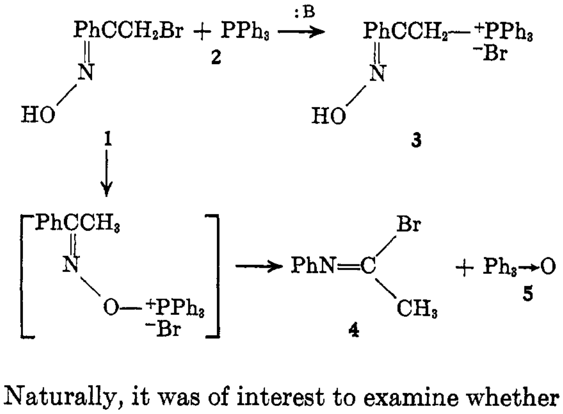
In the reaction of 2-bromoacetophenone with triphenylphosphine, the presence of a catalytic amount of base was remarkably effective for the formation of the α-ketophosphonium salt. The catalytic effect of the base was also observed in the reaction of triphenylphosphine with *para*-substituted 2-bromoacetophenone 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).