Experimental Section

Materials. All commercial compounds were distilled prior to use. Physical constants agreed with literature values and GLC analysis indicated minimal purities of 99%. Most of the substituted phenylacetonitriles were prepared similarly to the following example. Purities were comparable to those of the other compounds. Physical properties and IR and NMR spectra were in accord with literature values and/or expectation.

Preparation of (*p*-Methylphenyl)acetonitrile. (*p*-Methylphenyl)acetonitrile was prepared by the addition over 35 min of 50 g (0.43 mol) of *p*-methylbenzyl chloride in 50 g of ethanol to 25 g (0.51 mol) of sodium cyanide dissolved in 23 ml of distilled water. The mixture was refluxed at 82 °C with a water-cooled, glass helices packed condenser for 4 h, after which time the mixture had resolved into a dark-brown upper layer and a dark-amber lower layer. The mixture was cooled and suction filtered to remove the precipitated salt, and approximately 60 ml of ethanol was carefully distilled off at 77 °C. The remaining material was extracted with four times its volume of ethyl ether. The organic material was washed with equal volumes of sulfuric acid, saturated sodium bicarbonate, and concentrated sodium chloride solutions, and dried over a few grams of anhydrous magnesium sulfate. After filtration, the material was fractionally distilled. A yield of 5.5 g (13%) of 99.9% pure product was obtained.

Procedure for Kinetic Runs for the Reaction of Bromotrichloromethane with the Substituted Phenylacetonitriles. Solutions of the two phenylacetonitriles, bromotrichloromethane, and *o*-dichlorobenzene (or chlorobenzene) were prepared in the approximate molar ratio of 1:1:10:0.5. Approximately 0.75 ml of the solution was placed in each of the several ampules (usually eight ampules were prepared simultaneously). The ampules were cooled to dry ice–isopropyl alcohol temperature until the solutions solidified. The ampules were evacuated at 0.4–1.5 Torr, filled with nitrogen gas, and then warmed to room temperature. This process was repeated three times. After cooling and evacuation, the tubes were sealed and one was reserved for the analysis of the unreacted starting materials. The remainder were placed horizontally just below the surface of a mineral oil constant temperature bath maintained at 70.0 ± 0.5 °C. The samples were irradiated with ultraviolet light provided by a Sylvania 275-W sun lamp placed 20 cm above the surface of the oil. Reaction times varied from 91.25 to 144.25 h, by which time 33.74–89.89% of the phenylacetonitriles had reacted. The ampules were then cooled and opened. Analysis of the mixtures, both before and after reaction, was carried out via GLC on either a 3% SE-30 on Varaport 30 or a 12% Carbowax 20M on Chromosorb P column. Conversion of raw data to relative rate expressions followed standard techniques.[20]

Registry No.—Bromotrichloromethane, 75-62-7.

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The Facile Oxidation of Phenacyl Bromides with *N,N*-Dialkylhydroxylamines

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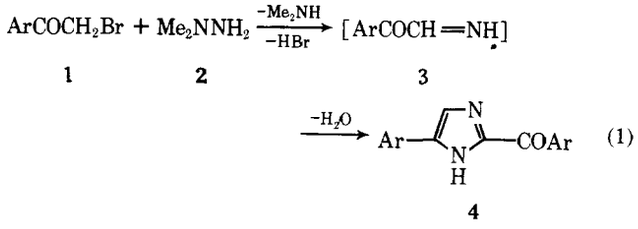
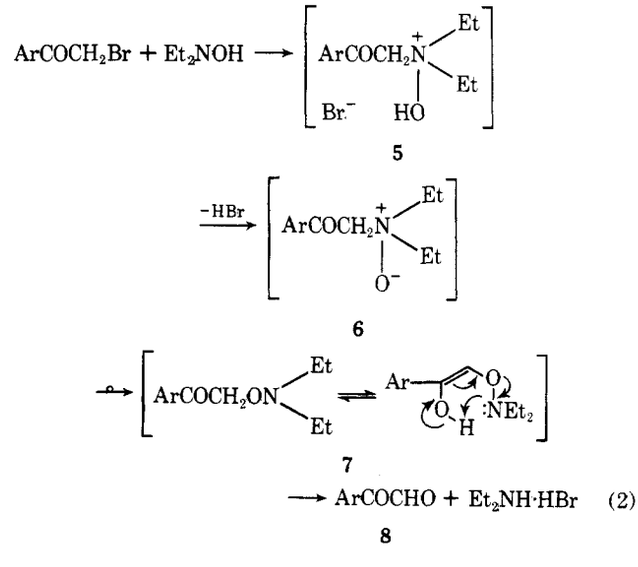
Semiionic compounds such as sulfoxides[1a,b] and amine *N*-oxides[1b–d] have been used to oxidize α-halocarbonyl compounds to α-dicarbonyl compounds. It has been shown recently that the reaction of phenacyl bromides (**1**) with 1,1-dimethylhydrazine resulted in the formation of arylglyoxaldimines (**3**) which then underwent further reactions.[2] Inas-



much as the net result of this reaction amounts to the conversion of the $-CH_2Br$ group to the $-CH{=}NH$ function, it was reasonable to anticipate that *N,N*-dialkylhydroxylamines might convert phenacyl bromides to the corresponding glyoxals. This note describes the results of our investigations of the reaction of phenacyl bromides with *N,N*-diethyl- and *N,N*-dibenzylhydroxylamines.

The reaction of phenacyl bromide with *N,N*-diethylhydroxylamine (DEHO) in methanol gave a 78% yield of phenylglyoxal as a thick, yellow-orange oil which slowly hydrated on standing, mp 90–91 °C, identical with an authentic sample.[3] Similarly, other phenacyl bromides were converted to the corresponding glyoxals in good to excellent yields (Table I), although no attempts were made to optimize the yields.

To our knowledge, this is the first report of the use of *N,N*-dialkylhydroxylamines as *oxidizing* agents for organic compounds,[4] which is to be contrasted with the recent disclosure of the *reduction* of *p*-benzoquinones to the corresponding hydroquinones with *N,N*-diethylhydroxylamine.[5] By analogy with the reaction of **1** with *N,N*-dimethylhydra-



† Taken from the B.A. Thesis of V. E. Gunn, University of Massachusetts at Boston, 1977.

Table I. Oxidation of Phenacyl Bromides with *N,N*-Dialkylhydroxylamine[a]

$ArCOCH_2Br$ (I), Ar	Registry no.	ArCOCHO (yield, %)[b]	Registry no.	Mp of hydrate (lit. mp), °C
Ph	70-11-1	78 (80)[c]	1074-12-0	90–91 (90)[d]
p-BrPh	99-73-0	68 (74)[c]	5195-29-9	119–122 (128–129)[e]
p-PhPh	135-73-9	90 (75)[c]	4974-58-7	113–117 (117–121)[f]
m-MeOPh	5000-65-7	55	32025-65-3	99–100 (98–101)[g]
β-Naphthyl[h]	613-54-7	76	22115-06-6	93–96 (98)[d]

[a] All reactions were carried out in methanol at reflux for 2 h, except as otherwise noted. [b] As the glyoxal hydrates. [c] Yields with *N,N*-dibenzylhydroxylamine, *without* distillation. [d] "Heilbron's Dictionary of Organic Compounds". [e] G. A. Russel and G. J. Mikol, *J. Am. Chem. Soc.*, **88**, 5498 (1966). [f] F. Krohnke and E. Borner, *Ber.*, **69B**, 2006 (1936). [g] R. B. Moffett, B. T. Tiffany, B. D. Aspergren, and R. V. Heinzelman, *J. Am. Chem. Soc.*, **79**, 1687 (1957). [h] Reaction time: 8 h.

zine, one can postulate the initial formation of 1,1-diethyl-1-phenacylhydroxylammonium bromides (**5**)[2,4a] followed by a Meisenheimer rearrangement[6] of the amine *N*-oxides (**6**) to the *O*-phenacylhydroxylamines (**7**).[7] These latter intermediates could then fragment to the arylglyoxals and diethylamine, which was isolated as its hydrobromide salt in each case in nearly quantitative yields. Extension of this oxidation to other α-halo carbonyls has so far been less successful. Although benzil was obtained from the reaction of desyl chloride and DEHO, albeit in only 25% yield, so far only complex products and recovered starting materials have been obtained with 2-chlorocyclohexanone and α-bromopropiophenone. In the case of benzil, a control experiment clearly indicated that *N,N*-diethylhydroxylamine reacted further with benzil to give less than 30% of recovered benzil; no definite product has yet been isolated from the dark residue of this reaction.[8]

The Cope elimination is a competitive reaction when β hydrogens are available in the amine *N*-oxides.[6,9] In order to investigate this possibility, the reaction of phenacyl bromide with *N,N*-dibenzylhydroxylamine[10] was carried out. The reaction proceeded much more slowly (an orangy color develops almost immediately after mixing phenacyl bromide with DEHO) and a longer reflux period had to be used for the reactions to take place. Although the yields of arylglyoxals were not substantially different (see Table I), the undistilled products in these cases were nearly as pure as those obtained with DEHO *after* the distillation. This suggests that the Cope elimination, though not a major problem, may be occurring to a small extent, thus explaining the lesser purity of the products obtained with DEHO.

Thus, the reaction of *N,N*-diethylhydroxylamine with phenacyl bromide offers a useful and mild "nonoxidative" route to arylglyoxals. We are at present investigating the scope and mechanism of this reaction, with particular attention to the possible intervention of radicals in the putative Meisenheimer rearrangement.

Experimental Section

All melting points are uncorrected. *N,N*-Diethylhydroxylamine was obtained from Pennwalt Corp. and was distilled prior to use. *N,N*-Dibenzylhydroxylamine was prepared according to a published procedure.[10] The phenacyl bromides were used as purchased or prepared according to literature directions.

Oxidation of Phenacyl Bromides with *N,N*-Dialkylhydroxylamines. A. With *N,N*-Diethylhydroxylamine. A solution of 8.56 g (0.043 mol) of phenacyl bromide and 3.83 g (0.043 mol) of *N,N*-diethylhydroxylamine in 80 ml of methanol was heated to reflux with stirring for 2 h. Evaporation of the solvent followed by addition of 75 ml of ether to the residue precipitated diethylamine hydrobromide, mp 203–206 °C dec (lit.[11] mp 205 °C), in nearly quantitative yield. Evaporation of the ethereal solution left a residue which was distilled in vacuo to yield 4.5 g (78%) of phenylglyoxal. The other glyoxals reported in Table I were obtained by the same procedure.

B. With *N,N*-Dibenzylhydroxylamine. A solution of 5.00 g (0.025 mol) of phenacyl bromide and 5.33 g (0.025 mol) of *N,N*-dibenzylhydroxylamine in 80 ml of methanol was heated to reflux with stirring for 48 h. Evaporation of the solvent followed by addition of 80 ml of ether to the residue precipitated 5.31 g (76%) of dibenzylamine hydrobromide, mp 262–265 °C (lit.[12] mp 266 °C). Evaporation of the ethereal solution left a residue whose infrared spectrum matched that of the distilled compound above. The other glyoxals reported in Table I were obtained by the same procedure.

Acknowledgment. It is a pleasure to acknowledge generous gifts of *N,N*-diethylhydroxylamine from Mr. L. Gilette of the Pennwalt Co., Philadelphia, Pa.

Registry No.—*N,N*-Diethylhydroxylamine, 3710-84-7; *N,N*-dibenzylhydroxylamine, 621-07-8; dibenzylamine hydrobromide, 103-49-1.

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Heterocyclic Derivatives Formed from 2-Alkoxyimino Aldehydes and 1,2-Disubstituted Ethanes

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The preparation of 2-alkoxyimino aldehydes, **1**, by selenium dioxide oxidation of alkoxyiminoalkanes[1] provided a functional group adjacent to an oxime which was susceptible to derivatization by nucleophilic reagents.[2] Derivatization of the aldehyde moiety with molecules containing two nucleophilic

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