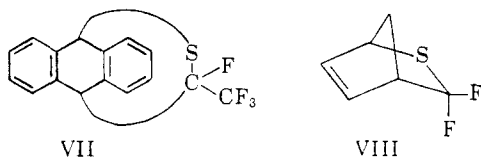


Hexafluorothioacetone is an exceedingly active dienophile. It reacts instantaneously with butadiene at  $-78^\circ$  to give a quantitative yield of the cyclic adduct, 2,2-bis-(trifluoromethyl)-3,6-dihydro-2H-1-thiapyran, b.p.  $65^\circ$  (30 mm.),  $n_D^{25}$  1.4042 (*Anal.* Found: S, 13.87). Under the same conditions, I also reacts rapidly with the two conjugated diene systems in styrene to give a 2:1 adduct, b.p.  $103-104^\circ$  (1.2 mm.),  $n_D^{25}$  1.4512 (*Anal.* Found: F, 48.62; S, 13.89).

Other fluorothiocarbonyl compounds, for example, trifluorothioacetyl fluoride (V) and thiocarbonyl fluoride (VI), are also very reactive dienophiles.

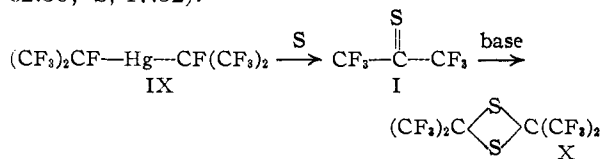


Although less reactive than I, trifluorothioacetyl fluoride (V) reacts with anthracene at room temperature to give the adduct VII, m.p.  $85^\circ$  (*Anal.* Found: S, 10.03). Thiocarbonyl fluoride (VI) reacts rapidly with cyclopentadiene at  $-20^\circ$  to give the adduct VIII, m.p.  $48^\circ$  (*Anal.* Found: S, 21.36).



Bistrifluoromethyl trithiocarbonate and ethyl dithiotrifluoroacetate are additional examples of fluorothiocarbonyls that are active dienophiles. Surprisingly, the diene reaction is also applicable to such non-fluorine-containing thiocarbonyl compounds as thiophosgene and thiofluorenone.

A general method for preparation of perfluorothioketones is reaction of perfluoro-*sec*-alkylmercurials with sulfur. Hexafluorothioacetate was obtained in 60% yield by dropwise addition of bis-(heptafluoroisopropyl)-mercury (IX)<sup>1</sup> to boiling sulfur. The thioketone is a deep blue liquid, b.p.  $8^\circ$ ,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  580 m $\mu$  (*Anal.* Found: C, 19.84; F, 62.41; S, 17.71). It is not sensitive to water or to oxygen but dimerizes in the presence of a trace of base to give the dithietane X, b.p.  $110^\circ$ , m.p.  $23.6^\circ$ ,  $n_D^{25}$  1.3357 (*Anal.* Found: C, 19.64; F, 62.36; S, 17.52).



The reaction of secondary fluoroalkylmercurials with sulfur has been used to prepare a number of other fluorothioketones.

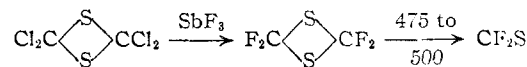
Trifluorothioacetyl fluoride was prepared in a similar manner from bis-(1-chloro-1,2,2,2-tetrafluoroethyl)-mercury<sup>2</sup> and sulfur. The thioacid fluoride was obtained in 80% yield and is a yellow gas, b.p.  $-21^\circ$  (*Anal.* Found: C, 18.31; F, 57.28; S, 24.38). Upon ultraviolet exposure, it dimerized to a mixture of *cis* and *trans* 2,4-bis-(trifluoro-

(1) E. G. Howard and W. J. Middleton, U. S. Patent 2,970,173 (1961).

(2) C. G. Krespan, *J. Am. Chem. Soc.*, **25**, 105 (1960).

methyl)-2,4-difluoro-1,3-dithietane, b.p.  $73^\circ$ ,  $n_D^{25}$  1.3378 (*Anal.* Found: C, 18.58; F, 57.47).

Thiocarbonyl fluoride was prepared in almost quantitative yields by pyrolysis at  $475-500^\circ$  of its cyclic dimer, 2,2,4,4-tetrafluoro-1,3-dithietane (XI). After distillation, the thiocarbonyl fluoride, b.p.  $-54^\circ$ ,<sup>3</sup> appeared to have no impurity other than about 15-25 ppm. of carbonyl sulfide. The dimer XI, b.p.  $48^\circ$ ,  $n_D^{25}$  1.3950 (*Anal.* Found: C, 14.73; F, 46.60; S, 39.16), was prepared from tetrachloro-1,3-diethietane<sup>4</sup> by reaction with antimony trifluoride in tetramethylene sulfone.



(3) (a) N. N. Yarovenko and A. S. Vasil'eva, *J. Gen. Chem. (U.S.S.R.)*, **29**, 3754 (1959), English Translation, report a boiling point range of  $-57$  to  $-54^\circ$  for impure thiocarbonyl fluoride. (b) A. J. Downs and E. A. V. Ebsworth, *J. Chem. Soc.*, 3516 (1960), also have made this compound and have reported an infrared spectrum, which is in agreement with one taken on our compound.

(4) A. Schonberg and A. Stephenson, *Ber.*, **66B**, 567 (1933).

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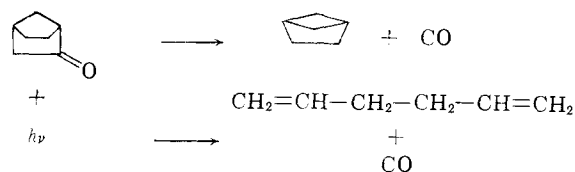
RECEIVED APRIL 26, 1961

#### A SIMPLE SYNTHESIS OF BICYCLO[2.1.1]HEXANE<sup>1</sup>

Sir:

Bicyclo[2.1.1]hexane has been synthesized recently.<sup>2</sup> Till now, the only satisfactory method for the formation of the bicyclo[2.1.1]hexane ring system has been the photolysis of a diazoketone derived from bicyclo[2.2.1]heptane.<sup>3</sup> The present method provides an alternative route to the synthesis of bicyclo[2.1.1]hexanes and may be particularly applicable to the hydrocarbons of this series.

It was found that the *vapor phase* photolysis of norcamphor led to the formation of bicyclo[2.1.1]hexane and 1,5-hexadiene along with an equivalent amount of carbon monoxide.



These reactions are analogous to the photochemical formation of bicyclo[2.2.0]hexane, 1,5-hexadiene, and carbon monoxide from bicyclo[3.2.0]heptanone-3.<sup>4</sup>

Bicyclo[2.1.1]hexane (m.p.  $21.6-22^\circ$ , b.p.  $70.9^\circ$  (751 mm.)) was separated from the other products by distillation and vapor phase chromatography.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{10}$ : C, 87.74; H, 12.26; mol. wt., 82. Found: C, 87.70; H, 12.25; mol.

(1) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18(600)1528 presently AF 49(638)679. Reproduction in whole or in part is permitted for any purpose by the United States Government.

(2) Professor K. Wiberg, private communication.

(3) L. Horner and E. Spietschka, *Ber.*, **88**, 934 (1955).

(4) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, No. 21, p. 24 (1960).

wt., 82 (mass spectrum). Its structure was deduced from these observations: since the compound showed no evidence of unsaturation in its ultraviolet and infrared spectra, the formula demands the presence of two rings. Of the possible bicyclohexanes, bicyclo[2.2.0]hexane has already been made<sup>4</sup> and bicyclo[3.1.0]hexane would show the presence of the cyclopropane ring in its spectra. The n.m.r. spectrum of the compound on hand (solvent: CCl<sub>4</sub>, chloroform and tetramethylsilane as internal standards) consisted of 2 protons at 7.47  $\tau$ -broad, 6 protons at 8.41  $\tau$ -apparent singlet; 2 protons at 9.13  $\tau$ -quartet, which would fit only the bicyclo[2.1.1]structure. The spectrum agreed closely with that of authentic bicyclo[2.1.1]hexane which was synthesized by another route.<sup>5</sup>

Preliminary studies have shown that this photochemical method is also applicable to the synthesis of 1,5,5-trimethylbicyclo[2.1.1]hexane from *dl*-camphor. The yields of the bicyclohexanes obtained by this method ranged from 25% in the case of norcamphor using mercury photosensitization<sup>6</sup> to 10% in the case of camphor using radiation from a medium pressure mercury arc. An increase in temperature generally decreased the yield. The improved yield as compared to the photochemical production of bicyclo[2.2.0]hexane by a similar process<sup>4</sup> is understandable when the degree of strain involved in the two systems is considered.

Although the yields obtained are only fair, the ready availability of the starting materials and the simplicity of the process should make this an attractive path to the synthesis of certain bicyclo[2.1.1]hexanes. It is to be noted that the alternative route<sup>3</sup> is also a photochemical reaction so that scaling up these methods should present similar problems.

**Acknowledgment.**—The author wishes to thank Professor W. Albert Noyes, Jr., for his advice and encouragement. He is grateful to Dr. Sheldon Cremer for helpful discussions.

(5) The author is deeply grateful to Professor K. Wiberg of the University of Washington for making this spectrum available to him for comparison.

(6) The photochemistry was more complex in this instance and led to derivatives of cyclopropane too.

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R. SRINIVASAN

RECEIVED APRIL 26, 1961

**RING CLOSURE TO THE NORBORNYL SYSTEM BY ANCHIMERICALLY ASSISTED SOLVOLYSIS OF 2-( $\Delta^3$ -CYCLOPENTENYL)-ETHYL TOSYLATE\***

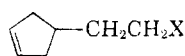
Sir:

2-( $\Delta^3$ -Cyclopentenyl)-ethanol (I) has been prepared by the addition of ethylene oxide to the Grignard reagent prepared from  $\Delta^3$ -cyclopentenyl bromide.<sup>1</sup> Phenylurethan of I, m.p. 60°; calcd. for C<sub>14</sub>H<sub>17</sub>O<sub>2</sub>N: C, 72.70; H, 7.41; N, 6.06; found: C, 72.53; H, 7.26; N, 6.06. The tosylate II was prepared by the method outlined by Tipson.<sup>2</sup> It was an oil down to -30°. The analytical

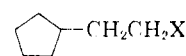
(\*) Presented before the Organic Division of the American Chemical Society at St. Louis, Missouri, March 27, 1961.

(1) Marian R. Rice, Thesis, Radcliffe College, 1957.

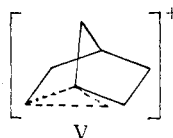
(2) R. S. Tipson, *J. Org. Chem.*, **9**, 238 (1944).



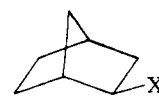
I, X = OH  
II, X = OTs



III, X = OH  
IV, X = OTs



V



VI, X = OH  
VII, X = OAc

sample still contained alcohol. Calcd. for a mixture of 88.7% II and 11.3% I: C, 62.13; H, 6.47. Found: C, 62.13; H, 6.57. These compounds showed infrared spectra consistent with the assigned structures. The corresponding saturated alcohol<sup>3</sup> III and its tosylate IV were prepared for comparative kinetic studies.

If the double bond does not participate anchimerically in the ionization of II, its rate of solvolysis in any given medium should differ inappreciably from that of IV, and would be expected to correspond to bimolecular displacement of tosylate ion by a solvent molecule and to increase in rate with the nucleophilic reactivity of the solvent. For the kinetic investigation three solvent mixtures were chosen with similar ionizing powers as reflected in their Grunwald-Winstein *Y* values (see Table I) but of widely different nucleophilic reactivities. Rates of appearance of *p*-toluenesulfonic acid in the solutions were followed conductometrically.

TABLE I  
SOLVOLYTIC RATE CONSTANTS (SEC.<sup>-1</sup>  $\times 10^4$ ) IN ABSENCE OF ADDED REAGENTS

Solvent	50% Ethanol (70°)	50% Acetic Acid (60°)	98% Formic acid (60°)
<i>Y</i> value	1.66	1.94	2.10
<i>k</i> <sub>1</sub> for IV	0.58	0.076	~0.003
<i>k</i> <sub>1</sub> for II	3.36	3.8	5.7
<i>k</i> <sub>II</sub> / <i>k</i> <sub>IV</sub>	5.8	50	~1900

As seen from the table, the solvolysis rate of the saturated IV declines about 200-fold in going from 50% alcohol to formic acid, while the solvolysis rate of the unsaturated II increases by 70%. Since any inductive effect of the double bond can only be unfavorable to ionization, the ratio *k*<sub>II</sub>/*k*<sub>IV</sub> is a measure of anchimeric driving force from the double bond, and this quantity amounts to 5.8 in 50% alcohol and about 1900 in formic acid.

The product of heating 0.341 g. of II in 50% acetic acid at 72° for 7 hours was isolated by neutralization and ether extraction. Vapor chromatography showed that 92% of the total product was a 60-40 mixture of *exo*-norbornyl acetate (VII) and *exo*-norborneol (VI), confirmed by comparison with known mixtures of these compounds. The mixture was converted into *exo*-norborneol (VI) by saponification with potassium hydroxide; this alcohol was isolated by continuous extraction with petroleum ether, careful evaporation of the solvent and sublimation of the VI as white crystals having the infrared spectrum of norborneol, identical with

(3) V. N. Ipatieff, W. W. Thompson and H. Pines, *J. Am. Chem. Soc.*, **73**, 553 (1951).