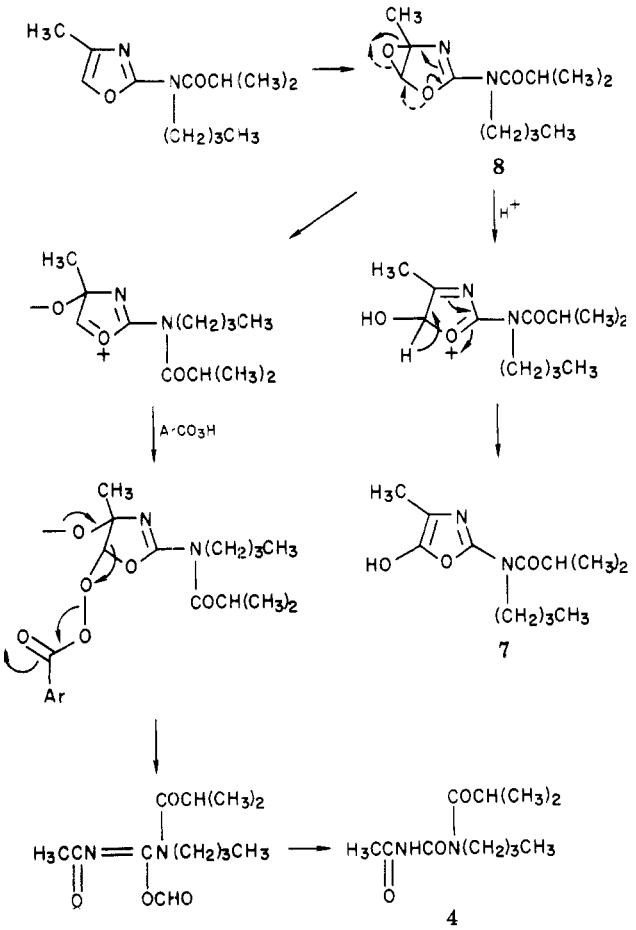
Scheme II



order to designate unambiguously the carbon atom responsible. 5-Ethoxy-4-methyl-2-isopropyloxazole was, therefore, synthesized,[9] and a signal at δ 112 in its ^{13}C spectrum attributed to C-4, the upfield shift being induced by the adjacent substituent. **7** is to our knowledge the first reported example of a 5-hydroxylated oxazole of this type. Our interest in this compound caused us to consider its direct chemical synthesis and, therefore, 1 was treated with excess *m*-chloroperbenzoic acid in dichloromethane. Two products were isolated. As anticipated one of these corresponded to the 5-hydroxy oxazole **7**, while surprisingly the second product was identified as the diacyl urea **4** previously isolated from singlet oxygen reaction. The formation of both of these products can be rationalized by rearrangement of the epoxide intermediate **8** as illustrated in Scheme II.

Experimental Section

Proton NMR spectra were determined on a Varian A-60A in $CDCl_3$ with Me_4Si as the internal standard. ^{13}C NMR spectra were obtained on a Bruker WH90 22.63-MHz instrument, infrared spectra on a Pye-Unicam SP 1000 spectrophotometer, and mass spectra on an LKB 9000. Methanol was distilled from calcium hydride prior to use, and oxygen was dried by passage through a Drierite column. Isamoxole was prepared as described.[1]

Photolysis of *N*-Butyl-*N*-(4-methyloxazol-2-yl)-2-methylpropanamide (1). A solution of **1** (1.2 g, 0.0535 mol) in dry methanol (600 mL) containing methylene blue (~5 mg) was photolyzed using a 150-W tungsten element lamp while passing dried oxygen through the stirred solution. After 60 h the solvent was removed in vacuo and the residue was distilled by bulb-to-bulb distillation at 150 °C (0.5 mm) to give a pale yellow oil (0.85 g). The major component (66% by GC) was identified as *N*-butylisobutyramide by comparison with an authentic sample. The minor component (22% by GC) was purified by chromatography on a Kieselgel preparative plate with elution by 5% methanol in chloroform to give pure **3**: IR (neat) 1690, 1670 cm^{-1}; MS *m/e* 242; ^1H NMR δ 2.1 (s, 3), 3.75 (s, 3).

Anal. Calcd for $C_{12}H_{22}N_2O_3$: C, 59.56; H, 9.16; N, 11.58. Found: C, 59.18; H, 8.93; N, 12.15.

N-Butyl-N-(5-hydroxy-4-methyloxazol-2-yl)-2-methylpropanamide (7). **1** (14.5 g, 0.065 mol) was heated at 70 °C in an open flask while passing air through a water bubbler into the reaction vessel. After 160 h, the resulting brown oil was eluted through a column of neutral alumina (400 g, Brockman grade 1) with 50% ethyl acetate–diethyl ether to remove unchanged starting material and with 10% methanol in ethyl acetate to yield **7** (3.1 g): IR (neat) 1765, 1720, 1680 cm^{-1}; MS *m/e* 240; ^1H NMR δ 2.39 (s, 3) ^{13}C NMR δ 117.7, 132.0, 154.5.

Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 60.06; H, 8.40; N, 11.67. Found: C, 59.83; H, 8.35; N, 11.71.

A sample of **7** in dry DMF was methylated using silver oxide–methyl iodide in the standard manner to yield the corresponding methyl ether: IR (neat) 1770 cm^{-1}; ^1H NMR δ 3.18 (s, 3), 1.99 (s, 3).

Anal. Calcd for $C_{13}H_{20}N_2O_3$: C, 61.47; H, 8.73; N, 11.03. Found: C, 61.64; H, 8.82; N, 11.31.

7 was acetylated using acetic anhydride in benzene at 80 °C to give an oily product: IR (neat) 1800 cm^{-1}; ^1H NMR δ 2.25 (s, 3), 2.62 (s, 3).

Reaction of 1 with *m*-Chloroperbenzoic Acid. **1** (15 g, 0.067 mol) in dichloromethane (100 mL) was stirred at 0 °C during the addition of *m*-chloroperbenzoic acid (16 g, 0.093 mol). Stirring was continued for 48 h at ambient temperature. The mixture was then filtered and most of the dichloromethane was removed in vacuo. The residue was taken into ether and stirred with 5% aqueous sodium bisulfite solution. The organic phase was washed with sodium bicarbonate solution and brine, and then dried and evaporated to leave an oil (13.9 g). This product (10 g) was taken into ether and washed with 1 N sodium hydroxide solution, and the aqueous phase was neutralized and back-extracted into ether. Washing of this ether phase with aqueous bicarbonate and water, drying, and evaporation gave an oil (4.07 g) identical with **7** as isolated in the previous experiment.

Nonacidic material was identified as a mixture of **1** and the acetyl urea **4**.

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Registry No. **1**, 57067-46-6; **2**, 6282-85-5; **3**, 71032-52-5; **4**, 71032-53-6; **7**, 57068-66-3; **7** acetate, 71032-54-7; **8**, 57068-97-0.

(9) Prepared from alanine ethyl carboxylate by reaction with isobutyric anhydride and cyclization of the resulting acyl derivative by refluxing in chloroform solution with phosphorus pentoxide.

A Novel Catalytic Effect of Tertiary Phosphine Oxides and Dichlorides for the Reaction of Chlorine with Carbon Monoxide. A Preparative Method of a Phosgene Solution

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Phosgene is a versatile reagent for organic syntheses.[1] Several methods for the preparation of phosgene have been known; they include the gas-phase reaction of chlorine with carbon monoxide on activated carbon, the decomposition of trichloromethyl chloroformate, and the reaction of carbon tetrachloride with oleum. This paper describes a

(1) H. Babad and A. G. Zeiler, *Chem. Rev.*, 73, 75 (1973).

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Table I. Preparation of Phosgene in Carbon Tetrachloride

catalyst	mol ratio cat./Cl_2	press of CO, atm	temp,[b] °C	time, min	yield[a] of $COCl_2$, %
$(n\text{-}C_4H_9)_3PO$ (1a)	1/50	60	rt	30	81
$(n\text{-}C_8H_{17})_3PO$ (1b)	1/57	60	rt	30	81
$(C_2H_5)_3PO$ (1c)	1/19	60	rt	40	69
$(C_6H_5)_3PO$ (1d)	1/50	60	rt	120	52
	0	60	rt	120	0
$(n\text{-}C_4H_9)_3PO$ (1a)	1/95	30	rt	135	96
	1/85	10	rt	195	80
	1/82	5	rt	360	84
	1/75	5	50	190	90

[a] Yields were based on chlorine, and the values are yields of *N,N'*-diphenylurea isolated in the treatment of the resultant phosgene solution with aniline and triethylamine and the subsequent separation of the products. [b] rt = room temperature.

catalytic effect of tertiary phosphine oxides and dichlorides for the reaction of chlorine and carbon monoxide in solution and a convenient preparative method of a phosgene solution, which is readily applicable even in the laboratory.

We recently reported the conversion of tertiary phosphine oxides (1) into tertiary phosphine dichlorides (2) by treatment with an equimolar amount of chlorine and pressurized carbon monoxide in carbon tetrachloride.[2] It is known that the reaction of 1 with phosgene gives 2,[3] but the formation of phosgene was not observed in a treatment of a solution of chlorine with carbon monoxide in the absence of 1 under the same conditions as in the transformation of 1 into 2.

We found that a catalytic amount of 1 promoted the reaction of chlorine with carbon monoxide in solution.

When a solution of chlorine in carbon tetrachloride was treated with pressurized carbon monoxide in the presence of a catalytic amount of tri-*n*-butylphosphine oxide (1a) at room temperature, an exothermic reaction occurred, giving phosgene as a solute in the solvent.

Tri-*n*-octylphosphine oxide (1b) also catalyzed the reaction for the production of phosgene, but triethylphosphine oxide (1c) and triphenylphosphine oxide (1d) were not so effective. The reaction rate depends remarkably on the kind of 1. Several experimental results are shown in Table I.

Since 1 is readily transformed into the corresponding 2 in the reaction system,[2] the reaction for the production of phosgene is catalyzed apparently by 2. 2 did not react with carbon monoxide in the absence of chlorine under the conditions applied for the phosgene formation.[4] In view of these facts, 2 seems to be not an intermediate but a catalyst.

The mechanism of these catalyses is not yet clear, but the catalytic effect is valuable since the quantitative conversion of chlorine into phosgene in solution became possible under mild conditions by the use of the catalyst 1.

Tetrachloroethane and *o*-dichlorobenzene could be used as the solvent in place of carbon tetrachloride.

The present preparative method of phosgene solution is very useful and has the following merits: (1) handling of highly toxic phosgene in the gaseous state can be avoided, since the greatest use of the reagent is done in solution, and (2) storage of highly toxic gas can be excluded, since the reagent can be produced only in a requisite amount just before use.

(2) M. Masaki and N. Kakeya, *Angew. Chem., Int. Ed. Engl.*, **16**, 552 (1977).

(3) G. Wunsch, K. Winterberger, and H. Geierhaas, *Z. Anorg. Allg. Chem.*, **369**, 33 (1966).

(4) The reaction of tertiary phosphine with phosgene is known to give 2 quantitatively: R. Appel, B. Blaser, and G. Siegemund, *Z. Anorg. Allg. Chem.*, **363**, 176 (1968).

Experimental Section

General Procedure for the Preparation of Phosgene. In an autoclave was placed a glass vessel containing a solution of 1a (0.72 g, 3.30 mmol) and chlorine (17.55 g, 247.53 mmol) in carbon tetrachloride (250 mL). The autoclave was pressurized with carbon monoxide to 5 kg/cm^2. The reaction mixture was stirred with a Teflon wing at 50 °C for 190 min, during which the pressure was maintained around 5 kg/cm^2 by intermittently supplying carbon monoxide. The autoclave was cooled to room temperature and then was brought to ordinary pressure. A colorless clear solution containing phosgene was obtained in the glass vessel. In order to determine the phosgene content, a solution of aniline (13.90 g, 149.24 mmol) and triethylamine (15.10 g, 149.18 mmol) in carbon tetrachloride (50 mL) was added to a portion (107.10 g) of the resultant solution (843.14 g) at 0 °C.

N,N'-Diphenylurea (5.99 g, 28.22 mmol) was separated from the resultant mixture by filtering followed by washing the collected crystalline product with water. The yield of *N,N'*-diphenylurea was 90%. This fact shows that the yield of phosgene in the solution obtained in the glass vessel was at least 90%.

Registry No. 1a, 814-29-9; 1b, 78-50-2; 1c, 597-50-2; 1d, 791-28-6; phosgene, 75-44-5; carbon monoxide, 630-08-0; chlorine, 7782-50-5.

Electronic Effects Exerted in the Thermolysis of 2-Oxetanone: Hammett Studies of the 3-Aryl and 4-Aryl Derivatives

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In spite of the widespread interest in the mechanism of the 2-oxetanone thermolysis,[1] only scanty reports describing the quantitative investigations of such reactions are available.[1b,e] As a result, the electronic effects exerted by the substituent at the C-3 or C-4 position have not yet been clarified.[2] Qualitatively, however, it has been fre-

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(2) Qualitatively, it has been stated that electron-withdrawing substituent(s) at either C-3 or C-4 stabilizes the 2-oxetanones.[1c]

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