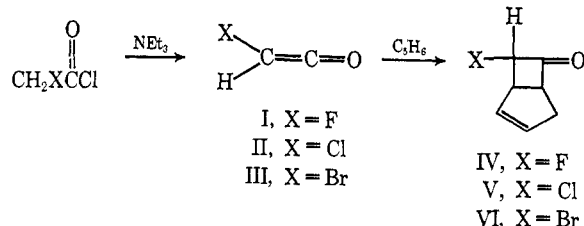


Halogenated Ketenes. VII. On Monohaloketenes<sup>1</sup>

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.<sup>2</sup> 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.<sup>3</sup> 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  $-78^\circ$ .<sup>4</sup> 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  $-10^\circ$ . 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;<sup>5,6</sup> bp  $73.5^\circ$  (4.5 mm); ir, 1800 (C=O) and  $1605\text{ cm}^{-1}$  (C=C); nmr ( $\text{CCl}_4$ ),  $\delta$  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);<sup>7</sup> the proton nmr employing a fluorine decoupler demonstrated the presence of fluorine. *Anal.* Calcd for  $\text{C}_7\text{H}_7\text{FO}$ : C, 66.65; H, 5.59. Found: C, 66.50; H, 5.55.

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  $50\text{--}51^\circ$  (0.7 mm); ir, 1832 (C=O) and  $1710\text{ cm}^{-1}$  (C=N); nmr ( $\text{CCl}_4$ ),  $\delta$  1.32

(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).

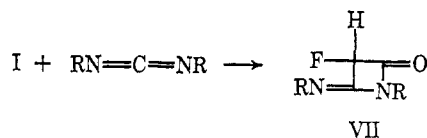
(3) G. Opitz, M. Kleemann, and F. Zimmermann, *Angew. Chem.*, **74**, 32 (1962).

(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  $\delta$  5.5 and 5.9 with equal areas.



R = isopropyl

(m, 12 H), 3.85 (m, 2 H), and 5.94 (d, 1 H;  $J_{\text{HF}} = 55$  cps). *Anal.* Calcd for  $\text{C}_9\text{H}_{15}\text{FN}_2\text{O}$ : C, 58.1; H, 8.07; N, 15.5. Found: C, 58.37; H, 8.26; N, 15.21.

Chloroketene (II) was readily prepared by the dehydrobromination of chloroacetyl bromide with triethylamine in ether at  $-78^\circ$ . 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  $64^\circ$  (0.6 mm); ir, 1795 (C=O) and  $1605\text{ cm}^{-1}$  (C=C); nmr ( $\text{CCl}_4$ ),  $\delta$  2.6 (m, 2 H), 3.84 (m, 2 H), 5.08 (m, 1 H), and 5.81 (m, 2 H). *Anal.* Calcd for  $\text{C}_7\text{H}_7\text{ClO}$ : 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  $-78^\circ$ . 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  $1617\text{ cm}^{-1}$  (C=C); nmr ( $\text{CCl}_4$ ),  $\delta$  2.6 (m, 2 H), 3.87 (m, 2 H), 5.14 (m, 1 H), and 5.8 (m, 2 H). *Anal.* Calcd for  $\text{C}_7\text{H}_7\text{BrO}$ : 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.

William T. Brady, Edwin F. Hoff, Jr.

Chemistry Department, North Texas State University  
Denton, Texas 76203

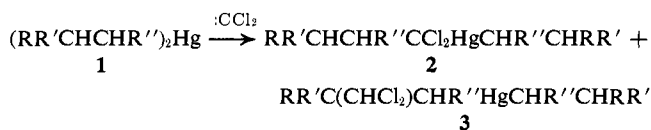
Received July 25, 1968

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

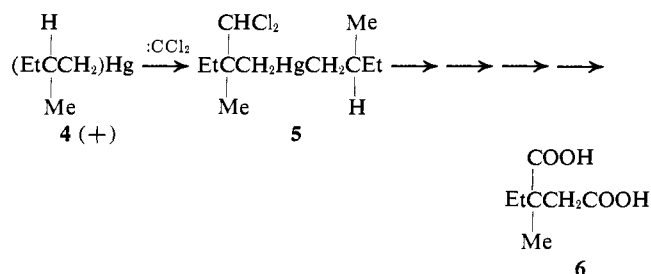
Sir:

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

2 and an unusual  $\beta$ -carbon-hydrogen insertion product 3.<sup>1-3</sup>



It was previously reported<sup>2</sup> that the insertion of dichlorocarbene into the  $\beta$ -C-H bond of (+)-bis((*S*)-2-methylbutyl)mercury (**4**) occurred with net inversion of configuration. Subsequent to the appearance of this publication, unpublished data<sup>4</sup> brought to the attention of the authors<sup>5</sup> indicated that the final degradation



product of their stereochemical sequence,  $\alpha$ -methyl- $\alpha$ -ethylsuccinic acid (**6**), has a concentration-dependent sign and magnitude of rotation in chloroform. For example, the rotations of samples of 85% optically pure (*S*)- $\alpha$ -methyl- $\alpha$ -ethylsuccinic acid in chloroform are  $[\alpha]^{24\text{D}} - 5.0^\circ$  (*c* 16.5),  $-0.6^\circ$  (*c* 10.6),  $+1.7^\circ$  (*c* 8.5),  $+9.4^\circ$  (*c* 4.3),  $+18.9^\circ$  (*c* 2.2), and  $+30^\circ$  (*c* 1.1).<sup>6</sup>

Because the rotation of our sample of diacid **6** was  $[\alpha]^{25\text{D}} - 6.41^\circ$  (*c* 1.4,  $\text{CHCl}_3$ ), there can be no doubt that it has the *R* configuration, clearly indicating that the dichlorocarbene insertion occurred primarily by retention of configuration. One can estimate from the data of Krow and Hill<sup>6</sup> that at *c* 1.4 the rotation of optically pure (*R*)- $\alpha$ -ethylsuccinic acid should be *ca.*  $30^\circ$ . Using this value we can calculate that the insertion took place with approximately 21% retention and 79% racemization.

More recent work on the extent of carbon-mercury and  $\beta$ -carbon-hydrogen insertion in a series of dialkylmercury compounds (Table I) provides convincing evidence for specificity of the carbon-hydrogen attack by dichlorocarbene at the  $\beta$  position. The data clearly show an increase in the ratio of  $\beta$ -C-H to C-Hg insertion products from 0 to *ca.* 9 as the  $\beta$ -C-H bond progresses from primary to tertiary. No other simple C-H insertion products were detected.<sup>6a</sup>

A particularly interesting example is that of diisooamylmercury in which the carbon-hydrogen insertion went exclusively into the secondary C-H bond at the  $\beta$  position, although there was a tertiary C-H bond at the  $\gamma$  position. Such an observation would appear to

(1) J. A. Landgrebe and R. D. Mathis, *J. Amer. Chem. Soc.*, **88**, 3545 (1966).

(2) J. A. Landgrebe and D. E. Thurman, *ibid.*, **89**, 4542 (1967).

(3) D. Seyferth and S. S. Washburne, *J. Organometal. Chem.*, **5**, 389 (1966).

(4) G. R. Krow, Ph.D. Dissertation, Princeton University, 1967.

(5) We are indebted to the astute observations of Dr. John Jacobus and the helpful correspondence with Professor K. Mislow and Dr. G. R. Krow.

(6) See footnote 6 in G. Krow and R. K. Hill, *Chem. Commun.*, 430 (1968).

(6a) NOTE ADDED IN PROOF. Dr. John Jacobus has communicated to us that he has independently carried out the  $\beta$ -C-H insertion reaction by dichlorocarbene on **4** with net retention of configuration.

Table I. Relative Distribution of C-Hg and  $\beta$ -C-H Insertion Products by Dichlorocarbene Attack on  $\text{R}_2\text{Hg}$ <sup>a,b</sup>

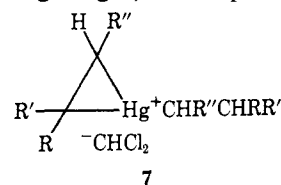
| R                 | $\beta$ -C-H | % C-Hg insertion | % $\beta$ -C-H insertion |
|-------------------|--------------|------------------|--------------------------|
| Ethyl             | Primary      | 100              | 0                        |
| Isopropyl         | Primary      | 100              | 0                        |
| <i>sec</i> -Butyl | Primary,     | 100              | 0                        |
|                   | secondary    |                  |                          |
| <i>n</i> -Propyl  | Secondary    | 53               | 47                       |
| <i>n</i> -Butyl   | Secondary    | 67               | 33                       |
| <i>n</i> -Amyl    | Secondary    | 67               | 33                       |
| Isoamyl           | Secondary    | 65               | 35                       |
| Isobutyl          | Tertiary     | 9                | 91                       |
| 2-Methylbutyl     | Tertiary     | 6                | 94                       |
| Cyclohexylmethyl  | Tertiary     | 13               | 87                       |

<sup>a</sup> Reactions were carried out at  $\leq 5^\circ$  in alkene-free pentane by treatment of ethyl trichloroacetate with commercial sodium methoxide in the presence of  $\text{R}_2\text{Hg}$ . <sup>b</sup> Product distribution data were obtained by vpc analysis of the brominated reaction mixture.

rule out a simple free-radical process in which tertiary C-H bonds at various positions along the alkyl chain other than the  $\beta$  position should be susceptible to attack.

We have previously expressed the belief that the initial attack of dichlorocarbene on a dialkylmercury compound might be at the mercury atom with the resultant formation of a complex or ylide structure which could then undergo further reaction.<sup>1</sup> While it is possible that dichlorocarbene could be transferred from its position in the complex directly into the  $\beta$ -C-H bond, a glance at approximate models would suggest that such a transfer should also be made into the  $\gamma$ -C-H bond and that the transfer process should be highly stereospecific, neither of which is realized experimentally.

Our current hypothesis attempts to account for the facts by postulating formation and collapse of an intermediate mercurinium ion pair,<sup>7a-c</sup> **7**. Experimental support, now being sought, will be published later.



(7) (a) K. Ichikawa, K. Nishimura, and S. Takayama, *J. Org. Chem.*, **30**, 1593 (1965); (b) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965); (c) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

(8) We wish to thank the National Science Foundation for generous support for our work.

John A. Landgrebe,<sup>8</sup> Duane E. Thurman  
Department of Chemistry, University of Kansas  
Lawrence, Kansas 66044

Received June 19, 1968

## The Photochemical Generation of a Subvalent Phenylaluminum Species from Triphenylaluminum(III)

Sir:

Recent interest in lower valent intermediates of groups IIIA and IVA, typified by numerous reports on carbenes,<sup>1</sup> as well as on silenes<sup>2</sup> and subvalent boron<sup>3</sup>

(1) Cf. W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1960, for a critical survey.

(2) (a) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964); (b) R. West and R. E. Bailey, *ibid.*, **85**, 2871 (1963).

(3) M. A. Kuck and G. Urry, *ibid.*, **88**, 426 (1966).