Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.81; H, 8.13.

3-Dimethylmalonyl-2-(2-pentynyl)cyclopentanone (7).—2-(2-Pentynyl)-2-cyclopentenone (59.2 g, 0.4 mol) in dry methanol (50 ml) was added in a nitrogen atmosphere over a 0.5-hr period at −5° to a solution of dry methanol (200 ml), sodium metal (1.15 g, 0.05 g-atom), and dimethyl malonate (66 g, 0.5 mol). After the reaction mixture had been stirred for 1 hr at −5°, acetic acid (6 g, 0.1 mol) was added and the solvent removed *in vacuo*. The residue was extracted twice with ether, the organic layers were washed with water and dried over magnesium sulfate, and the ether was removed *in vacuo*. Distillation through a small Vigreux column afforded the pure (1.5 m, vpc, silicone rubber SE-30, 10%, 225°) Michael adduct: 107 g (95.5%); bp 140–145° (0.01 mm); $n^{23}D$ 1.800; ir (liquid) 3460, 1735, 1430, 1165 cm^{-1}; nmr (CCl_4) δ 1.08 (3 H, t), 1.5–2.5 (10 H, m), 3.65 (2 H, d), 3.72 (6 H, s); mass spectrum *m/e* (rel intensity) 280 (0.1), 251 (17.7), 148 (100), 133 (48), 122 (36), 107 (26.3).

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.00; H, 7.29.

Dehydrojasmonic Acid (8).—Sodium hydroxide (32 g, 0.8 mol) dissolved in water (320 ml) was added slowly under a nitrogen atmosphere to the malonate **7** (107 g, 0.382 mol) at 15° over 3 hr. The reaction mixture was stirred overnight at room temperature. By extraction with ether, pure 2-(2-pentynyl)-2-cyclopentenone (3 g, 5.3%) (retro-Michael product) was removed from the reaction mixture. The aqueous solution was acidified with sulfuric acid (50 g, 0.5 mol) in water (100 ml) and heated at reflux until gas evolution ceased (3–4 hr). After two extractions with ether, the organic layers were washed with water and dried over magnesium sulfate, and the solvent was removed *in vacuo*. Distillation through a small Vigreux column afforded pure dehydrojasmonic acid:[2] 63.6 g (80%); bp 155–160° (0.01 mm); $n^{23}D$ 1.4895; ir (liquid) 3150, 2670, 1735, 1705 cm^{-1}; nmr (CCl_4 + $CDCl_3$) δ 1.09 (3 H, t), 1.8–3.1 (10 H, m), 8.6 (1 H, s); mass spectrum *m/e* (rel intensity) 208 (0.1), 179 (29), 122 (100), 107 (54).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.76; H, 7.81.

Racemic Methyl Dehydrojasmonate (9).—Dehydrojasmonic acid (**8**) (63.6 g, 0.306 mol) and dry methanol (200 ml) in the presence of concentrated sulfuric acid (3 g) was heated at 40° for 3 hr. The reaction mixture was cooled and sodium bicarbonate (5 g) was added. Methanol was removed *in vacuo*, the residue was extracted twice with ether, the organic layers were washed with water and dried over magnesium sulfate, and the solvent was removed *in vacuo*. Distillation through a Vigreux column afforded pure (2.5 m, vpc, Carbowax 20M, 5%, 200°) methyl dehydrojasmonate:[1] 63.5 g (93.5%); bp 100–103° (0.01 mm); $n^{23}D$ 1.4779; ir (liquid) 3460, 1735 cm^{-1}; nmr (CCl_4) δ 1.09 (3 H, t), 1.7–2.9 (12 H, m), 3.63 (3 H, s); mass spectrum *m/e* (rel intensity) 222 (0.1) 193 (43.3), 122 (100), 107 (52).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.39; H, 8.36.

This compound gave a semicarbazone, mp 167–169°.

Anal. Calcd for $C_{14}H_{21}O_3N_3$: C, 60.19; H, 7.58. Found: C, 60.23; H, 7.88.

Racemic Methyl Jasmonate (1).—Methyl dehydrojasmonate (63 g, 0.284 mol) in petroleum ether (bp 50–70°, 500 ml) was hydrogenated in the presence of Lindlar[11] catalyst (1 g). After 3 hr 1 equiv of H_2 had been absorbed. Filtration, removal of the petroleum ether *in vacuo*, and distillation through a Widmer column afforded methyl jasmonate: 59.5 g (93.5%); bp 88–90° (0.01 mm); $n^{23}D$ 1.4720; ir (liquid) 3450, 1735, 1690, 703 cm^{-1}; nmr (CCl_4) δ 0.96 (3 H, t), 1.7–2.7 (14 H, m), 3.61 (3 H, s), 5.25 (1 H, m); mass spectrum *m/e* (rel intensity) 224 (36), 151 (58), 83 (100). Infrared and nmr spectra were indistinguishable from those of authentic material.[1,2]

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.52; H, 8.98.

Ketone 10.—A solution of 171 mg (1.15 mmol) of ketone **6** in 5 ml of hexane was hydrogenated in the presence of 10 mg of Lindlar[11] catalyst. Hydrogen uptake after 45 min at 20° (760 mm) was 25.5 ml (0.92 equiv). The mixture was filtered, evaporated, and distilled to yield 157 mg (91%) of ketone **10**: bp ~70° (0.05 mm); ir ($CHCl_3$) 1690, 1630 cm^{-1}; nmr (CCl_4) δ 1.0 (3 H, t, J = 7 Hz), 1.5–3.0 (8 H, m), 5.4 (2 H, m), 7.2 (1 H, m); uv (EtOH) 227 mμ (ε 10,500).

(11) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.23; H, 9.50.

Jasmone (12).—To an ice-cold solution of 115 mg (0.75 mmol) of ketone **10** in 2 ml of ether was added 1 ml (1.5 mmol) of 1.5 *M* methyllithium in ether. After 10 min at room temperature the mixture was poured into cold water. It was extracted with pentane, washed with water, dried (Na_2SO_4), and evaporated to give 121 mg of alcohol **11**: ir ($CHCl_3$) 3610, 3430 cm^{-1}.

The crude carbinol was dissolved in 2 ml of ether and then a solution of 80 mg of CrO_3 in 0.8 ml of aqueous 5% H_2SO_4 was added dropwise at 5°. After being stirred for 15 min at 5° water was added and the mixture was extracted with pentane. The organic layer was subsequently washed with 5% $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated to afford 113 mg of crude jasmone (**12**). A pure sample was obtained by vpc collection: ir ($CHCl_3$) 1685, 1640 cm^{-1}; nmr (CCl_4) δ 1.0 (3 H, t, J = 7 Hz), 2.0 (3 H, s), 2.1–2.6 (6 H, m), 2.9 (2 H, d, J = 6 Hz), 5.2 (2 H, m). Ir and nmr spectra and retention time on vpc were identical with those of an authentic[12] sample of jasmone.

Registry No.—**1**, 20073-13-6; **3**, 29119-42-4; **4**, 29119-43-5; **6**, 29119-44-6; **7**, 29119-45-7; **8**, 29119-46-8; **9**, 29119-47-9; **9** semicarbazone, 29119-48-0; **10**, 29119-49-1; **12**, 488-10-8.

Acknowledgments.—We are indebted to Firmenich et Cie., Geneva, for generous financial support. High-resolution mass spectra were measured in the National Institutes of Health supported facility at Massachusetts Institute of Technology (Grant FR 00317) under the direction of Professor K. Biemann.

(12) G. Büchi and H. Wüest, *J. Org. Chem.*, **31**, 977 (1966).

Synthesis and Stereochemistry of *syn*- and *anti*-*p*-Nitrophenyl Phenacyl Methylphosphonate Oxime[1]

PETER BLUMBERGS,* CHANDRAKANT B. THANAWALLA, AND ARTHUR B. ASH

Ash Stevens Inc., Detroit, Michigan 48202

CLAIRE N. LIESKE AND GEORGE M. STEINBERG

Medical Research Laboratory, Research Laboratories, Edgewood Arsenal, Maryland 21010

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Studies of neighboring oxime group participation in phosphonate ester hydrolysis have been in progress in our laboratories for the past several years. We have reported[2-4] on the very large rate enhancements in the solvolytic displacement of *p*-nitrophenol exhibited by *syn*-*p*-nitrophenyl phenacyl methylphosphonate oxime (**1**) and *anti*-*p*-nitrophenyl phenacyl methylphosphonate oxime (**2**) relative to that of ethyl *p*-nitrophenyl methylphosphonate (10^9 and 10^7 times, respectively). The experimental data in these papers support hy-

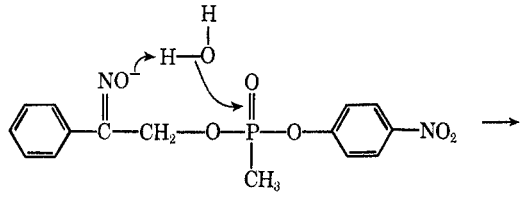
(1) This work was performed under Edgewood Arsenal Contract Nos. DA 18-035-AMC-703(A) and DAAA 15-67-C-0080. Presented in part at the 1st Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 1968.

(2) C. N. Lieske, J. W. Hovanec, G. M. Steinberg, and P. Blumbergs, *Chem. Commun.*, 13 (1968).

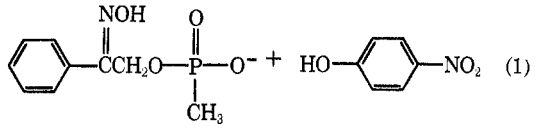
(3) J. W. Hovanec, C. N. Lieske, G. M. Steinberg, J. N. Pikulin, A. B. Ash, and P. Blumbergs, Abstracts, 1st Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 1968, p 97.

(4) C. N. Lieske, J. W. Hovanec, and P. Blumbergs, *Chem. Commun.*, 976 (1969).

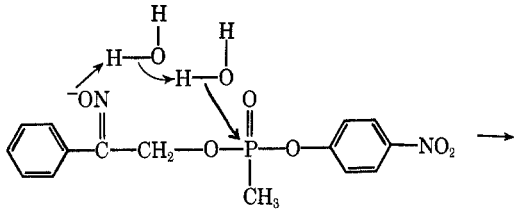
drolysis mechanisms for **1** and **2** involving oximate anion catalyzed, water-mediated reactions (eq 1 and 2).



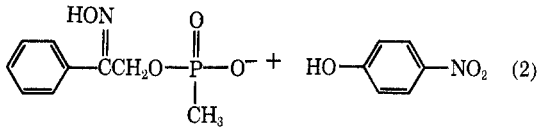
syn-**1**



(1)



anti-**2**



(2)

This paper reports the synthesis of **1** and **2**. While the isolation of **1** as a pure isomer was not achieved, a reproducible experimental procedure for *in situ* conversion of **2** to a mixture of isomers in which **1** predominates is described. Finally, from kinetic data and mechanistic considerations, assignments are made of the configurations of **1** and **2**. In light of the current controversy[5,6] in assigning oxime configurations from nmr data, the use of kinetic–mechanistic considerations, as illustrated in this work, provides a powerful tool for the stereochemical assignment of oximes in those situations where it may be invoked.

Experimental Section

General.—All melting points are uncorrected and were determined on a Hoover melting point apparatus, oil bath capillary technique, with a calibrated thermometer. Infrared spectra were recorded using a Perkin-Elmer 237B spectrophotometer. Nmr spectra were determined on a Varian A-60A spectrometer. Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

***p*-Nitrophenylmethylphosphonic Acid (3).**—Bis(*p*-nitrophenyl methylphosphonate),[7] mp 121.5–122.5°, was dissolved in acetonitrile and 1.85 equiv of 1 *N* sodium hydroxide solution added over a 3-hr period. Acetic acid was added to adjust the pH to *ca.* 5. The reaction mass was diluted with water and extracted with ether until the extracts showed the absence of *p*-nitrophenol. Five extractions were usually required. The aqueous layer was acidified to pH *ca.* 2 with hydrochloric acid and extracted three times with chloroform. The combined chloroform extracts were dried and charcoaled, the solvent was removed, and the residual solid was recrystallized twice from chloroform–*n*-hexane to give a 70% yield of *p*-nitrophenylmethylphosphonic acid as white crystals, mp 111–111.5° (lit.[8] mp 90–91°).

Anal. Calcd for $C_7H_8NO_5P$: C, 38.72; H, 3.71; N, 6.45; P, 14.27. Found: C, 38.70; H, 3.70; N, 6.70; P, 14.10.

Silver Salt of *p*-Nitrophenylmethylphosphonic Acid (4).—*p*-Nitrophenylmethylphosphonic acid (2.17 g, 10 mmol) was dissolved in a minimum amount of cold distilled water. The solution was treated with powdered silver carbonate (1.88 g, 6.8 mmol) and the precipitate washed with hot water. The filtrate was lyophilized and the resulting residue washed with cold chloroform to provide 3.2 g (quantitative) of silver *p*-nitrophenyl methylphosphonate, mp 207–209°. Recrystallization from a mixture of anhydrous methanol and anhydrous diethyl ether gave white plates, mp 208–210°.

Anal. Calcd for $C_7H_7AgNO_5P$: C, 25.95; H, 2.17; P, 9.56. Found: C, 25.87; H, 2.27; P, 9.37.

Phenacyl Bromide Oxime (5).—Phenacyl bromide was dissolved in a minimum amount of methanol and treated with an aqueous solution of 1 equiv of hydroxylamine sulfate. The suspension was stirred for 1 day at room temperature and the methanol evaporated under reduced pressure. The residue was extracted with benzene and the extract dried over anhydrous sodium sulfate. The drying agent was removed by filtration. Following removal of the solvent, the residue was recrystallized from chloroform–petroleum ether (bp 30–60°) without heating. The yield was 60% (by reworking the mother liquor) of phenacyl bromide oxime, mp 97–98.5° (lit.[9] mp 97–98°). The nmr spectrum ($CDCl_3$) was as follows: δ 4.42 (s, 2, CH_2Br, 9.66 (s, 1, OH), 7.41 and 7.72 (m, 5, phenyl).

Anal. Calcd for C_8H_8BrNO: Br, 37.33. Found: Br, 37.20.

Sublimation of the oxime at 70° (0.01 mm) effected no change in melting point. Further recrystallization gave a product with mp 99–100°. The nmr spectrum was unchanged. Attempts to obtain crystals suitable for X-ray diffraction studies were unsuccessful; the crystals were fibrous in structure.

Beckmann Rearrangement of Phenacyl Bromide Oxime Using Polyphosphoric Acid (PPA).—Phosphorus pentoxide (50 g) was dissolved in 85% H_3PO_4 (32 ml). Phenacyl bromide oxime, mp 97–98.5° (0.50 g, 2.3 mmol), was added to 10 g of the PPA and the mixture was immersed in an oil bath at 135° for 5 min while stirring manually. The reaction mass was poured over cracked ice and the solid filtered to provide 0.41 g (82%) of α-bromoacetanilide, mp 132.5–134.5°. Admixture of this material with an authentic sample (mp 134–136°) did not depress the melting point of the latter.

Beckmann Rearrangement of Phenacyl Bromide Oxime Using Phosphorus Pentachloride in Ether.—Phosphorus pentachloride (1 g) was added portionwise to a cold solution (0°) of phenacyl bromide oxime, mp 97–98.5° (215 mg, 1 mmol), in 10 ml of anhydrous diethyl ether. The reaction mixture was allowed to come to room temperature, stirred for 48 hr, poured onto cracked ice, and extracted with diethyl ether. The ether extract was washed several times with water, dried (sodium sulfate), and evaporated under reduced pressure (aspirator) to furnish a light pink pasty mass. Crystallization from a mixture of methylene chloride and petroleum ether gave 60 mg (27%) of a light pink crystalline solid, mp 128–130°. Admixture of this compound with an authentic sample of α-bromoacetanilide did not depress the melting point of the latter.

***anti*-*p*-Nitrophenyl Phenacyl Methylphosphonate Oxime (2).**—A solution of phenacyl bromide oxime, mp 99–100° (432 mg, 2 mmol), in 10 ml of anhydrous acetonitrile was added to a solution of silver *p*-nitrophenyl methylphosphonate (649 mg, 2 mmol) in 240 ml of acetonitrile. The reaction solution was stirred for 2.5 hr and filtered. The oily residue obtained by evaporation of the filtrate was dissolved in methylene chloride and the solution filtered to remove traces of silver bromide. Removal of the solvent and two crystallizations of the residue from a mixture of methylene chloride and 30–60° petroleum ether without heating gave 420 mg (60%) of *anti*-*p*-nitrophenyl phenacyl methyl-

(5) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958); E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961); R. H. Mazur, *J. Org. Chem.*, **28**, 248 (1963); G. J. Karabatsos, R. A. Taller, and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 2327 (1963); G. Slomp and W. J. Wechter, *Chem. Ind. (London)*, 41 (1962); W. B. Benson and A. E. Pohland, *J. Org. Chem.*, **30**, 1129 (1965); A. C. Huitric, D. B. Roll, and J. R. DeBoer, *ibid.*, **32**, 1661 (1967).

(6) H. Saito, *J. Chem. Soc. Jap.*, **85**, 724 (1964); H. Saito, K. Nukada, and M. Ohno, *Tetrahedron Lett.*, 2124 (1964); H. Saito and K. Nukada, *J. Mol. Spectrosc.*, **18**, 1 (1965); H. Saito and K. Nukada, *Tetrahedron Lett.*, 2117 (1965).

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(8) R. J. Withey, *Can. J. Chem.*, **47**, 4383 (1969).

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

phosphonate oxime, mp 115–117°. The nmr spectrum ($CDCl_3$) was as follows: δ 5.02 (d, 2, J = 9.5 Hz, $POCH_2$), 1.65 (d, 3, J = 18 Hz, PCH_3).

Anal. Calcd for $C_{15}H_{15}N_2O_6P$: C, 51.43; H, 4.31; N, 7.99. Found: C, 51.36; H, 4.28; N, 8.15.

syn- **and** *anti-p*-**Nitrophenyl Phenacyl Methylphosphonate Oximes (1 and 2).**—A mixture of phenacyl bromide oxime, mp 99–100° (5.16 g, 24.2 mmol), and silver *p*-nitrophenyl methylphosphonate (7.8 g, 23.9 mmol) in 390 ml of anhydrous acetonitrile was stirred at room temperature for 2.5 hr and filtered through a sintered-glass funnel. The filtrate was evaporated under reduced pressure to provide an oily residue. The residue was dissolved in anhydrous methylene chloride and refiltered to remove the remaining silver bromide. The filtrate was evaporated to dryness under reduced pressure and the resulting residue recrystallized from a mixture of methyl ethyl ketone and 30–60° petroleum ether. The first crop of white crystals weighed 2.91 g (34%) and had mp 115–117.5° (designated sample A).

Anal. Calcd for $C_{15}H_{15}N_2O_6P$: C, 51.43; H, 4.31; N, 7.99; P, 8.84. Found: C, 51.39; H, 4.56; N, 7.90; P, 8.68.

The nmr spectrum ($CDCl_3$) of this sample contained two distinct pairs of doublets: δ 1.65 [d, J = 17 Hz, PCH_3) (minor)], 1.66 [d, J = 17 Hz, PCH_3 (major)], 5.02 [d, 2 (35%), J = 9.5 Hz, $POCH_2$], 5.31 [d, 2 (65%), J = 9.5 Hz, $POCH_2$].

A portion of sample A was dissolved in freshly distilled, dry acetonitrile and allowed to stand for 15 min. It was then evaporated to dryness (total time of 30 min). There was obtained a colorless oil which solidified to a white solid, mp 115–118° (designated sample B), with acceptable elemental analysis. The nmr spectrum of sample B ($CDCl_3$) indicated that isomerization had occurred during this treatment: δ 1.65 [d, J = 17 Hz, PCH_3 (major)], 1.66 [d, J = 17 Hz, PCH_3 (minor)], 5.02 [d, 2 (56%), J = 9.5 Hz, $POCH_2$], 5.31 [d, 2 (44%), J = 9.5 Hz, $POCH_2$]. In addition to the first crop (sample A), 2.91 g of a second crop with mp 111–116.5° (designated sample C) was isolated which contained only the upfield (δ 5.02) isomer. Further, the original sample A, after standing 10 days in the solid state, contained only the upfield (δ 5.02) isomer. As discussed in the text, the upfield isomer is assigned the anti configuration **2** and the downfield isomer is assigned the syn configuration **1**.

Isomerization of 2 to 1 by Glacial Acetic Acid.—The following *in situ* isomerization of **2** to a mixture of **1** and **2** in the ratio of 3 to 1 was found to be consistently reproducible and without accompanying decomposition. In a typical experiment, 5.58 mg of **2** was dissolved in 450 μl of glacial acetic acid (Pioneer Chemical Co., Long Island City, N. Y.). The extent of isomerization was measured by a spectrophotometric kinetic procedure (see Results and Discussion) and found to reach a maximum of 75% conversion to **1** within 15 min.

Results and Discussion

The original synthesis of phenacyl bromide oxime, mp 89.5°, was accomplished by Korten and Scholl[10] in 1901 using phenacyl bromide and hydroxylamine hydrochloride. The Beckmann rearrangement, using phosphorus pentachloride in ether, gave α-bromoacetanilide. Korten and Scholl drew the structure as anti (syn phenyl), whereas present-day interpretation of the Beckmann reaction would lead to a syn (anti phenyl) assignment.[11] Fischer and Grob[12] in 1962 repeated the synthesis of Korten and Scholl to obtain phenacyl bromide oxime, mp 91°. Based on ultraviolet spectral data and metal complexing reactions of some α-dialkylaminomethyl derivatives, they also assigned the configuration as anti.

In these laboratories, the synthesis of Korten and Scholl was repeated to yield a product with mp 88.5–89°. In agreement with the recent findings of Masaki[9] and coworkers, it was found that the Korten and Scholl product contained significant quantities of phenacyl chloride oxime. Using hydroxylamine sulfate, we isolated chloride-free phenacyl bromide oxime with mp 97–98.5°. The nmr spectrum identified it as a single isomer. The Beckmann rearrangement using either phosphorus pentachloride in ether or by heating in polyphosphoric acid for 5 min at 135° gave α-bromoacetanilide (yields of 27 and 82%, respectively). These results strongly support pure phenacyl bromide oxime, mp 97–98.5°, having a syn configuration.

The synthesis of *anti-p*-nitrophenyl phenacyl methylphosphonate oxime (**2**) from pure phenacyl bromide oxime (**5**) and the silver salt of *p*-nitrophenyl methylphosphonic acid (**4**) was accomplished repeatedly in yields of 40–60%. The product represented a single isomer based on nmr spectral data. In a later, typical larger-scale experiment, somewhat modified (heterogeneous), 34% of a product was obtained as a first crop and shown by nmr to be a mixture of isomers consisting of 65% *syn-* and 35% *anti-p*-nitrophenyl phenacyl methylphosphonate oxime. A portion was dissolved in dry acetonitrile. The solvent was removed and the product now contained 44% syn and 56% anti oxime. Furthermore, the first crop, after standing for 10 days in the solid state, was reexamined by nmr and found to contain only the anti isomer. Clearly, the upfield isomer (anti), where there is no opportunity for hydrogen bonding between the oximino proton and the phosphoryl oxygen, is the thermodynamically more stable isomer. This observation is consistent with the results of Cherry[13] and coworkers. They found that the internally hydrogen bonded syn isomer of 3-hydroximinocamphor was less stable than the anti form.

Controlled and reproducible isomerization of the more stable upfield isomer of *p*-nitrophenyl phenacyl methylphosphonate oxime (**2**) to a mixture containing 75% of the downfield isomer **1** and 25% of the upfield isomer **2** was accomplished by dissolving **2** in glacial acetic acid at room temperature. Less reproducible was the thermal isomerization of **2** to **1** in deuteriochloroform at ambient temperature catalyzed by DCl–D_2O.

These conversions, established in the latter two cases by nmr spectral measurements, were confirmed by solvolysis rate studies (the hydrolysis rates of the isomers were independent of the isomerization procedure used) reinforced with supporting stoichiometric *p*-nitrophenol production. That is, spectrophotometric kinetic analysis of the isomer mixtures at the appropriate pH reflected *p*-nitrophenol production corresponding to the same percentage of the isomer in the nmr analysis. These results also established unequivocally that an isomerization step is not involved in the hydrolysis reaction. Such a diagnostic tool was made possible, of course, only by the fortuitous 100-fold difference in hydrolysis rates of the two isomers. The upfield isomer **2**, which has a half-life of 1.34 min at pH 4.90 (25°)[2] is virtually inert at pH 2.48 (25°), where the lower field isomer **1** has a half-life of 2.72 min.[4] As the kinetic and mechanistic data accumulated on the two isomers[2–4] excludes mechanistic pathways other than an oximate–anion, water-mediated reaction, correlation of the nmr data and the hydrolysis rate data identifies the upfield isomer as *anti-p*-nitrophenyl phenacyl methylphosphonate oxime (**2**) and the downfield isomer

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(11) L. G. Donaruma and W. Z. Heldt, *Org. React.*, **11**, 4 (1960).
(12) H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, **45**, 2528 (1962).
(13) P. C. Cherry, W. R. T. Cotthrell, G. D. Meakins, and E. E. Richards, *J. Chem. Soc. C*, 459 (1968).

as *syn*-*p*-nitrophenyl phenacyl methylphosphonate oxime (**1**). Reversal of these assignments, resulting in the anti isomer hydrolysis rate exceeding the syn isomer hydrolysis rate, would be, to the knowledge of the authors, without published precedent. In view of the current controversy[5,6] surrounding the assignment of oxime configurations from nmr data alone, the value of kinetic data and mechanistic considerations has been demonstrated. While not as universally applicable or as readily obtainable as nmr data, it does represent a useful approach in those situations where it may be invoked. To a limited extent, it is related to Meisenheimer's[14] elucidation of the configuration of ketoximes and to the work of Brady and Bishop[15] with aldoximes. In a larger sense, it is sufficiently different to offer future workers in the field of oxime configuration additional latitude in their approach to the problem of configurational assignment.

Registry No.—**1**, 25273-22-7; **2**, 25273-21-6; **4**, 29119-53-7; **5**, 14181-72-7.

(14) J. Meisenheimer, *Chem. Ber.*, **54**, 3206 (1921).
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Cyanomethylidenebis(triphenylphosphonium) Dibromide. Its Use in a Convenient Modification of the Wittig Reaction

JAMES W. WILT* AND ALEXANDER J. HO[1]

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

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In the course of some studies on dibromoacetonitrile, we discovered a convenient modification of the Wittig[2] reaction that affords unsaturated nitriles in generally good yields.

Dibromoacetonitrile reacted with triphenylphosphine in benzene to produce the bisphosphonium salt I. Although somewhat little studied, bisphosphonium salts such as I have been reported before.[3] It is of passing

$$Br_2CHCN + PPh_3 \xrightarrow[\text{heat}]{\text{benzene}} Ph_3\overset{+}{P}CH\overset{+}{P}Ph_3\ 2Br^- \quad (\text{I: } CN)$$

$$I + Ar(R)CHO \xrightarrow[\text{PhH, } H_2O, \text{ heat}]{\text{NaOH}} Ar(R)CH{=}CHCN + 2Ph_3PO$$

interest that trisphosphonium salts were reported long ago by Hofmann.[4] The report was incorrect, however, and trisphosphonium salts remain unknown.[5]

When I, together with an appropriate aldehyde, was refluxed with sodium hydroxide in a benzene–water solvent, the unsaturated nitrile and triphenylphosphine oxide resulted.

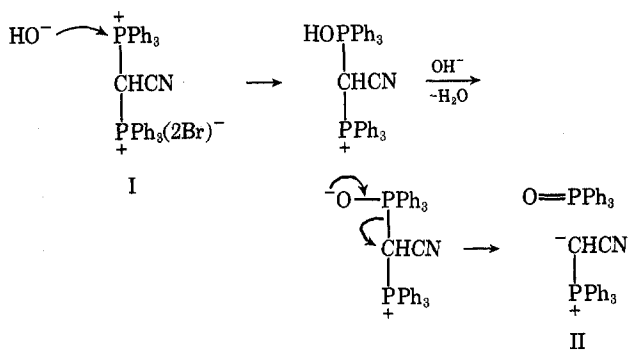
The reaction was applied to a variety of available aldehydes with the results given in Table I. Cyclohexanone failed to undergo the reaction, as might be anticipated because ketones normally fail to react with cyano-stabilized ylides.[6]

TABLE I

Starting aldehyde[a]	Isolated yield of nitrile, %	Trans:cis, %[b]
Benzaldehyde	84.7	74:26
p-Nitrobenzaldehyde	80.7	All trans
p-Isopropylbenzaldehyde	73.3	61:39
p-Methoxybenzaldehyde	72.9	All trans
α-Hexylcinnamaldehyde	78.2	*c*
Furfural	38.1	60:40
n-Heptaldehyde	74.1 (88:12)[d]	*c*
Isovaleraldehyde	66.6 (75:25)[d]	*c*
α-Ethylhexaldehyde	65.3[e]	*c*

[a] For experimental details, see the Experimental Section. [b] *Via* nmr spectral analysis. [c] Not determined because of complexity of the spectrum. [d] Ratio of α,β- and β,γ-unsaturated nitriles (see text). [e] All β,γ isomer.

In the aliphatic cases, the isolated product was partly or wholly isomerized to the (presumably equilibrated) β,γ-unsaturated nitrile, a well-investigated phenomenon in such systems.[7] The low yield of nitrile from furfural reflects the sensitivity of this aldehyde to hot base. Probably the somewhat lower yields in the aliphatic cases can be rationalized in this same way. Otherwise, the yields seem relatively insensitive to substituents, while the stereochemistry favors the more stable trans olefinic nitrile predominantly.[8] The pathway for this process seems clear. In the absence of aldehyde, treatment of I with aqueous sodium hydroxide produced the ylide II and triphenylphosphine oxide, possibly as



indicated. In the presence of aldehyde and the benzene cosolvent, II would be partitioned to some

(1) Taken from the M.S. Thesis of A. J. H., Loyola University of Chicago, 1970.
(2) G. Wittig, *Pure Appl. Chem.*, **9**, 245 (1964), A. Maerker, *Org. React.*, **14**, 270 (1965), and A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, are recent reviews of this process.
(3) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Amer. Chem. Soc.*, **83**, 3539 (1961); C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *ibid.*, **84**, 4349 (1962); J. S. Driscoll, D. W. Grisley, Jr., J. E. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, **29**, 2427 (1964).
(4) A. W. Hofmann, *Proc. Roy. Soc., London*, **10**, 189 (1860).
(5) *Cf.* G. H. Birum and C. N. Matthews, *J. Amer. Chem. Soc.*, **88**, 4198 (1966).
(6) J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y.,1968, p 704.
(7) *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 562–566.
(8) Mixtures of cis and trans products are commonly found in Wittig reactions: L. D. Bergel'son and M. M. Shemyakin, *Angew. Chem., Int. Ed. Engl.*, **3**, 250 (1964). No determination of isomeric stability was made in the present study, however, so no claim is made that the isolated nitriles represent the kinetic products. Most certainly in the aliphatic cases they do not.