of 2-oxazoline (**3b**), bp 110–111° (0.01 mm). A second distillation gave an analytically pure sample: nmr (DMSO-d_6) δ 7.01 (m, 4 H), 4.35 (quartet, 2 H), 2.23 (s, 3 H), 1.87 (quartet, 4 H), 1.27 (t, 3 H), 0.85 (t, 6 H). *Anal.* Calcd for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08; N, 10.21; mol wt, 274.4. Found: C, 70.30; H, 8.13; N, 9.97; mol wt, 280.

Isolation of 4-*N*-(*p*-Tolyl)imino-2-oxazolidinone (4a and 4b).—A 1.0-g sample of **3a** (4.06 mmol) was placed in 20 ml of acetone and 1 ml of 3 *N* acetic acid was added. Water was added until the liquid **3a** began to separate. After 3 hr at room temperature, the mixture was filtered with suction and washed with water. After air drying, 0.7 g of crystalline material was collected. Further addition of water to the filtrate, followed by filtration, gave another 0.1 g of crystalline material. Infrared analysis indicated that both samples were identical. One recrystallization from petroleum ether–THF gave an analytically pure **4a**: mp 231–232.5°; nmr (DMSO-d_6) δ 7.45 (m, 4 H), 2.28 (s, 3 H), 1.57 (s, 6 H), 10.40 (broad s, 1 H). *Anal.* Calcd for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84; mol wt, 218.3. Found: C, 66.06; H, 6.38; N, 12.76; mol wt, 218.

The same procedure produced **4b**: mp 246–247.5°; uv max (100% C_2H_5OH) 268 mμ (ϵ −16,900); ir (KBr) 1730, 1630, 1575, and 3297 cm^{-1} (NH); nmr (DMSO-d_6) δ 7.42 (m, 4 H), 2.27 (s, 3 H), 1.95 (quartet, 4 H), 0.74 (t, 6 H), 10.34 (broad s, 1 H, disappeared upon addition of D_2O). *Anal.* Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.36; 11.37; mol wt, 246. Found: C, 68.46; H, 7.44; N, 11.21; mol wt, 245.

Compound **4b** was also isolated by column chromatography of the initial crude reaction product **3b**. A sample of 0.9 g of the crude reaction product was chromatographed on 60 g of neutral alumina. The column was developed with the following order of solvents: 350 ml of hexane, 300 ml of petroleum ether, 150 ml of 50% petroleum ether–ether, 300 ml of ether, 100 ml of 50% ether–THF, 200 ml of THF, and 200 ml of ethanol. A total of 0.6 g of **4b** was isolated from the THF and ethanol elutions.

Attempted Photolytic Preparation of 2-Oxazoline (3b).—Photolysis of an equal molar solution of ethylazidoformate and diethylketene-*N*-(*p*-tolyl)imine in degassed methylene chloride solution (10%) was attempted. The experiment was conducted in a cylindrical glass vessel fitted with a quartz immersion well. A 200-W Hanovia high-pressure lamp constituted the light source and the solution was stirred with the aid of a magnetic stirrer. After 24 hr the solution was concentrated on a rotary evaporator. Distillation under vacuum gave 93% recovery of the starting ketenimine.

Acid Hydrolysis of 4a and 4b.—Acidic hydrolysis was completed upon reaction of 5.0 g of **4a** or **4b** in 20 ml of ethanol and 50 ml of concentrated hydrochloric acid at reflux for 10 hr. After the solution cooled to room temperature, it was concentrated to one-half its volume on a rotary evaporator at reduced pressure, and 10 ml of water was added. The solution was extracted four times with 30-ml portions of ether. The combined ethereal extracts were dried and concentrated. The material isolated (mp 75–76°) possessed carbonyl absorption at 1812 and 1730 cm^{-1} with the latter absorption more intense. The nmr spectrum of **5a** in benzene indicated no *p*-tolyl group was present, but only a singlet at δ 1.10 and a broad singlet at δ 7.95. Comparison of the ir, nmr, and mixture melting point with authentic 5,5-dimethyl-2,4-oxazolidinedione (mp 76–77°) verified the structural assignments. In the case of compound **5b**, the residue after ether extraction was distilled. The 5,5-diethyl-2,4-oxazolidinedione had bp 117–120° (1.5 mm) and mp 27° [lit.[8] 146–147° (6.0 mm), and 28°]; nmr (DMSO-d_6) δ 11.01 (broad s, 1 H), 1.80 (quartet, 4 H), 0.82 (t, 6 H).

The aqueous acidic layer was made strongly basic by the addition of 40% sodium hydroxide solution and extracted with ether. After drying and concentrating the ethereal extracts, *p*-toluidine was isolated. This was confirmed by mixture melting point and ir.

When hydrolysis was attempted using 6 *N* hydrochloric acid and 8 hr reflux, **4a** and **4b** were recovered. The ethereal extracts of the acidic and basic aqueous layers yielded only traces of material. The starting materials **4a** and **4b** were observed to be soluble in the strongly acidic and basic layers and precipitated upon neutralization of the aqueous solution.

Registry No.—**1**, 817-87-8; **2a**, 18779-86-7; **2b**, 26212-59-9; **3a**, 26212-60-2; **3b**, 26212-61-3; **4a**, 26212-62-4; **4b**, 26212-63-5.

The Oxidation of Alcohols with Phenyl *N*-Bromoketimine[1a]

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The use of phenyl *N*-bromoketimine (**1**) as a brominating agent similar to *N*-bromosuccinimide was reported a few years ago.[2] We wish now to report the results of a study of the use of this compound as a reagent for the oxidation of alcohols to aldehydes or ketones.

A number of *N*-halo compounds such as *N*-haloamides,[3] *N*-haloimides,[4] and *N*-halobenzotriazole[5] are known to effect the mild oxidation of alcohols to the corresponding carbonyl analogs usually with moderate to high yields. Compound **1** appears to be at least as effective as these other *N*-halo compounds. Experiments involving benzhydrol, benzyl alcohol, 1-phenylethanol, 2-propanol, 2-butanol, and cyclohexanol revealed rates of oxidation by **1** ranging from essentially quantitative conversion in a few minutes for the first three to 75% conversion in 450 min for cyclohexanol. All of these oxidations were carried out in benzene at reflux temperature under sunlamp irradiation, and the progress was conveniently followed by ir and glpc and weighing the imine hydrobromide salt as it was formed.

The oxidation of 1-phenylethanol was explored in some detail. The stoichiometry of this reaction was investigated by varying the ratio of **1** to alcohol over the range of 2:1, 1:1, 1:2, and 1:5. Analysis of the reaction mixtures showed the stoichiometry to always be 1 mol of **1** to 1 mol of alcohol. The reaction progress was found to be retarded or stopped by the addition of 5 mol % of quinone or chloranil, by using lower temperatures, or by excluding the sunlamp irradiation. Most significant is the observation that the addition of 2 mol % of norbornene as a bromine trap[6] completely inhibits the reaction. The results of this study of the effects of such variables on the oxidation of 1-phenylethanol are summarized in Table I. Furthermore, it was found that 1-phenylethanol is not converted to acetophenone under conditions of irradiation in benzene at reflux temperature in the absence of **1** but can be quantitatively oxidized under these conditions if molecular bromine is added in minute quantities at regular intervals until no more is consumed.

These observations suggest that the oxidation of alcohols by phenyl *N*-bromoketimine proceeds by a radical chain mechanism as shown below. This mechanism is similar to the ones proposed for the oxidation of alcohols by *N*-haloimides[7] and *N*-halobenzotriazole[5] in that the *N*-haloimine (**1**) is simply serving as a source of molecular halogen in low concentration throughout the re-

(1) (a) Taken from the Ph.D. Thesis of C. G. L., West Virginia University, 1970. (b) To whom inquiries should be addressed.
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TABLE I

OXIDATION OF 1-PHENYLETHANOL WITH PHENYL *N*-BROMOKETIMINE[a]

Alcohol, mmol	Bromoimine, mmol	Temp, °C	Inhibitor, mol %[b]	Yield of acetophenone, % (time)
0.49	0.98	80	None	94 (2 min)
0.49	0.98	80	Chloranil, 5	70 (2 min), 94 (4 min)
0.49	0.98	15	None	71 (15 min), 98 (30 min)
0.98	0.98	15	Chloranil, 5	41 (20 min), 80 (35 min)
0.49	0.98	15	Norbornene, 2	0 (80 min)
0.98	0.49	15	Light excluded	0 (30 min)
0.98	0.49	80	None	52[c]
2.45	0.49	80	None	21[c]

[a] All reactions were carried out in 3.0 ml of benzene at the indicated temperatures. Continuous stirring was accomplished with a magnetic stirring bar and except for the one experiment where light was excluded all reactions were under sunlamp irradiation, G.E. sunlamp at 6 in. [b] Based on bromoimine initially present. [c] Maximum accumulation of acetophenone. Yield is based on amount of alcohol initially present.

action. Evidence for the dissociation of **1** as shown in the first step and for its reaction with HBr as shown in the third step has been reported earlier.[2]

$$(C_6H_5)_2C{=}NBr \xrightarrow[\text{or } \Delta]{h\nu} (C_6H_5)_2C{=}N\cdot + Br\cdot$$

1

$$Br\cdot + {>}CHOH \longrightarrow \cdot{>}COH + HBr$$

$$HBr + \mathbf{1} \longrightarrow (C_6H_5)_2C{=}NH + Br_2$$

$$\cdot{>}COH + Br_2 \longrightarrow \begin{matrix} OH \\ | \\ C \\ | \\ Br \end{matrix} + Br\cdot$$

$$\begin{matrix} OH \\ | \\ C \\ | \\ Br \end{matrix} \longrightarrow {>}C{=}O + HBr$$

$$HBr + (C_6H_5)_2C{=}NH \longrightarrow (C_6H_5)_2C{=}NH_2^+\ Br^-\downarrow$$

Although the scope of possible oxidations with **1** has not been fully investigated, the results reported here suggest that this compound may be a very useful reagent for oxidations which need to be carried out under mild conditions. It offers certain advantages over other *N*-halo compounds in that it is extremely soluble in common organic solvents and it shows no tendency to add to olefins.[8]

Experimental Section[9]

Phenyl *N*-bromoketimine (1) was prepared from benzophenone imine hydrochloride and bromine in aqueous sodium carbonate solution.[10] The product thus obtained was crystalline, mp 34–35° (lit.[10] mp 37°), and shown to be 99.9% pure by titration for the active bromine.

Reactions of 1 with Alcohols.—All alcohols (benzhydrol, benzyl alcohol, 1-phenylethanol, 2-propanol, 2-butanol, and cyclohexanol) were purified by recrystallization or distillation prior to use and checked for the absence of the corresponding aldehyde or ketone by ir and glpc. All reactions were carried out in refluxing benzene using a 2:1 ratio of *N*-bromoimine to alcohol. The mixtures were stirred throughout the reaction and irradiated with a G.E. sun lamp from a distance of about 6 in. Aliquots were withdrawn at intervals and thermally quenched. Qualitative analyses of reaction progress were made by ir spectroscopy but quantitative analyses were made using glpc in the following manner. A series of standard solutions containing known amounts of starting alcohol and anticipated oxidation product was made up in benzene for each reaction. These solutions were then analyzed by glpc and peak area ratios were plotted against the concentration of oxidation product. The resulting working curves were used to determine percentage composition of reaction mixtures. Identification of peaks corresponding to the alcohols and oxidation product was accomplished by comparing the glpc retention volumes with the retention volumes of authentic samples on the same column.

This general procedure was used to acquire the results shown in Table I except the molar ratio of alcohol to imine was varied, the temperature was varied, and inhibitors were sometimes added.

Reaction of Bromine with 1-Phenylethanol.—A solution of 0.059 g (0.49 mmol) 1-phenylethanol in 3 ml of benzene was irradiated with a sun lamp while the temperature was maintained at 25–30°. Bromine was added at the rate of 1 drop every 15 sec until the pale yellow color produced by a drop of bromine did not disappear. At this point an aliquot of the mixture was withdrawn for analysis by glpc for percentage conversion of alcohol to ketone. The mixture was found to contain 0% alcohol and 100% acetophenone (based on initial alcohol concentration).

Registry No.—**1**, 7699-75-4; 1-phenylethanol, 98-85-1.

(8) C. G. McCarty and C. G. Leeper, unpublished results.

(9) Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer and a Beckman Model IR-8 spectrophotometer. A Micro-Tek GC-2503R gas chromatograph equipped with a Sargent GC recorder and Disc integrator was used for all glpc analyses.

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α-Lactams. VIII.[1,2] *O*-Alkylation of α-Lactams

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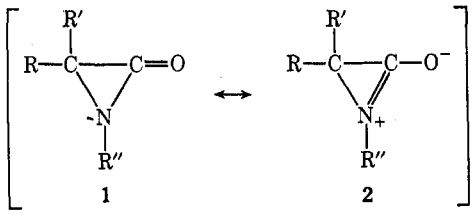
In an earlier report[4] on the photochemistry of α-lactams **1**, a dipolar resonance form **2** was proposed in



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