Laser Raman Kinetics .- Routine laser Raman spectra of solutions were measured with the sample contained in a melting point capillary aligned coaxially with the laser beam. While 2 absorbed no light at the laser frequency, prolonged exposure to the beam (20-30 min) inevitably resulted in some deterioration of the sample. To minimize this problem in the kinetic study, the sample was contained in a 3-mm-o.d. Pyrex tube having one end flat; the other end was sealed after degassing the sample in vacuo. The larger diameter of this tube permitted thermal mixing of the solution in the vicinity of the laser beam, reducing the amount of laser-induced decomposition. The sample was kept in a thermostatted oil bath at 67.0 \pm 0.1° and removed only long enough to record the two peaks for each point.

Registry No.-1, 38512-16-2; 2, 35099-79-7; 3, 35099-80-0.

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Communications

See Editorial, J. Org. Chem., 37, No. 19, 4A (1972).

The Electrophilic Addition of Chlorosulfonyl Isocyanate to Ketones. A Convenient Synthesis of Oxazines, Oxathiazines, and Uracils¹

Summary: CSI is found to react with ketones 1 in ether solution to produce 1,2,3-oxathiazines 5 and 1,3oxazines $\mathbf{6}$ but, in CH₂Cl₂ solution, only $\mathbf{6}$ is formed; oxazines 6 are readily converted into uracils 7.

Chlorosulfonyl isocyanate (CSI) has received Sir: considerable attention recently owing to its reactivity in various cycloadditions and its use in heterocyclic syntheses.² This remarkable electrophile reacts with a variety of compounds, including olefins,^{2b} acetylenes,^{2c} strained bicyclic hydrocarbons,^{2d} and ketene thioacetals.^{2e} Recent evidence^{3a} has been interpreted mechanistically as involving $[\pi 2_s + \pi 2_a]$ cycloaddition of CSI to olefins; heterolytic ring opening of the initially formed β -lactam to a 1,4 dipole may then lead to rearranged products. However, 1,4 dipoles may still be the primary intermediates, giving 1,2 addition under kinetic control and rearranged products under thermodynamic control.^{3b}

We wish to report the first examples of the electrophilic addition of CSI to simple ketones 1,⁴ a reaction which provides a facile entry into the 3,4-dihydro-4oxo-1,2,3-oxathiazine 2,2-dioxide (5) and the 3,4dihydro-2H-2,4-dioxo-1,3-oxazine (6) systems (Scheme I). The former represents a new heterocyclic system,⁵ the novel reactions of which are currently under study.

(1) Cycloadditions. XII. For paper XI, see A. Hassner and D. J. Anderson, J. Amer. Chem. Soc., 94, 8255 (1972).

(3) (a) T. J. Barton and R. J. Rogido, J. Chem. Soc., Chem. Commun., 878 (1972); T. J. Barton and R. J. Rogido, Tetrahedron Lett., 3901 (1972); (b) J. R. Malpass and N. J. Tweddle, J. Chem. Soc., Chem. Commun., 1244, 1247 (1972); J. R. Malpass, ibid., 1246 (1972).

(4) CSI has been reported to react with a few β diketones such as dimedone and acetylacetone, leading to β -ketoamides. See ref 2a, p 180.

(5) The only previously reported examples appear to be the 5,6-dimethyl compound [K. Clauss and H. Jensen, Tetrahedron Lett., 119 (1970)] and the 6-phenyl compound [K.-D. Kampe, ibid., 123 (1970)].

SCHEME I RÖCH₃R' OH RĊCHĊNSO₂Cl OH R' 2 RĊ CHR' 1 **RCCHCNHSO₂Cl** RÜCHÜNÜNHSO,CI k' Ŕ1 \$0.Cl 3 4 ΙH NH₃ Ŕ′ Ŕ′ 5 6

The latter are readily converted into uracil derivatives 7.8

Treatment of 1⁷ with 2.3 equiv of CSI in ether or dichloromethane solution under nitrogen at room temperature for up to 7 days, followed by reductive hydrolvsis with aqueous sodium sulfite solution,⁸ provided 5 and 6 as the major isolated products (Table I).

As depicted in Scheme I, electrophilic addition of CSI to the enol form of 1 would produce the 1,4 dipole 2,⁹ which yields amide 3 by a proton shift. We have succeeded in trapping intermediate 3 by the isolation of various derivatives. These results will be described in our full paper. Reaction of 3 with a second equiva-

(9) None of our experimental results, however, would preclude initial β -lactam formation followed by rapid ring opening to 2.

^{(2) (}a) For a recent review, see R. Graf, Angew. Chem., Int. Ed. Engl., 7, 172 (1968); (b) E. J. Moriconi and J. F. Kelly, J. Org. Chem., 33, 3036 (1968); E. J. Moriconi and W. C. Meyer, *ibid.*, 36, 2841 (1971); L. A. Paquette, T. Kakihana, J. R. Hansen, and J. C. Phillips, J. Amer. Chem. Soc., 93, 152 (1971); L. A. Paquette, S. Kirschner, and J. R. Malpass, *ibid.*,
 92, 4330 (1970); (c) E. J. Moriconi and Y. Shimakawa, J. Org. Chem., 37, 196 (1972); (d) E. J. Moriconi and C. P. Dutta, *ibid.*, 35, 2443 (1970); L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, J. Amer. Chem. Soc. 93, 4503 (1971); (e) F. A. Carey and J. R. Neergaard, J. Org. Chem., 36, 2731 (1971).

⁽⁶⁾ Satisfactory elemental analyses (+0.3%) were obtained for all new compounds, and the nmr, ir, and mass spectral data were in complete agreement with the structural assignments.

⁽⁷⁾ Ketones in which neither R nor R' is any appear to react in an entirely \mathbf{R} different manner. For example, 4-heptanone reacts with CSI in CH2Cl2 to yield butyric acid in 75% yield following work-up. Further investigation of this novel reaction is in progress.
(8) T. Durst and M. J. O'Sullivan, J. Org. Chem., 35, 2043 (1970).

			Т	ABLE	I		
	REACT	TION C	F KETO	ves 1	WITH CSI TO	YIEL	D
Oxathiazines 5 and Oxazines 6^{α}							
Compd	R	R'	$\mathbf{Solvent}$	% 5	Mp, °C	% 6	Mp, °C
a	Ph	Me	$Ether CH_2Cl_2$	41.5	122.5	$28.4 \\ 43.0$	184,5
b	Ph	Et	$Ether CH_2Cl_2$	41.2	113-113.5	7.7 14.8^b	132.5-133
c	Me	\mathbf{Ph}	Ether			70.6	166.5
d	$PhCH_2$	\mathbf{Ph}	$\mathbf{E}\mathbf{ther}$			61.0	137-137.5
e	Ph	Ph	Ether	28.4	233.5-234.5	13.6	220-222
f	U.)	Ether	30.3	258.5-260	19.8	210-211

^a Yields are for pure isolated products. ^b After 11 days' reaction time; 2-benzoylbutyramide [J. Büchi, P. Schneeberger, and R. Lieberherr, *Helv. Chim. Acta*, **36**, 1402 (1953)] was also isolated from this reaction in 34.5% yield.

lent of CSI, cyclization, and hydrolysis on work-up leads to 6. Alternatively, cyclization of 3 with loss of HCl would give oxathiazines 5. Further mechanistic studies are in progress and will be detailed in our full paper.

Despite the biological importance of uracil derivatives, and the intense interest in their chemistry,¹⁰ few examples are known containing alkyl or aryl substituents on both the 5 and 6 positions.^{10,11} The ready availability of starting materials and the nearly quantitative conversion of oxazines 6 to uracils 7 by treatment with concentrated aqueous ammonia provide a new regiospecific two-step synthesis of 5,6-disubstituted uracils which is more advantageous than most conventional routes.¹²

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(10) D. J. Brown, "The Pyrimidines," Wiley-Interscience, New York'
N. Y., 1962.
(11) (a) M. Draminski and B. Fiszer, *Rocz. Chem.*, 43, 499 (1969); *Chem.*

(11) (a) M. Draminski and B. Fiszer, Rocz. Chem., 43, 499 (1969); Chem. Abstr., 70, 115100v (1969). (b) M. Ohoka, S. Yanagida, and S. Komori, J. Org. Chem., 37, 3030 (1972).
(12) Reference 11, pp 31-115, 227-237.

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Syntheses of 11-Dehydro-13,14-dihydro-PGE₁ and PGD₂

Summary: The syntheses of 11-dehydro-13,14-dihydro-PGE₁ (9b) and PGD₂ (6b) was achieved from diols 8 or 4, respectively.

Sir: The formation of the triketo acid 2a by oxidation of PGE₁ (1a) with Jones reagent has been reported by Pike, et al.¹ Similarly, we obtained the mixture of 2b and 3, at the ratio of 1:3 by oxidation of PGE₂ (1b) under the same condition (at 0°, for 20 min). 2b had the following properties: uv $\lambda_{\text{max}}^{50\% \text{ EtOH}}$ 282 nm; ir (liquid film) ν 3500-2500, 1707, 1560 cm⁻¹; nmr (CDCl₃) δ 6.50 (t, 1 H, C₁₃ proton), 5.47 (s, 1 H, C₁₀ proton), 5.35 (m, 2 H, C₅ and C₆ protons), 3.41 (d, 2 H, C₁₄ protons). 3 had the following properties: uv

(1) J. E. Pike, F. H. Lincoln, and W. P. Schneider, J. Org. Chem., **34**, 3552 (1969).

 $\lambda_{\rm max}^{50\% \ {\rm EtOH}} 231 \ {\rm nm}$; ir (liquid film) ν 3400, 3400–2500, 1740, 980 cm⁻¹; nmr (CDCl₃) δ 6.80 (dd, 1 H, C₁₃ proton), 6.28 (d, 1 H, C₁₄ proton), 5.38 (m, 2 H, C₅ and C₆ protons), 4.27 (q, 1 H, C₁₁ proton).

5 was formed, together with 6a and 7a, by oxidation of 4 under the same condition. There is a presumption that migration of the trans double bond to C_{12} will lower PG-like biological activity, and it is known that the saturation of the trans double bond to single bond retains its activity.² For these reasons we have synthe-



(2) E. Ånggard, Acta Physicol. Scand., 66, 509 (1966).