26305-81-7; **10b**, 26305-82-8; **10c**, 26305-83-9; **10d**, 26305-84-0.

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Reaction of Ethyl Azidoformate with Dimethyl- and Diethylketen-*N*-(*p*-tolyl)imine

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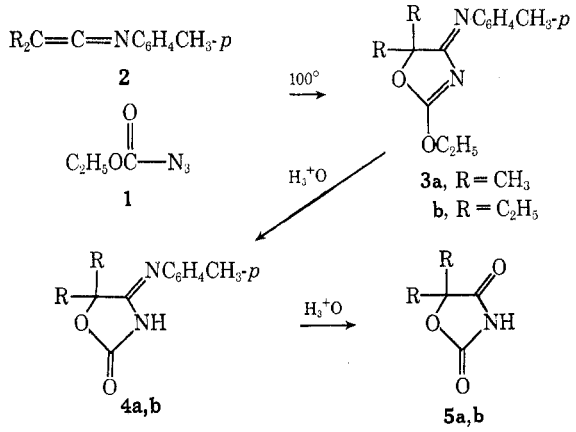
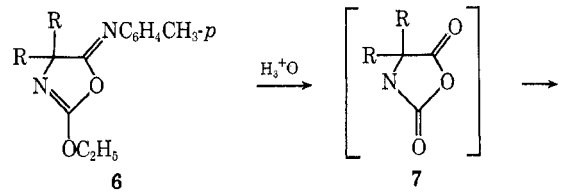
The formation of heterocyclic ring systems from cycloaddition reactions of ketenimines has recently received attention.[1,2] Since detailed studies on carbethoxynitrene from ethyl azidoformate have been reported,[3,4] and a variety of methods for preparing ketenimines are available,[5-7] the previously unreported cycloaddition reaction of ethyl azidoformate with two ketenimines was investigated. Reaction occurred under thermal but not photolytic conditions.

Thermolysis of a mixture of ethyl azidoformate (**1**) and ketenimines (**2a** or **2b**) at 100° led to the formation of the corresponding 4-*N*-(*p*-tolyl)imino-2-ethoxy-2-oxazolines (**3**) in 70% yields. The products were isolated by distillation at 0.01 mm; analyses and spectral data were consistent with structure **3**.



Mild acid hydrolysis of the adducts **3a,b** gave the tautomeric oxazolidinones **4a,b**; the latter compounds were isolated directly when the crude thermolysis products were chromatographed on neutral alumina. Vigorous acid hydrolysis of **4a,b** gave 5,5-dimethyl-2,4-oxazolidindione (**5a**), identified by comparison with an authentic sample, and 5,5-diethyl-2,4-oxazolidindione (**5b**), identified by comparison of spectral and physical data reported in the literature.[8] This hydrolytic sequence establishes the 4-imino structure **3** of the adducts as opposed to the alternate 5-imino oxazolidinones (**6**). Hydrolysis of the latter would lead to the 2,5-oxazolidinediones (**7**) which are unstable under the conditions used and would be subject to further degradation.[9]



6 **7**

The formation of the adducts **3** suggests that the adducts may arise by rearrangement of an acyltriazoline or aziridine. In view of the polarity of a ketenimine, cycloaddition of singlet carbethoxynitrene would be expected to give **6** rather than **3**.

Experimental Section

Melting points are uncorrected. Elemental analyses and molecular weight determinations were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared absorption spectra were obtained with a Perkin-Elmer spectrophotometer, Model 337. The nmr spectra were determined on a JOEL Company 100 Mc nmr. Chemical shifts are given in δ (ppm) downfield from TMS as an internal standard. The uv spectra were run on a Beckman DK-2A spectrophotometer. Ethyl azidoformate was prepared and purified as previously reported.[3] The 5,5-dimethyl-2,4-oxazolidinedione was purchased from Chemical Procurement Laboratories, Inc.

Preparation of Dimethyl- and Diethylketene-*N*-(*p*-tolyl)imine (2a, 2b).—The ketenimines (**2**) were prepared according to the method of Stevens and French[5] from the corresponding imidoyl chlorides in 65% yields. Proof of structure was accomplished by ir, nmr, and hydrolysis to the corresponding amides. Dimethylketene-*N*-(*p*-tolyl)imine (**2a**) had a bp of 63–65° (0.05 mm) [lit.[5] 64–65° (0.05 mm)]: nmr (neat) δ 7.03 (m, 4 H), 2.18 (s, 3 H), 1.61 (s, 6 H). Diethylketene-*N*-(*p*-tolyl)imine (**2b**) had a bp of 62–64° (0.01 mm): nmr (neat) δ 7.07 (m, 4 H), 2.19 (s, 3 H), 1.97 (quartet, 4 H), 1.01 (t, 6 H).

Preparation of 2-Oxazolines (3a and 3b).—A mixture of ethyl azidoformate (5.5 g, 0.047 mol) and dimethylketene-*N*-(*p*-tolyl)imine (8.05 g, 0.047 mol) was placed in an oil bath at 100 ± 1°. The mixture was stirred, and after 24 hr, it was cooled to room temperature. Distillation *in vacuo* gave 8.2 g (70%) of light yellow liquid, bp 103–104° (0.01 mm). This material was placed in a refrigerator and after 4 hr it solidified. The solid was low melting and could not be recrystallized. A second distillation gave an analytical sample of the 2-oxazoline (**3a**): uv max (cyclohexane) 283 mμ (ϵ −9530) and conjugated aromatic band 207 mμ (ϵ −13,000); ir (neat) 1710 (C=N exocyclic) and 1675 (C=N cyclic); nmr (DMSO-d_6) δ 7.04 (m, 4 H), 4.35 (quartet, 2 H), 2.24 (s, 3 H), 1.53 (s, 6 H), 1.27 (t, 3 H). *Anal.* Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.36; N, 11.37. Found: C, 68.16; H, 7.10; N, 11.10.

The procedure was repeated for the reaction with diethylketene-*N*-(*p*-tolyl)imine. Distillation *in vacuo* gave a 70% yield

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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-

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