1,1,1′,1′-tetraphenyldimethylamine (349 mg, 1.00 mmol) under the conditions described above resulted in a confirmation of the produce identity and yields described by a previous researcher[1] except for the isolation of biphenyl in 9% yield. It was necessary to separate biphenyl and diphenylmethane by preparative GLC (10% OV-1 on 80/100 mesh Chromosorb W at 170°).

Vycor-Filtered Irradiation of Bis(diphenylmethyl) Sulfide (4). Irradiation of bis(diphenylmethyl) sulfide[4] (366 mg, 1.00 mmol) for 0.25 hr was conducted under the conditions described above. Fractions 18–20 produced 102 mg (0.31 mmol, 44%) of 1,1,2,2-tetraphenylethane (7), identified by NMR and melting point comparison with an authentic sample. Fractions 21–28 afforded a mixture of two compounds which upon rechromatography in the manner described above gave in fractions 21–22 110 mg of unreacted starting material and in fractions 23–25 31 mg (0.10 mmol, 14%) of bis(diphenylmethyl) disulfide.[13]

Quantum Yield Determinations and Quenching Experiments. The apparatus and procedures used in conducting these experiments have been previously described.[2a] The quantum yields are recorded in Table I. The results of the quenching experiments are plotted in Figure 1.

Acknowledgment. The authors wish to thank Drs. T. W. Flechtner and A. H. Andrist for their helpful discussion of this work.

Registry No.—**1**, 5350-71-0; **2**, 36171-50-3; **3**, 574-42-5; **4**, 1726-03-0; **7**, 632-50-8; **8**, 92-52-4; **9**, 17953-97-8; **10**, 100-52-7; **11**, 55520-57-5; **12**, 1439-07-2; bis(diphenylmethyl) disulfide, 27080-90-6.

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(6) See ref 2 for the definition of the π-interaction reaction.
(7) Percent yields may exceed a total of 100 since reaction can cleave **3** into two compounds.
(8) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966), have found that photolysis of stilbene oxide in methanol gives benzyl methyl ether in high yield.
(9) This fact has been described previously for irradiation of **2** in methanol.
(10) The following ranges for bond-energy values (kilocalories per mole) have been assembled by J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N.Y., 1968, p 26: C–O, 85–91; C–C, 83–85; C–N, 69–75; C–S, 66.
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Reactions of Dichloroketene with 2-Protio- and 2-Methyl-Δ^2-oxazolines

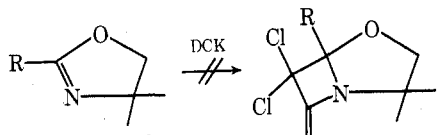
Peter Y. Johnson* and John W. Caldwell

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Received March 21, 1975

Recent reports on the syntheses of active[1] β-lactam-containing antibiotics in which the ring sulfur had been replaced by oxygen,[1,2] together with the interest[3,4] in azetidine-2,3-dione modifications of penicillins as synthons for other β-lactam-containing systems, prompt us to report our approach toward molecules containing both structural features.

In a previous study,[5] we showed that the reaction of dichloroketene[6] (DCK) with 2-aryl-Δ^2-oxazolines (1) did not form the desired azetidinone **2** (R = aryl) as is generally the case when dichloroketene is treated with acyclic imines,[7] but rather formed 2:1 ketene:oxazoline adducts.



1, R = aryl
3a, R = CH_3
3b, R = H

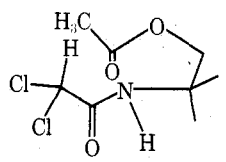
2

In these studies, it was postulated that the initially formed zwitterionic adducts were stabilized via charge delocalization due to the aromatic substituents at the 2 position,[7] and hence discouraged from ring closure to give β-lactam-containing products, but not from further reaction with the dichloroketene. In order to prevent delocalized zwitterion formation, thus hopefully encouraging β-lactam formation, the reactions of dichloroketene with 2-methyl and 2-protio oxazolines were studied.

Results

Monoaddition of dichloroketene to 2,4,4-trimethyloxazoline (**3a**) was attempted using three methods of reaction. The first method involved formation of the ketene via dehydrohalogenation of dichloroacetyl chloride with triethylamine[6b] in dry ether at −78° followed by addition of the oxazoline. The second method, which entailed formation of the ketene in the presence of the oxazoline, was accomplished by the addition of the acid chloride to a cool solution of oxazoline containing triethylamine. The third mode of reaction involved formation of the ketene in the presence of the oxazoline via dehalogenation of trichloroacetyl chloride using zinc powder.[6a]

Reaction of **3a** by either method 1 or method 2 led to the same products, amido ester **4** and vinylogous amide **5** (and small amounts of diadduct **6**), but in ratios which varied greatly with the method used. While reaction of **3a** with preformed ketene resulted in formation of **4** and **5** in a 7:1 ratio, reaction of **3a** with ketene formed in situ gave **4** and **5** in a 1:4 ratio. The zinc procedure gave a poor (13%) yield of **5** as the only isolable product.



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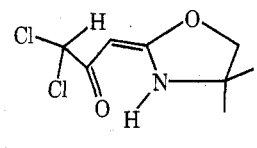

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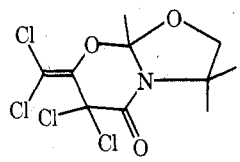
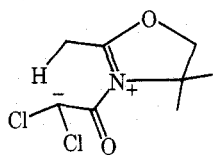
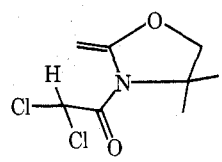


6

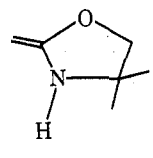
We feel that products **4** and **5** are formed by two pathways whose relative importance depends upon the experimental conditions. Pathway 1 would involve reaction of **3a** and preformed DCK to give a zwitterion[8] **7a**, which would be expected to undergo a rapid "ene" reaction[9,10] forming **7b**. Attempted isolation of **7b** by column chromatography



7a



7b



7c

gave hydrolysis product **4**. Attempted GLC isolation or distillation of **7b** after anhydrous removal of salts and in

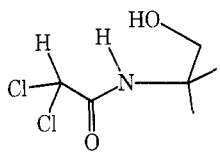
vacuo removal of solvent resulted in polymerization. ^{1}H NMR spectra of the crude reaction mixture, however, were compatible with a syn–anti mixture of **7b** (=CH_2, δ 5.8 → 6.1, 2 AB patterns). Addition of dichloroacetyl chloride to the mixture did not affect the olefinic portion of the ^{1}H NMR spectrum, indicating that **7b** was not reactive to further acylation under mild conditions. This is not surprising, as **7b** is an en*amide* and not an en*amine*.

Pathway 2, we believe, involves an equilibrium between imine **3a** and enamine **7c**[9-11] promoted by the excess base (triethylamine) and longer reaction times. Reaction of **7c** with either the acid chloride or DCK would give **5**. Attempts to methylate **5** on either nitrogen or carbon (enamine reaction) resulted in no reaction, supporting our view that **5** should be looked upon as a relatively unreactive vinylogous amide and not as an enamine. Our results do not rule out other possible mechanisms, however.

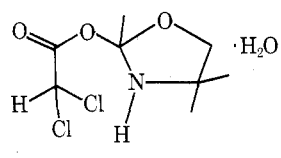
Compound **5** was identified on the basis of its spectral and analytical data, while **4** was synthesized via intermediate **8** (see Experimental Section).

The identification of the diadduct **6** was based on its spectral data. The mass spectrum of **6**, which shows a parent ion at *m/e* 333 containing four chlorine atoms, indicates a 2:1 stoichiometry. Comparison of the carbonyl portion of the ir spectrum of **6** (1725 cm^{-1}) with those of similar diadducts[5] strongly indicated the structure given. No attempt was made to further characterize **6**.

Dichloroacetic acid was found to react with **3a** to give the ether-soluble adduct **9**[10] in nearly quantitative yield.



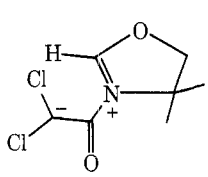
8



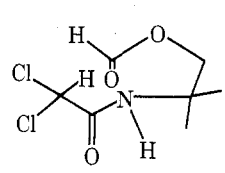
9

The presence of **9** in a few of the reaction mixtures was taken as evidence that totally anhydrous conditions had not been realized, and such runs were ignored.

Reaction of dichloroketene with 4,4-dimethyloxazoline (**3b**) would be expected to proceed via N-acylation of the substrate to give zwitterion **10**.[8] Adduct **10** is apparently stable and closure to β-lactam **2** (R = H) was not observed, but rather amido ester **11** was isolated upon work-up followed by chromatography. Longer reaction times, higher temperatures, and varying solvents did not alter the course of this reaction.



10



11

That zwitterionic intermediates of type **10** (and **7a**) were involved in this reaction was demonstrated by reducing **10** with sodium borohydride followed by mild hydrolysis[9] to yield the previously formed amido alcohol **8** which could be formylated to yield **11** or acetylated to yield **4**. Compound **11** was shown not to revert to **8** under the conditions used for the work-up of the $NaBH_4$ reduction reaction.

Experimental Section

Melting points were taken with a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 grating instrument, while ^{1}H NMR data were collected on a Jeol MH-100 spectrometer utilizing Me_4Si as internal standard. Mass spectra were taken with a Hitachi RMU 6-D mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Flame-dried glassware and nitrogen atmospheres were used for all reactions involving dichloroketene.

2,4,4-Trimethyloxazoline (**3a**) and 4,4-dimethyloxazoline (**3b**) were prepared by the method of Allen and Ginos[12] but were observed to codistill with water. Distillation from sodium hydride into dried containers provided dry material which could be kept for several weeks in a desiccator.

Reaction of 3a with Dichloroketene. Method 1. Freshly distilled dichloroacetyl chloride (1.47 g, 0.01 mol) dissolved in dry ether was dripped slowly into a solution containing 1 equiv of freshly distilled triethylamine in ether at −78°. The immediate appearance of triethylamine hydrochloride indicated the formation of dichloroketene. After the mixture was allowed to stir for 30 min at −78°, 1.13 g (0.01 mol) of freshly dried oxazoline **3a** was added to it over a period of 30 min. The mixture was warmed to 25° and allowed to stir for 1–4 hr. Vacuum filtration of the slurry followed by evaporation of the solvent in vacuo resulted in the isolation of a yellow oil which, when chromatographed on silicic acid (hexane–ether eluent), gave **4** (60–80%), **5** (5–15%), and **6** (2–5%).

Method 2. Freshly distilled dichloroacetyl chloride (1.47 g, 0.01 mol) in dry ether was added to a stirred solution of 0.01 mol each of dry oxazoline and triethylamine at −78°. The immediate formation of a white precipitate was observed. The mixture was stirred at −78° for 1 hr, warmed at 25°, and allowed to stir for another 1–48 hr. The solid was removed via vacuum filtration and the filtrate was concentrated in vacuo to yield a pale yellow oil which, when chromatographed on silicic acid, alumina (acidic or basic), or Florisil (hexane–ether eluent), provided **4** (10–20%), **5** (55–65%), and **6** (3–5%).

Method 3. To 50 ml of dry ether under nitrogen was added 1.13 g (0.01 mol) of freshly dried oxazoline and 1.5 g of finely powdered zinc. Freshly distilled trichloroacetyl chloride (1.13 g, 0.01 mol) was added to the mixture with vigorous stirring over a period of 3 hr. After 12 hr of further stirring at 25°, the dark mixture was vacuum filtered and concentrated in vacuo to give a tarry oil. Chromatography on Florisil (hexane–ether eluent) provided **5** (13%) as the only isolated product.

For 6: mp 128°; ir (CCl_4) 2995, 1725, 1380, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3), 1.56 (s, 3), 1.76 (s, 3), 3.90 (AB, 2); mass spectrum (70 eV) *m/e* 333 (parent, 4 Cl), 298 (3 Cl), 270 (3 Cl), 262 (3 Cl), 223 (2 Cl).

For 5: mp 123°; ir (CCl_4) 3300, 2990, 1639, 1545, 1390, 1370 and 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 6), 4.08 (s, 2), 5.14 (s, 1), 5.70 (s, 1); mass spectrum (70 eV) *m/e* 223 (parent, 2 Cl), 208 (2 Cl), 140, 72.

Anal. Calcd for $C_8H_{11}NO_2Cl_2$: C, 42.89; H, 4.91. Found: C, 43.05; H, 4.91.

Reaction of 3b with Dichloroketene. Methods 1 and 2 described above were utilized substituting **3b** for **3a** and giving after work-up **11** as a semisolid in yields from 70 to 90%.

Synthesis of Dichloroacetamido-2-methylpropanol (8). Alcohol **8** was synthesized in 80% yield from 2-amino-2-methylpropanol and dichloroacetyl chloride using Schotten–Baumann conditions. For **8:** mp 125–125.5°; ir ($CHCl_3$) 3420, 2995, 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 6), 2.96 (s, 1, Br), 3.62 (s, 2), 5.76 (s, 1) 6.54 (s, 1, Br).

Synthesis of 2-Dichloroacetamido-2-methylpropanol Acetate Ester (4). Compound **4** was synthesized by acetylation of alcohol **8** with 1.2 equiv of acetic anhydride in pyridine. Acid–base work-up gave a pale yellow oil which solidified upon standing to give **4** in 80% yield.

For **4:** mp 81–82°; ir (CCl_4) 3440, 3380, 2995, 1752, 1711, 1520, 1378, 1240, and 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 6), 2.04 (s, 3), 4.12 (AB, 2, J = <1 Hz), 5.72 (s, 1), 6.5 (s, 1, broad); mass spectrum (70 eV) *m/e* 241 (parent, 2 Cl), 184 (2 Cl), 168 (2 Cl), 116, 72.

Anal. Calcd for $C_8H_{13}Cl_2NO_3$: C, 39.70; H, 5.38. Found: C, 39.85; H, 5.26.

Synthesis of 2-Dichloroacetamido-2-methylpropanol Formate Ester (11). A solution of formic–acetic anhydride[13] was prepared by adding 0.02 mol of acetic anhydride to 50 ml of 88% formic acid. To this mixture was added 0.01 mol of alcohol **8** in formic acid. After stirring for 1 hr, the solution was added to an ice-cold carbonate solution, which was extracted with $CHCl_3$, dried, and evaporated in vacuo to give a residual oil which was found to be in excess of 95% **11** by ^{1}H NMR. This material could not be recrystallized in our hands and distillation resulted in an O to N formyl shift and decomposition.

For **11:** ir (CCl_4) 3420, 2985, 2940, 1780, 1720, 1540, 1155 cm^{-1};

^{1}H NMR ($CDCl_3$) δ 1.36 (s, 6), 4.28 (s, 2), 5.84 (s, 1), 6.60 (Br, 1), 8.10 (s, 1); mass spectrum (70 eV) *m/e* no parent ion, 181 (2 Cl), 168 (2 Cl), 116, 101, 72, 58.

Synthesis of 2-Dichloroacetoxy-2,4,4-trimethyloxazolidine (9) Monohydrate. Dichloroacetic acid (1.29 g, 0.01 mol) was added dropwise to 1.13 g (0.01 mol) of **3a** in ether to yield an initial precipitate which later dissolved. Concentration of the solution in vacuo produced a pale yellow oil which crystallized upon standing at 5°. Recrystallization with ether–hexane gave **9** monohydrate in 85% yield.

For **9** monohydrate: mp 110°; ir (CCl_4) 3000, 1755, 1680, 1390, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 6), 2.13 (s, 3), 4.12 (s, 2), 5.82 (s, 1), 7.6 (Br, 3); mass spectrum (70 eV) *m/e* no parent ion, 113, 98, 83, 70, 57.

Anal. Calcd for $C_8H_{15}Cl_2NO_4$: C, 36.94; H, 5.81; Cl, 27.26; N, 5.38. Found: C, 37.05; H, 5.84; Cl, 27.43; N, 5.40.

Reduction of 10 by Borohydride. Zwitterion **10** was formed by reaction of dichloroketene and **3b** using either methods 1 or 2 described above and treated with a threefold excess of sodium borohydride. The resulting slurry was stirred for 3 days under nitrogen, quenched with ice water acidified to pH 5, and extracted with ether which was then dried (Na_2SO_4) and evaporated in vacuo to yield a pale yellow oil. The oil, when saturated with ether, produced 65% of a white, crystalline material shown to be amido alcohol **8**.

Some ester **11** resulting from incomplete reduction of **10** was also recovered. Compound **11** was shown not to be hydrolyzed to **8** under the work-up conditions employed.

Acknowledgment. We thank the National Institutes of Health (AI 10389) for support of this work.

Registry No.—**3a**, 1772-43-6; **3b**, 30093-99-3; **4**, 55428-39-2; **5**, 55428-40-5; **6**, 55428-41-6; **8**, 55428-42-7; **9**, 55428-43-8; **10**, 55428-44-9; **11**, 55428-45-0; dichloroacetyl chloride, 79-36-7; triethylamine, 121-44-8; dichloroketene, 4591-28-0; oxazoline, 504-77-8; 2-amino-2-methylpropanol, 124-68-5; formic–acetic anhydride, 2258-42-6; dichloroacetic acid, 79-43-6; sodium borohydride, 16940-66-2.

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Synthesis of 3,11-Dimethyl-2-nonacosanone, a Sex Pheromone of the German Cockroach

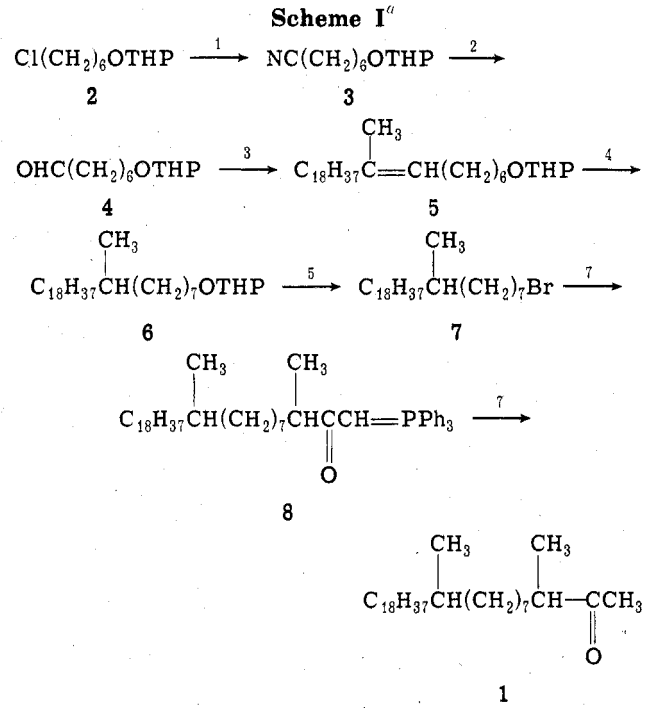
Meyer Schwarz,* James E. Oliver, and Philip E. Sonnet

Agricultural Environmental Quality Institute, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Maryland 20705

Received March 31, 1975

Recently Nishida et al.[1] reported the isolation of a sex pheromone of the German cockroach, *Blattella germanica* (L.), from its cuticular waxes. The compound was identified as 3,11-dimethyl-2-nonacosanone (**1**) with no information given concerning its absolute configuration. We wish to report a synthesis of the mixture of diastereomers of **1** as outlined in Scheme I.[2]

Scheme I[a]



[a] 1, NaCN–NaI–DMSO; 2, $Li(EtO)_2AlH_2$; 3, $C_{18}H_{37}C(CH_3)$=PPh_3; 4, H_2–Pd/C; 5, PPh_3Br_2; 6, $C_2H_5C(=O)CH=PPh_3$; 7, OH^-.

6-Chlorohexyl tetrahydro-2-pyranyl ether[3] **2** was converted to the corresponding cyanohexyl tetrahydropyranyl ether (**3**) with sodium cyanide in Me_2SO in the presence of a catalytic amount of sodium iodide. Reduction of **3** with lithium diethoxyhydroaluminate[4] yielded the corresponding aldehyde **4**. The Wittig reaction between **4** and (1-methylnonadecylidene)triphenylphosphorane (see Experimental Section) afforded presumably a cis and trans mixture of 8-methyl-7-hexacosenyl tetrahydropyranyl ethers (**5**) which was hydrogenated to compound **6**. Treatment of tetrahydropyranyl ether **6** with dibromotriphenylphosphorane[5] in methylene chloride gave 1-bromo-8-methylhexacosane (**7**) in excellent yield.[6] (2-Oxobutylidene)triphenylphosphorane,[7] prepared according to Cooke,[8] was converted to its anion by treatment with *n*-butyllithium and was alkylated with bromide **7**. Title compound **1**[9] was finally obtained by the hydrolysis of the crude alkylation product **8**. This extension of Cooke's procedure[8] thus represents a useful method for the preparation of α-branched methyl ketones.

Experimental Section[10]

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Ir spectra were obtained with CCl_4 solutions on a Perkin-Elmer Model 457A grating spectrophotometer. NMR spectra were obtained on a Varian Model T-60 spectrometer with tetramethylsilane (Me_4Si) as an internal standard. Reported chemical shifts are in δ, parts per million downfield from Me_4Si. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

6-Cyanohexyl Tetrahydropyranyl Ether (3). A heterogeneous mixture of 6-chlorohexyl tetrahydropyranyl ether[3] (50 g, 0.227 mol), NaCN (17.2 g, 0.35 mol), and NaI (4.5 g, 0.03 mol) in dry DMSO (50 ml) was stirred at ambient temperature for 16 hr. The mixture was diluted with water and extracted with petroleum ether. The organic phase was washed with H_2O (2 × 100 ml) and dried ($MgSO_4$). Concentration followed by distillation afforded 44.0 g (90%) of **3**: bp 105–115° (0.7 mm); $n^{25}D$ 1.4550; ir 2260 cm^{-1}; NMR δ 2.30 (m, 2, CH_2CN), 3.2–4.0 (m, 4, CH_2O), 4.47 (s, 1,