limed Mg (43.7 g, 1.80 mol) and 200 ml of purified Et_2O under argon were stirred while 348 g (1.46 mol) of **3b** in 800 ml of purified Et_2O was added at such a rate as to maintain reflux. The solution was stirred for 30 min after addition and then filtered. The Grignard solution was added slowly to 548 g (1.60 mol) of $HgBr_2$ in 200 ml of purified Et_2O and stirred overnight. (The slurry had the consistency of paste at this point.) The slurry was then poured into a large excess of H_2O and filtered, and the solid was air dried. The Et_2O filtrate was distilled, and the solid remaining was combined with the precipitate. The material was divided into two batches, and each was recrystallized from *ca.* 15 l. of benzene. The first crops were pure **4a**, mp 182.1–183.0° dec (sealed tube), and weighed 158 g (0.36 mol). The benzene solution was evaporated down in stages, taking various crops, and the final residue of 90 g was discarded. The last crops were recrystallized from EtOH to yield 130 g (0.226 mol) of impure **4b**, mp 109–111°. There was also isolated 158 g (0.360 mol) of additional impure **4a**. The total yield was 70% based on **3b**. *Anal.* Calcd for $C_{12}H_{15}HgBr$: C, 32.75; H, 3.44. Found: C, 32.47; H, 3.48.

***cis*-4-Phenylcyclohexylmercuric Bromide (4b).**—Impure **4b** from above was recrystallized from EtOH until the melting point was 120°. The material was then chromatographed using Woelm activity I neutral Al_2O_3 with Et_2O–benzene as eluent, followed by recrystallization from EtOH, mp 134.0–134.3°. *Anal.* Calcd for $C_{12}H_{15}HgBr$: C, 32.75; H, 3.44. Found: C, 32.71; H, 3.44.

***trans*-4-Phenylcyclohexyl Bromide (3a).**—After 132.2 g (0.301 mol) of **4a** was dissolved in 500 ml of pyridine, a solution of 15.5 ml (0.301 mol) of Br_2 in 100 ml of pyridine was added slowly with stirring over a 15-min period at 25° with cooling. The solution was cooled to 15° for 1 hr and then poured into a mixture of ice, 200 ml of pentane, and 1200 ml of 6 *N* HCl. The organic layer was separated, washed with $NaHSO_3$ solution, washed several times with H_2O, and dried over anhydrous $MgSO_4$. After removal of the pentane, 54.2 g (76% yield) was obtained. After recrystallization from pentane, the melting point was 62.8–63.2°, ν_{max} 687 cm^{-1} (C–Br), nmr δ 4.66 (m, =CBrH). *Anal.* Calcd for $C_{12}H_{15}Br$: C, 60.28; H, 6.32; Br, 33.40. Found: C, 60.04; H, 6.45; Br, 33.43.

Reaction of the Grignard Reagent Prepared from Pure *cis*-4-Phenylcyclohexyl Bromide (3b) with Mercuric Bromide.—**3b** (12.0 g, 0.0502 mol) in 40 ml of Et_2O was added slowly to just maintain reflux to 1.80 g (0.0741 mol) of sublimed Mg and 25 ml of Et_2O under N_2. The soln. was refluxed for 1 hr after addition. The Grignard formed in 69% yield. This solution was added to 22.6 g (0.0618 mol) of $HgBr_2$ in 50 ml of Et_2O. After the mixture was stirred for 20 hr, 40 ml of H_2O was added, and the precipitate was dissolved in benzene, washed with H_2O, dried, and filtered. After the volume of the filtrate was reduced to 75 ml, 5.28 g of **4a** was isolated and recrystallized, mp 182.5–184.0° dec. The impure residue, 5.6 g, was chromatographed over Woelm activity I neutral Al_2O_3 with Et_2O–benzene eluent. The combination of the latter fractions gave 1.22 g of **4b**, mp 133–134°. The total weight of 4-phenylcyclohexylmercuric bromide obtained from the Grignard reaction was 10.9 g (72%). **4b**, therefore, constituted 12% of the alkylmercuric bromide compounds formed.

Carbonation of the Grignard Reagent from *cis*-4-Phenylcyclohexyl Bromide (3b).—Sublimed Mg (0.35 g, 0.0144 mol) in 12 ml of purified Et_2O was refluxed and stirred under N_2, while 2.00 g (0.0084 mol) of **3b** in 22 ml of purified Et_2O was added slowly. The reaction mixture was refluxed for 1.75 hr and poured into an Et_2O–Dry Ice mixture. This mixture was acidified and CH_2Cl_2 was added. The organic layer was washed several times with H_2O and dried over anhydrous Na_2SO_4; the solvent was removed to give 1.59 g (93% yield) of the acids. The ir showed the mixture to be only carboxylic acids. After esterification with CH_2N_2, the ester mixture was analyzed by glc. **5a** was found to be 98.2% of the total methyl ester mixture. The glc retention time and the ir spectra of authentic samples corresponded with those obtained by the Grignard carbonation. Pure **5a** was obtained by recrystallization from pentane, mp 29–31°. The same Grignard formation and carbonation procedure using *trans*-4-phenylcyclohexyl bromide (**3a**) gave 99.8% **5a** after esterification followed by glc analyses.

***cis*-4-Cyclohexylcyclohexyl Bromide (6b).**—**7a** was obtained by the recrystallization of commercial 4-cyclohexylcyclohexanol from cyclohexane until the melting point was 103.8–104.2° (lit.[3] mp 103–104°).

To 4.00 g (0.022 mol) of **7a** was added 5.96 g (0.022 mol) PBr_3 at −40°. The solution was warmed slowly to room temperature and stirred for 3 days. The solution was then poured over ice-isopentane. (A large amount of phosphite ester was still present, indicating that the reaction had not gone to completion.) The yield was 1.81 g (35%), mp 29–32°. *Anal.* Calcd for $C_{12}H_{21}Br$: C, 58.87; H, 8.66. Found: C, 58.76; H, 8.61.

***trans*-4-Cyclohexylcyclohexyl Bromide (6a).**—**7b** was prepared by the reduction of 21.0 g (0.124 mol) of *p*-phenylphenol in 150 ml of HOAc with H_2 and Rh–Al_2O_3, at 50 psi and 70°. After H_2 absorption ceased, the solution was cooled and poured into H_2O. The precipitate was dissolved in CH_2Cl_2, washed with aqueous base, and dried over anhydrous $MgSO_4$ and the solvent was removed to yield 19.2 g (85%) of impure **7b**. A small amount of this alcohol was chromatographed over Woelm activity II neutral Al_2O_3 with pentane–Et_2O eluent, mp 94.0–94.5° (lit.[3] mp 92–93°).

To 1.05 g (0.0058 mol) of **7b** at −40° was added 1.60 g (0.0059 mol) of PBr_3 and the solution was stirred for 3 days at room temperature. The solution was poured into ice-pentane, washed with concentrated H_2SO_4 and H_2O, and then dried over anhydrous $MgSO_4$. After the solvent was removed, 0.49 g (0.0020 mol) of **6a** was obtained (35% yield). The material could not be crystallized at room temperature. *Anal.* Calcd for $C_{12}H_{21}Br$: C, 58.87; H, 8.66. Found: C, 59.17; H, 8.87.

Reduction of the *cis*- and *trans*-4-Phenylcyclohexyl Bromides (3b and 3a).—To 30 ml of HOAc were added 0.300 g (0.0013 mol) of **3a** and 0.088 g of PtO_2. The H_2 pressure was kept at 40 mm for 12 hr. The ir spectrum showed complete reduction of **3a** bromide, and was identical with that prepared using **7b**. The material could not be crystallized at room temperature, nmr δ 4.56 (m, =CBrH).

The same procedure was used with **3b**. The ir spectrum was identical with that of the cis bromide **6b** prepared from **7a** and the mixture melting point was not depressed. The yield was 54%, mp 33–34°, nmr δ 5.40 (s, =CBrH).

Summary of Nmr. Bromide-Substituted Carbon Methine Absorption for Cyclohexyl Bromides: *cis*-4-phenylcyclohexyl bromide (**3b**), 5.54 (s); *trans*-4-phenylcyclohexyl bromide (**3a**), 4.66 (m); *cis*-4-cyclohexylcyclohexyl bromide (**6b**), 5.40 (s); *trans*-4-cyclohexylcyclohexyl bromide (**6a**), 4.56 (m); axial methine in cyclohexyl bromide at −81°, 4.70[8] (m)[6]; equatorial methine in cyclohexyl bromide at −81°, 5.56[8] (s).[6]

Acknowledgment.—I wish to thank Professor F. R. Jensen for his guidance and support during the course of this research.

Registry No.—**2a**, 5769-13-1; **3a**, 42367-11-3; **3b**, 42367-12-4; **4a**, 42367-13-5; **4b**, 42367-14-6; **5a**, 36296-69-2; **6a**, 42367-15-7; **6b**, 42367-16-8; **7a**, 7335-42-4; **7b**, 7335-11-7.

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[8] A. J. Berlin and F. R. Jensen, *Chem. Ind.* (*London*), 998 (1960).

The Addition of Dichloroketene to 2-Aryl-Δ^2-oxazolines

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Dichloroketene formed by the *in situ* dehydrohalogenation of dichloroacetyl chloride[1] has been shown[2] to react with many Schiff bases to form α,α-dichloro-β-lactams. In our hands, however, many variations of this reaction with the substrate 4,4-dimethyl-2-phenyl-Δ^2-oxazoline (**1**) have not produced the desired oxygen-containing penicillin-like lactam, **4**, but rather a 2:1 ketene diadduct, **3**.

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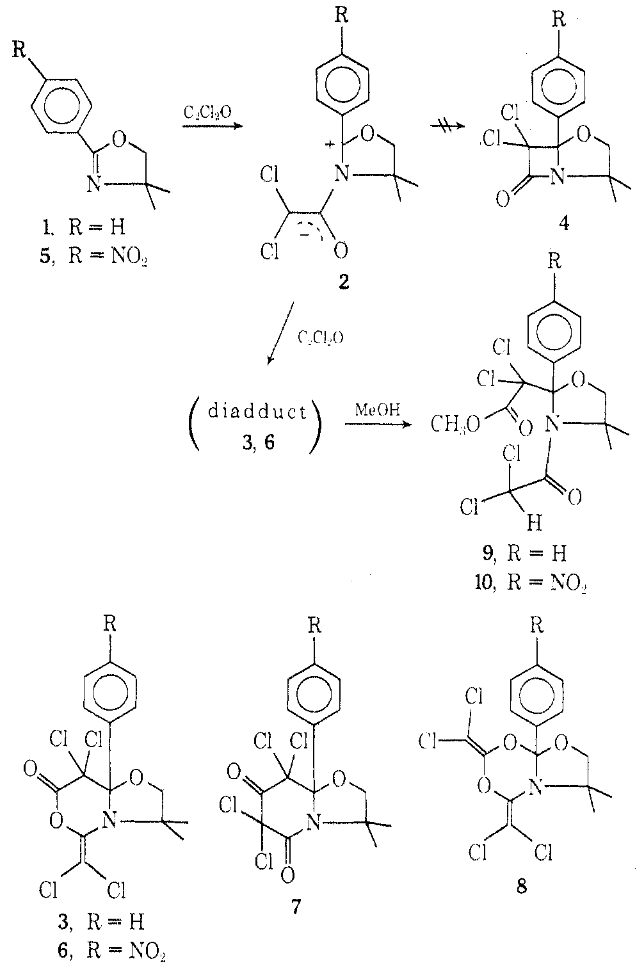
[1] L. Ghosez, R. Montaigne, and D. Mollet, *Tetrahedron Lett.*, 135 (1966); W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966).

[2] F. Duran and L. Ghosez, *Tetrahedron Lett.*, 245 (1970).

SCHEME I

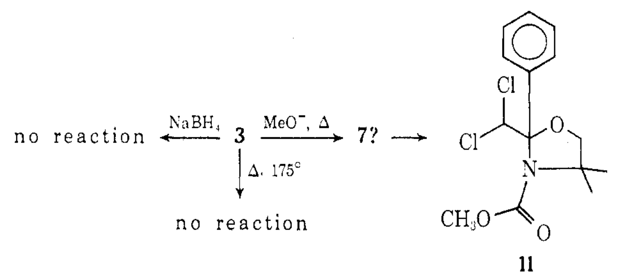


Determination of the structure of **3** was complicated by the possible formation of a number of other isomers, chiefly **7** and **8**. While the absence of protons on the ketene dimer portion of the molecule hindered the structure assignment, the infrared spectra provided some information. The presence of a carbonyl absorption in the ir at 1809 cm^{-1} can be rationalized[3] only in terms of structures **3** or **7**, not **8**. Also the formation of ester **9** (Scheme I) by solvolysis of the ketene diadduct in warm methanol could result from either isomer **3** or **7**. The inertness of the diadduct to sodium borohydride (Scheme II) in warm ether for 5 days, however, suggests structure **3**, as the ketone group in **7** would be expected to be reduced to an alcohol under the conditions employed.

Neither changes in the stoichiometry nor alteration of the order of reactant addition affected the formation of **3**, which was the only observed product of either 1:1 or 2:1 ratios of ketene precursors to substrate and of reaction conditions ranging from −78° to reflux in cyclohexane, ether, THF, and THF–DMF. When 1:1 ratios were used, oxazoline **1** could be recovered from the reaction mixtures.

Consideration of the reaction mechanism which, reportedly,[4,5] involves zwitterion **2** led to the idea that destabilization of the benzylic carbonium ion could encourage collapse of **2** to give β-lactam **4** in preference to attack by the intermediate on a second molecule of ketene. When dichloroketene was treated with oxazoline **5**, the *p*-nitrophenyl derivative of **1**, under varying conditions as mentioned above, only product **6** was observed, in direct analogy to the unsubstituted oxazoline.

SCHEME II



Dimethyl- and diphenylketene have been reported[6,7] to react with some Schiff bases to form the tetrasubstituted ketene dimers analogous to **3**. These have been shown[6] to undergo a base-catalyzed rearrangement to yield piperidinediones analogous to ketene dimer **7**. Attempts to rearrange compound **3** to **7** using sodium methoxide in refluxing benzene, however, gave only methyl ester **11** rather than the expected dione **7**, although **7** may have served as an intermediate in this reaction. Isomer **3** was found to be thermally stable to 175° in the absence of sodium methoxide.

Experimental Section

Melting points were taken with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 grating instrument, while nmr data were collected on a JOEL MH 100 spectrometer utilizing TMS as internal standard. Mass spectra were taken with a Hitachi RMU6-D mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

4,4-Dimethyl-2-phenyl-Δ^2-oxazoline (**1**) and 4,4-dimethyl-2-*p*-nitrophenyl-Δ^2-oxazoline (**5**) were prepared by the method of Boyd and Hansen,[8] and gave satisfactory spectral data.

Synthesis of 8,8-Dichloro-5-dichlorovinylidene-3,3-dimethyl-8a-phenyltetrahydrooxazolo[3,2-*a*]oxazin-7-one (3) and *p*-Nitrophenyl Analog 6.—Either oxazoline **1** or **5** (0.01 mol) was placed in a dry flask equipped with magnetic stirrer, addition funnel, condenser, and drying tube. One or two equivalents of freshly distilled triethylamine was then added along with 100 ml of dry solvent (either, cyclohexane, THF, or THF–DMF). The solution was brought to the desired temperature, at which time 1 or 2 equiv of dichloroacetyl chloride was added slowly. A white precipitate, amine hydrochloride, became immediately evident. After addition, the mixture was stirred for an additional 1 hr, at which time a theoretical yield of amine salt was recovered by vacuum filtration. About 90% of the solvent was removed from the filtrate *in vacuo*, and the resulting liquid was triturated with hexane to cause precipitation of the diadduct after 1 hr at 0°. Sublimation of the product afforded analytically pure material.

For compound **3**: yield 90% (average for 0.01–0.03-mol scale); mp 91–92°; ir (CCl_4) 1809, 1660, and 1182 cm^{-1}; nmr (CCl_4) δ 1.08 (s, 3), 1.37 (s, 3), 3.66 (AB pattern, 2), 7.28–7.85 (aromatic, 5); mass spectrum[9] (70 eV) parent ion at *m/e* 397; chlorine isotope ratio shows four chlorines.

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[3] For a recent article dealing with the controversy of diadduct formation in ketene addition reactions to imines see A. Hassner and M. J. Haddadin, *J. Org. Chem.*, **38**, 2650 (1973).

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[5] R. Huisgen, B. A. Davis, and M. Morikawa, *Angew. Chem.*, **80**, 802 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 826 (1968); W. T. Brady and E. D. Dorsey, *J. Org. Chem.*, **35**, 2737 (1970).

[6] A. Hassner, M. J. Haddadin, and A. B. Levy, *Tetrahedron Lett.*, 1015 (1973).

[7] J. C. Martin, K. C. Brannock, R. D. Burpitt, P. G. Gott, and V. A. Hoyle, *J. Org. Chem.*, **36**, 2211 (1971).

[8] R. N. Boyd and R. H. Hansen, *J. Amer. Chem. Soc.*, **75**, 5896 (1953).

[9] We thank Dr. C. Fenslau of The Johns Hopkins School of Hygiene and Public Health for providing us with this spectrum.

Anal. Calcd for $C_{15}H_{13}Cl_4NO_3$: C, 45.37; H, 3.30; N, 3.53. Found: C, 45.37; H, 3.28; N, 3.53.

For **6**: yield 85% (average for 0.01–0.03-mol scale); mp 154–155°; ir (CCl_4) 1809, 1658, 1535, 1350, 1175 cm^{-1}; nmr ($CDCl_3$) δ 1.10 (s, 3,), 1.46 (s, 3), 3.65 (AB pattern, 2), 7.62–7.92 and 8.10–8.32 (aromatic, 4).

Preparation of 3-Dichloroacetyl-4,4-dimethyl-2-(methyldichloroacetoxy)-2-phenyloxazolidine (9) and *p*-Nitrophenyl Analog 10.—Diadduct **3** or **6** was placed under gentle reflux in an excess of methanol for 3 hr. Addition of warm water precipitated the methyl esters, which were purified by recrystallization from methanol–water.

For oxazolidine **9**: yield >95% on 0.01-mol scale; mp 192–193°; ir (CCl_4) 1755, 1674, 1401, 1070 cm^{-1}; nmr (CCl_4) δ 1.39 (s, 3), 1.73 (s, 3), 3.60 (s, 3), 3.76 (AB pattern, 2), 6.34 (s, 1), 7.20–7.64 (aromatic, 5); mass spectrum (70 eV) no parent ion, *m/e* 285 ($-C_2Cl_2O$), 181, 104.

Anal. Calcd for $C_{16}H_{17}Cl_4NO_4$: C, 44.78; H, 3.99; N, 3.26; Cl, 33.05. Found: C, 44.90; H, 3.93; N, 3.17; Cl, 33.16.

For **10**: yield >95% on 0.01-mol scale; mp 229°; ir (CCl_4) 1756, 1670, 1525, 1415, 1350, 1250 cm^{-1}; nmr (CCl_4) δ 1.40 (s, 3), 1.76 (s, 3), 3.68 (s, 3), 3.80 (AB pattern, 2), 6.38 (s, 1), 7.67–8.32 (aromatic, 4).

Anal. Calcd for $C_{16}H_{16}Cl_4N_2O_6$: C, 40.53; H, 3.41; N, 5.91. Found: C, 40.40; H, 3.25; N, 5.79.

Methyl-2-dichloromethyl-4,4-dimethyl-2-phenyloxazolidine-3-carboxylic Acid (11).—Compound **3** (0.01 mol) was placed in 50 ml of dry benzene and brought to reflux. One equivalent of sodium methoxide in methanol was added *via* syringe and the reflux was continued for 1 hr. The solvent was removed *in vacuo*, and the remaining solid was recrystallized from methanol–water. For **11**: yield 70%; mp 142–143°; ir (CCl_4) 1691, 1450, 1380, 1260 cm^{-1}; nmr ($CDCl_3$) δ 1.65 (s, 6, broad), 3.48 (s, 3), 3.66 (AB pattern, 2), 6.05 (s, 1), 7.38–7.61 (aromatic, 5). The mass spectrum (70 eV) shows a parent ion at *m/e* 317 containing two chlorines (isotope ratio).

Anal. Calcd for $C_{14}H_{17}Cl_2NO_3$: C, 52.84; H, 5.38; N, 4.43. Found: C, 52.97; H, 5.26; N, 4.36.

Ester **9** was also formed in 10% yield from this reaction.

Acknowledgment.—We thank the National Institutes of Health for support for this work.

Registry No.—**1**, 19312-06-2; **3**, 42449-39-8; **5**, 42407-05-6; **6**, 42449-40-1; **9**, 42449-41-2; **10**, 42449-42-3; **11**, 42449-43-4; dichloroketene, 4591-28-0.