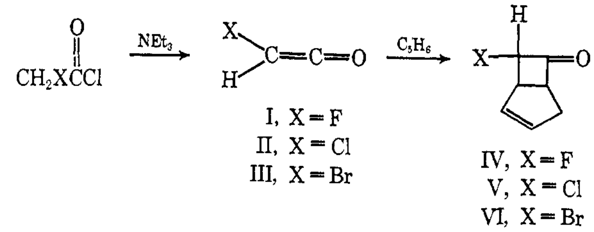
Halogenated Ketenes. VII. On Monohaloketenes[1]

Sir:

Although the chemistry of dihaloketenes has been explored to a considerable extent during the past 3 years, the monohaloketenes (aldohaloketenes) have received essentially no attention.[2] The only report we can find on these new materials is simply the mention by Opitz and coworkers of the cycloaddition of chloroketene and an enamine.[3] We now wish to report some chemistry of the monohaloketenes, fluoro-, chloro-, and bromoketenes. This is the first report on these elusive reactive materials which represent a new class of ketenes.

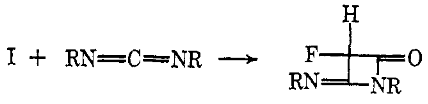
Fluoroketene (I) is easily prepared by the dehydrochlorination of fluoroacetyl chloride with triethylamine in anhydrous ether at −78°.[4] I appears to be quite stable in the reaction mixture at this temperature for at least 2 days. Upon warming to room temperature, I polymerizes to a black solid material over a period of about 20 hr. The ketene does not appreciably react with cyclopentadiene at −78 or at −10°. However, upon warming to room temperature, a 1,2-cycloaddition reaction occurs to produce 7-fluorobicyclo[3.2.0]hept-2-en-6-one (IV) in 40% yield:[5,6] bp 73.5° (4.5 mm); ir, 1800 (C═O) and 1605 cm^{-1} (C═C); nmr (CCl$_4$), δ 2.6 (m, 2 H), 3.45 (m, 1 H), 3.85 (m, 1 H), 5.52 (m, 1 H), and 5.87 (m, 2 H);[7] the proton nmr employing a fluorine decoupler demonstrated the presence of fluorine. *Anal.* Calcd for C_7H_7FO: C, 66.65; H, 5.59. Found: C, 66.50; H, 5.55.



I, X = F
II, X = Cl
III, X = Br

IV, X = F
V, X = Cl
VI, X = Br

When I was generated in the presence of N,N′-diisopropylcarbodiimide in refluxing hexane, 3-fluoro-1-isopropyl-4-isopropyliminoazetidin-2-one (VII) was produced in 40% yield: bp 50–51° (0.7 mm); ir, 1832 (C═O) and 1710 cm^{-1} (C═N); nmr (CCl$_4$), δ 1.32 (m, 12 H), 3.85 (m, 2 H), and 5.94 (d, 1 H; J_{HF} = 55 cps). *Anal.* Calcd for $C_9H_{15}FN_2O$: C, 58.1; H, 8.07; N, 15.5. Found: C, 58.37; H, 8.26; N, 15.21.



VII

R = isopropyl

Chloroketene (II) was readily prepared by the dehydrobromination of chloroacetyl bromide with triethylamine in ether at −78°. This monohaloketene also appeared to be quite stable in the reaction mixture at this temperature but quickly polymerized to a dark solid material upon warming to room temperature. II readily undergoes cycloaddition with cyclopentadiene to produce 7-chlorobicyclo[3.2.0]hept-2-en-6-one (V) in 60% yield: bp 64° (0.6 mm); ir, 1795 (C═O) and 1605 cm^{-1} (C═C); nmr (CCl$_4$), δ 2.6 (m, 2 H), 3.84 (m, 2 H), 5.08 (m, 1 H), and 5.81 (m, 2 H). *Anal.* Calcd for C_7H_7ClO: C, 58.8; H, 4.91. Found: C, 58.55; H, 4.93.

II also readily underwent cycloaddition with a carbodiimide to produce the corresponding azetidinone.

Bromoketene (III) was obtained by the dehydrobromination of bromoacetyl bromide with triethylamine in ether at −78°. However, this ketene, unlike I and II, was apparently not very stable in the reaction mixture at the low temperature as only a 5% yield of 7-bromobicyclo[3.2.0]hept-2-en-6-one (VI) was obtained when III was trapped with cyclopentadiene. Because of the small yield it was necessary to purify VI by vpc; ir, 1795 (C═O) and 1617 cm^{-1} (C═C); nmr (CCl$_4$), δ 2.6 (m, 2 H), 3.87 (m, 2 H), 5.14 (m, 1 H), and 5.8 (m, 2 H). *Anal.* Calcd for C_7H_7BrO: C, 44.8; H, 3.74. Found: C, 45.1; H, 3.96.

All of the monohaloketenes studied are thermally unstable with our preliminary studies, suggesting that III is much less stable than I and II. Also, these results indicate that I and II can be easily trapped with activated cycloaddition partners such as cyclopentadiene and carbodiimides to produce the corresponding 1,2-cycloaddition products. A more detailed report on further chemistry of the monohaloketenes is forthcoming.

Acknowledgment. The authors express their gratitude to Dr. William H. Glaze for helpful discussions concerning the nmr spectra. Support of this investigation by the Robert A. Welch Foundation and a National Science Foundation grant (GP-7386) is gratefully acknowledged.

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[1] Paper VI: W. T. Brady and R. Roe, Jr., *Tetrahedron Letters*, 1977 (1968).

[2] These are only among the first reports on dichloro-, dibromo-, difluoro-, and chlorofluoroketenes, respectively: H. C. Stevens, D. A. Reich, D. R. Brandt, D. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965); L. Ghosez, R. Montaigne, and P. Mollet, *Tetrahedron Letters*, 135 (1966); W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966); W. T. Brady, *ibid.*, **31**, 2676 (1966); D. C. England and C. G. Krespan, *ibid.*, **33**, 816 (1968); Y. A. Cheburkov, A. M. Platoshkin, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **173**, 1117 (1967).

[3] G. Opitz, M. Kleemann, and F. Zimmermann, *Angew. Chem.*, **74**, 32 (1962).

[4] Fluoroacetyl chloride was prepared by the method described by W. E. Truce, *J. Amer. Chem. Soc.*, **70**, 2828 (1948).

[5] The yield is not higher because of the competing polymerization of I as evidenced by a black solid residue remaining after the distillation of IV.

[6] The double bond location in IV was assigned on the basis of the diene acting as a nucleophile which would be expected to yield the above substituted cyclobutanone regardless of whether an ionic, diradical, or near-concerted mechanism was operative. See, for example, J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 26 (1962); W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 2704 (1967); W. T. Brady and B. M. Holifield, *Tetrahedron*, **23**, 4251 (1967).

[7] The fluorine had split the methinyl proton on C-7 so that half of the multiplet was hidden under the vinyl proton resonance. However, bromination of IV revealed two multiplets at δ 5.5 and 5.9 with equal areas.

Extreme Selectivity for a Carbon–Hydrogen Insertion Reaction by Dichlorocarbene. A Corrected Stereochemical Assignment

Sir:

The attack of dichlorocarbene on relatively simple dialkylmercury compounds **1** results in the formation of both the expected carbon–mercury insertion product