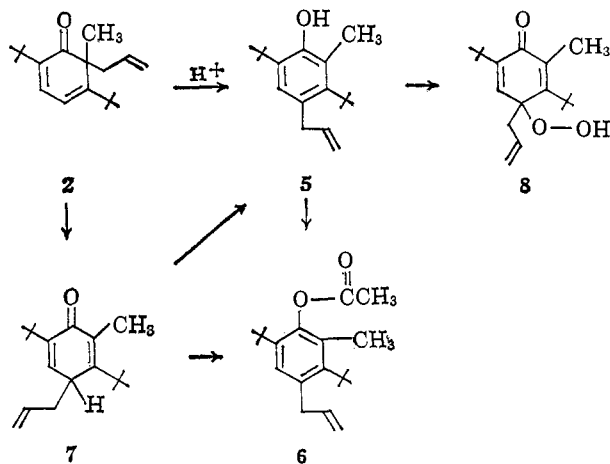


expected conjugated cyclohexadienone 2.<sup>4</sup> The structure assigned to 2 was confirmed by isolation of dienone 3 [b.p. 115–116° (1.0 mm.),  $\lambda_{\max}$  310 m $\mu$  ( $\epsilon$  3900)] in an over-all 69% yield from 1 by hydrogenation of 2 in benzene using a Pd on CaCO<sub>3</sub> catalyst. Irradiation of the cross-conjugated dienone 4 provided an independent synthesis of 3.

Although the identity of 2 as the principal photo-rearrangement product of 1 was established, 2 could not be isolated in a pure state. On attempted chromatography on alumina, silica gel, or Florisil, as well as on a variety of g.l.p.c. columns, 2 underwent a Cope rearrangement to phenol 5. Reaction of 2 with a 1% solution of sulfuric acid in acetic acid also converted it, essentially instantaneously, to 5, while reaction of 2 with acetic anhydride gave a 59% yield (based on 1) of the acetate 6 [b.p. 137–138° (0.1 mm.)], which could also be obtained by acetylation of 5.



Although its acetate was stable and easily isolated, phenol 5 could be isolated and stored only when extreme care was taken to avoid contact with oxygen. On exposure of 5 to air for even a few minutes, crystals of the keto hydroperoxide 8 [m.p. 123–124.5°,  $\lambda_{\max}$  (MeOH) 242 m $\mu$ ,  $\lambda_{\max}$  3.00 and 6.18  $\mu$ ] began to form.

When 2 is heated to 110° for 5 min. or to 70° for 1 hr., its characteristic absorption maxima at 310 m $\mu$  and 6.35  $\mu$  disappear. The product, however, retains an intense conjugated carbonyl peak at 6.17  $\mu$  and an ultraviolet band (in methanol) at 244 m $\mu$  ( $\epsilon$  9400) typical of cross-conjugated cyclohexadienones. No hydroxyl peak appears in its infrared spectrum.

No changes occur in the spectra of the ketonic product when it is kept at room temperature for 5 months. After heating to 220°, however, or on attempted chromatography on alumina, silica gel, or Florisil, only phenol 5 can be isolated from the product. Com-

pound 5 is also obtained instantly by dissolving the product in 1% sulfuric acid in acetic acid or in 1 N sodium methoxide in methanol.<sup>5</sup> Reaction of the crude ketone with sulfuric acid in acetic anhydride gave 6 in 62% yield.

The properties of the product of thermal rearrangement of 2 require its formulation as the cross-conjugated cyclohexadienone 7.<sup>6</sup>

The thermal stability of 7,<sup>7</sup> as well as the remarkably rapid autoxidation of 5, may be attributed to steric interference between the adjacent allyl and *t*-butyl groups in 5. Since this interference is decreased when 5 is converted to cyclohexadienones, the rate of aromatization of 7 to 5 under neutral conditions is much lower than usual, and the rate of oxidation of 5 much higher. As the work of Burgstahler, *et al.*,<sup>2</sup> indicated, however, once the phenolic form is obtained no detectable amounts of dienone remain in equilibrium with it.

The elemental analyses and n.m.r. spectra of all new compounds agree with the assigned structures.

(5) In contrast, 2 is stable in basic solutions.

(6) Formations of ketonic tautomers of phenols by thermal rearrangements have long been postulated as intermediate steps in the *ortho* and *para* Claisen rearrangements. It has been assumed, however, that aromatization of the dienones would be much faster than allylic rearrangements. See S. J. Rhoads in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., pp. 660–677.

(7) Thermal rearrangements of other 6-allylcyclohexa-2,4-dienones under similar conditions give only phenols, with no indications of the presence of the ketonic tautomers; *e.g.*, D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, 79, 3156 (1957).

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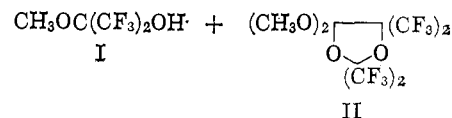
Received October 5, 1965

## Cyclic Ethers from Hexafluoroacetone

Sir:

We wish to report several new reactions of hexafluoroacetone which may involve dialkoxycarbene<sup>1</sup> and "silene"<sup>2</sup> intermediates.

Hexafluoroacetone reacts with trimethyl orthoformate at 150°, in a 3:1 mole ratio, to give the hemiketal I<sup>3</sup> and 2,2,4,4-tetrakis(trifluoromethyl)-5,5-dimethoxy-1,3-dioxolane (II) [79.4%, b.p. 161° (760 mm.), b.p. (CH<sub>3</sub>O)<sub>3</sub>CH + 3(CF<sub>3</sub>)<sub>2</sub>C=O →



— 1 to 0°,  $n_D^{25}$  1.3225].<sup>4</sup> The reaction proceeds readily

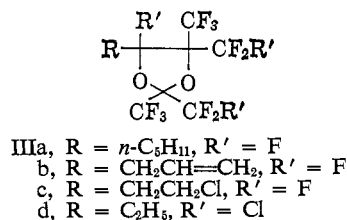
(1) Dialkoxycarbene intermediates have been proposed as intermediates in several reactions recently: (a) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, 85, 2677 (1963); (b) D. M. Lemal, *Tetrahedron Letters*, 11, 579 (1964); (c) J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, p. 70.

(2) (a) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, 86, 1442 (1964); (b) O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, 76, 270 (1964).

(3) C. Woolf, Abstracts of Papers Presented at the 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 1957, p. 23M.

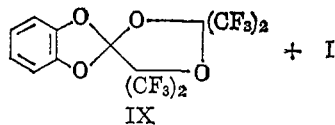
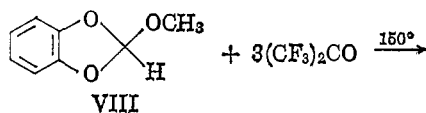
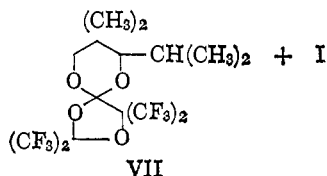
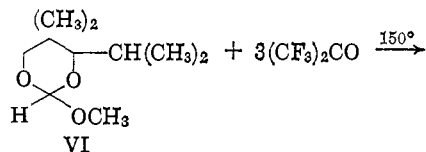
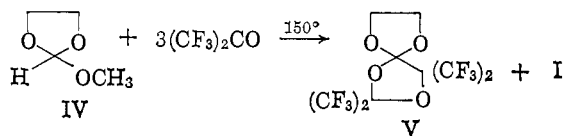
(4) Satisfactory elemental analyses and infrared and proton n.m.r. spectra for all of the new compounds were obtained. The fluorine n.m.r. and mass spectra of compounds II and X are in agreement with the proposed structures.

with a variety of orthoformates and hexafluoroacetone at 150°: tri-*n*-amyl orthoformate yields *n*-C<sub>5</sub>H<sub>11</sub>OC-(CF<sub>3</sub>)<sub>2</sub>OH and IIIa [57.0%, b.p. 152° (45 mm.), *n*<sup>25</sup><sub>D</sub>



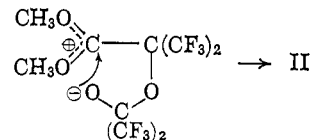
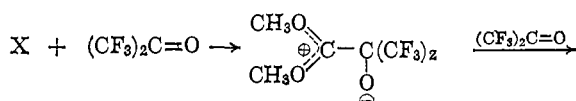
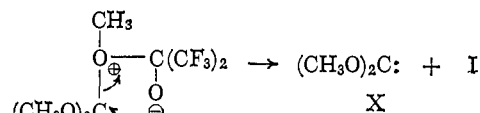
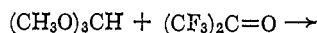
1.3717]; triallyl orthoformate and hexafluoroacetone yields CH<sub>2</sub>=CHCH<sub>2</sub>OC(CF<sub>3</sub>)<sub>2</sub>OH and IIIb [64.2%, b.p. 67° (4.3 mm.), *n*<sup>25</sup><sub>D</sub> 1.3532]; tri-β-chloroethyl orthoformate and hexafluoroacetone yields ClCH<sub>2</sub>-CH<sub>2</sub>OC(CF<sub>3</sub>)<sub>2</sub>OH and IIIc [28.4%, b.p. 86° (1.5 mm.), *n*<sup>25</sup><sub>D</sub> 1.3684]. Chloropentafluoroacetone and triethyl orthoformate undergo an analogous reaction, yielding C<sub>2</sub>H<sub>5</sub>OC(CF<sub>3</sub>)(CF<sub>2</sub>Cl)OH and III d [64.7%, b.p. 110° (23 mm.), *n*<sup>25</sup><sub>D</sub> 1.3728]. On the other hand, perhalo-ketones containing more chlorine undergo a different reaction with orthoformates, which will be the subject of a later communication.

Analogous reactions occur with hexafluoroacetone and cyclic orthoformates such as IV, VI, and VIII to

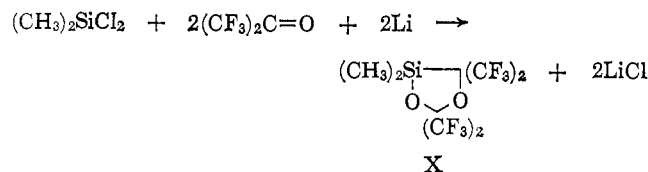


give I in each case and the spiroortho esters V [74.7%, b.p. 176° (760 mm.), m.p. 24°], VII (90.0%, m.p. 73–74°), and IX [75.2%, b.p. 207° (760 mm.), m.p. 71–72°].

The first step in these reactions could be the attack on the orthoformate in which hexafluoroacetone acts as a Lewis acid and the orthoformate as a Lewis base. The complex so formed could decompose in the indicated manner, liberating the hemiketal and dialkoxycarbene. Hexafluoroacetone may be an effective trap for the carbene, and steric considerations strongly favor reaction of 2 moles of hexafluoroacetone and formation of the 1,3-dioxolane (II).



Working from the hypothesis that 2 moles of hexafluoroacetone can react with a mole of dialkoxycarbene to give the observed products such as II, III, V, VII, and IX, experiments were devised to observe the reaction of dimethylsilene [(CH<sub>3</sub>)<sub>2</sub>Si:] with hexafluoroacetone. The reaction of dimethyldichlorosilane (1 mole) and hexafluoroacetone (2 moles) in tetrahydrofuran at 10° with lithium metal dispersion (2 moles) gave the analogous product 1,1-dimethyl-3,3,5,5-tetrakis(trifluoromethyl)-2,4-dioxo-1-silacyclopentane (X) (63.5%, b.p. 149–150°, m.p. –4°, *n*<sup>25</sup><sub>D</sub> 1.3342).



Details of these reactions and the reaction of perhalo-ketones with other ortho esters and acetals will appear in subsequent papers.

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 Received September 27, 1965

### Preferential Formation of the *cis* Olefin in an E2 Elimination

Sir:

We wish to report that the second-order reaction of potassium *t*-butoxide in *t*-butyl alcohol with 2-butyl, 2-pentyl, and 3-pentyl arenesulfonates produces the *cis* 2-alkene in considerable excess over the *trans*. All E2 reactions previously reported of alkyl halides and alkyl arenesulfonates produce the more stable *trans* alkene preferentially.<sup>1–3</sup>

For example, 2-butyl tosylate yields 62% 1-, 24% *cis*-2-, and 14% *trans*-2-butene. Similarly, 2-pentyl tosylate yields 74% 1-, 18% *cis*-2-, and 8% *trans*-2-

(1) W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Am. Chem. Soc.*, **87**, 3401 (1965).

(2) A. K. Colter and R. D. Johnson, *ibid.*, **84**, 3289 (1962). Very high yields of the *trans* isomer in eliminations involving 3-methyl-2-butyl arenesulfonates have recently been reported: A. K. Colter and D. R. McKelvey, *Can. J. Chem.*, **43**, 1282 (1965).

(3) High yields of *cis*-4-nonene have been realized in E2 eliminations of 5-nonyl onium salts and attributed to an incursion of an E1cb-like process: J. Zavada and J. Sicher, *Proc. Chem. Soc.*, 96 (1963).