clopentenone), 1628 cm$^{-1}$ (conjd C=C); NMR $\delta_{(CH_3)_4Si}$ (CCl$_4$) 0.80 (s, 3 H), 0.92 (s, 3 H), 1.18 (s, 3 H), 1.68 (d of d, $J$ = 2 Hz, 3 H), 4.90 ppm (br absorption, 1 H); $m/e$ (70 eV) 234.162 (calcd 234.162); $[\alpha]^{25}$D −152° ($c$ 0.111, CHCl$_3$). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.64; H, 9.48. The uv absorption maximum at 251 nm indicated that the 1 hydrogen and the cyclopropane ring had the trans relationship in the photoproduct.[9] The cis relationship of the 1 hydrogen and the 10-hydroxyl group was assigned by analogy with the stereochemical results for related cases, e.g., the $\alpha$-santonin–isophotosantonic lactone type rearrangements.[7b,10] Subsequent transformations provided support for this assignment.

Our original objective was to convert **8** into (−)-globulol (**2a**) by introduction of the appropriate stereochemistry at positions 4 and 5 by reduction and conversion of the carbonyl group to a methylene group. While this objective has not been realized as yet, we have been able to prepare (−)-4-epiglobulol (**2b**) in good yield. On treatment of **8** with 2.2 equiv of lithium in liquid ammonia and addition of ammonium chloride a single dihydro ketone having the structure **9** was produced in ~97% yield. Hydroxy ketone **9** had the following spectral properties: mp 68–69°; ir $\nu_{max}$ (CCl$_4$) 3600 (free OH), 3420 (hydrogen-bonded OH), 1740 cm$^{-1}$ (cyclopentanone); NMR $\delta_{(CH_3)_4Si}$ (CDCl$_3$) 0.99 (s, 3 H), 1.06 (d, $J$ = 6.5 Hz, 3 H), 1.09 (s, 3 H), 1.12 (s, 3 H); $m/e$ (70 eV) 236.175 (calcd 236.178); $[\alpha]^{25}$D −86° ($c$ 0.072, CHCl$_3$). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.11; H, 10.27. Compound **9** was unchanged on treatment with base which indicated that the more thermodynamically stable 4 epimer had been produced. Piers and Cheng[10f] have reported that on lithium–ammonia reduction the tricyclic hydroazulene **10** related to **8** gave a dihydro product having a trans ring fusion and a 4$\beta$-methyl substituent. They pointed out that, when the ring fusion is trans, the 4$\alpha$-methyl group would be a destabilized by an eclipsed interaction with C-6. While this type of interaction would also exist in the 4$\alpha$ epimer of **9**, examination of models suggested that the 4$\beta$-methyl substituent might be destabilized to some extent by a steric interaction with the *endo*-methyl group on the cyclopropane ring. Thus it was hoped that a mixture of 4 epimers would be present at equilibrium. However, this was not the case, and no evidence for the presence of any of the 4$\alpha$ epimer of **9** was obtained.

Wolff–Kishner reduction of **9** afforded a single product which after chromatography on silica gel was isolated in 55% yield. This material showed mp 49–50°; ir $\nu_{max}$ (CCl$_4$) 3600 cm$^{-1}$ (OH); NMR $\delta_{(CH_3)_4Si}$ (CDCl$_3$) 0.94 (d, $J$ = 5.9 Hz, 3 H), 0.96 (s, 3 H), 1.02 (s, 3 H), 1.09 ppm (s, 3 H); $m/e$ (70 eV) 222.196 (calcd 222.198); $[\alpha]^{25}$D −16° ($c$ 0.115, CHCl$_3$). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.04; H, 11.79. The spectral properties of this alcohol were very similar to but not identical with those of natural (−)-globulol[11] and the compounds had slightly different GLC retention times on a 6 ft × ⅛ in. 10% Carbowax K-20M on Chromosorb W column.

These results indicated that the Wolff–Kishner reduction product was 4-epiglobulol, i.e., **2b**. This was confirmed by reaction of the alcohol with thionyl chloride in pyridine at 0° followed by treatment with sodium acetate in acetic acid (to dehydrohalogenate the 10-chloro compound which was partially formed as an intermediate in the reaction). A 55% yield of a 4:1 mixture of two olefins was obtained. The major component was collected by preparative GLC using a 10 ft × ¼ in. 20% SE-30 on Chromosorb W column and exhibited identical spectral properties (ir and NMR) with those of (−)-4-epiaromadendrene.[2,12] Thus it had the structure **1b**. This olefin showed a specific rotation ($[\alpha]^{25}$D +33° ($c$ 0.050, CHCl$_3$) of nearly the same magnitude but of opposite sign to that reported ($[\alpha]^{25}$D −31.4° ($c$ 0.881, CHCl$_3$)) for its enantiomer.[2] The minor product obtained from dehydration of **2b** exhibited spectral properties which corresponded to the endocyclic olefin structure **11**. The formation of the exocyclic olefin as the major dehydration product of **2b** confirmed the assignment of the cis relationship between the 1-hydrogen atom and the 10-hydroxy group in the photoproduct **8**.[13]

The above results show that cyclohexadienone photolysis provides an excellent method of preparing tricyclic hydroazulenes containing a cyclopropane ring. Possible routes to allow the conversion of **8** into natural (−)-globulol (**2a**) are being explored.

**Supplementary Material Available.** Procedures for the preparation of new compounds reported in this paper will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W. Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-809.

## References and Notes

(1) This investigation was supported by Public Health Service Grant No. Ca 12193 from the National Cancer Institute.

(2) G. Büchi, H. Hofheinz, and J. V. Paukstelis, *J. Am. Chem. Soc.*, **91**, 6473 (1969).
(3) J. A. Marshall and J. A. Ruth, *J. Org. Chem.*, **39**, 1971 (1974).
(4) D. Caine and P. F. Ingwalson, *J. Org. Chem.*, **37**, 3751 (1972).
(5) A. E. Greene, J. C. Muller, and G. Ourisson, *Tetrahedron Lett.*, 4147 (1971).
(6) D. Caine and J. T. Gupton III, *J. Org. Chem.*, **39**, 2654 (1974).
(7) (a) P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, **32**, 4118 (1967); (b) J. Streith and A. Blind, *Bull. Soc. Chem. Fr.*, 2133 (1968).

(8) The steroidal dienone, *O*-acetyl-1-dehydro-6$\alpha$,7$\alpha$-methylenetestosterone, which is related to **4a** is stable to uv irradiation in dioxane while the corresponding 6$\beta$,7$\beta$-methylene derivative which is related to **5** undergoes photochemical rearrangement in the expected manner: J. Pfister, H. Wehrli, and K. Schaffner, *Helv. Chem. Acta*, **50**, 166 (1967). For an explanation of the difference in the behavior of these isomeric sterodial systems which also appears to apply to the case of **4a** and **5**, see K. Schaffner, "Organic Reactions in Steroid Chemistry", Vol. II, J. Fried and J. A. Edwards, Ed., Van Nostrand-Reinhold, New York, N.Y., 1972, Chapter 13, pp 335–337.

(9) G. Büchi, J. M. Kaufmann, and H. J. E. Loewenthal, *J. Am. Chem. Soc.*, **88**, 3403 (1966).
(10) (a) D. H. R. Barton, P. De Mayo, and M. Shafiq, *J. Chem. Soc.*, 929 (1957); (b) D. Caine and J. B. Dawson, *J. Org. Chem.*, **29**, 3108 (1964); (c) P. J. Kropp, *ibid.*, 29, 3110 (1964); (d) E. Piers and K. F. Cheng, *Can. J. Chem.*, **45**, 1591 (1967); (e) E. Piers and K. F. Cheng, *Chem. Commun.*, 562 (1969); (f) E. Piers and K. F. Cheng, *Can. J. Chem.*, **48**, 2234 (1970).

(11) We are grateful to Professors F. Šorm and P. R. Jefferies for providing us with authentic samples of (−)-globulol.
(12) We are grateful to Professor G. Büchi for providing us with copies of spectra of (−)-aromadendrene and (−)-4-epiaromadendrene.
(13) See paragraph regarding the availability of supplementary material for this paper.

*School of Chemistry*
*Georgia Institute of Technology*
*Atlanta, Georgia 30332*

**Drury Caine***
**John T. Gupton III**

*Received December 10, 1974*

---

## Highly Fluorinated Acetylenes. Preparation and Some Cyclization Reactions

*Summary:* Simplified preparations of new highly fluorinated acetylenes are described and a representative model undergoes thermal cycloaddition reactions to afford a cyclohexadiene, triazole, and cyclobutene.

*Sir:* Highly fluorinated acetylenes have been prepared previously by multistep synthetic routes[1] that invariably involve a high-pressure reaction. A recent report,[2] disclosing the formation of a highly fluorinated acetylene from the copper initiated coupling between a perfluoro ($F^3$) primary alkyl iodide and an iodoacetylene, prompts this communication. We have found that fluorinated acetylenes also can be prepared from commercially available materials in ordinary apparatus by the following sequence of reactions.

$$R_fI + PhCH{=}CHBr \xrightarrow{i^a} \underset{70\text{–}95\%}{R_fCH{=}CHPh} \xrightarrow[2.\ iii]{1.\ ii} \underset{60\text{–}90\%}{R_fC{\equiv}CPh}$$

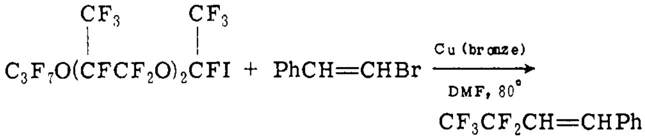
$$R_fI + ICH{=}CHCl \xrightarrow{i} R_fCH{=}CHCl \xrightarrow{iii} \underset{50\text{–}70\%}{R_fC{\equiv}CH}$$

$R_f$ = $F$-alkyl or alkylene ether

[a] i, DMF or DMAC, Cu (bronze), 100–120°, 16 hr; ii, $Br_2$, Freon 113, 25°, ~1–4 hr; iii, powdered KOH, distillation.

Several new fluorinated acetylenes prepared by these reactions which include, to the best of our knowledge, the first highly fluorinated diacetylene, are shown in Table I.

The reaction between $F$-alkyl iodides and halo olefins, the first step in our sequence, has been reported[4] for primary $F$-alkyl iodides; similar reactions using secondary $F$-alkyl[5] and $F$-vinyl[6] iodides also have appeared in the literature. We have observed that this reaction can be extended to certain $F$-alkylene ether iodides. Thus, structures such as $R_fOCF_2CF_2I$ give the expected product while $R_fOC(CF_3)FI$ structures afford only decomposition products involving scission at the C—O bond of the latter fluoro ether.



$$C_3F_7O(\overset{CF_3}{\overset{|}{C}}FCF_2O)_2\overset{CF_3}{\overset{|}{C}}FI + PhCH{=}CHBr \xrightarrow[DMF,\ 80^\circ]{Cu\ (bronze)} CF_3CF_2CH{=}CHPh$$

With regard to the above reaction it is suspected that the expected organocopper reagent forms and then decomposes to an $F$-ethylcopper species which subsequently reacts to give the observed product. This particular reaction is under further experimental scrutiny.

Once prepared, the highly fluorinated olefins can be converted to their corresponding acetylenes; however, in some cases complications arise. Compounds of the general structure $R_fCH{=}CHPh$ brominate and dehydrobrominate (KOH) smoothly to give the expected acetylene as the sole product. In contrast, the formation of $R_fC{\equiv}CH$ is accompanied by $R_fH$ and other low boiling components. Since the $R_fCH{=}CHCl$ precursors studied were >95% trans, it is suspected that, on KOH treatment, trans loss of a positive chlorine ($Cl^+$) and negative $R_f$ ($R_f^-$) leads to $R_fH$ in competition with the acetylene-forming cis HCl loss.

Along these lines, it is noteworthy that the following reaction gives the internal acetylene only as a minor liquid product.

$$trans\text{-}C_7F_{15}CH{=}CHCF_3 \xrightarrow[2.\ KOH]{1.\ Cl_2}$$
$$[C_7F_{15}CCl{=}CHCF_3 \text{ and/or } C_7F_{15}CH{=}CClCF_3] \xrightarrow{KOH}$$
$$C_7F_{15}H + C_7F_{15}C{\equiv}CH + C_7F_{15}C{\equiv}CCF_3$$

(4.5:4:1 relative ratio)

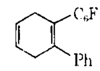
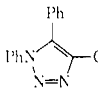
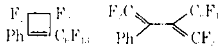
Our interest in highly fluorinated acetylenes stems from a possible polymer-forming reaction[7] between a diacetylene and various diunsaturates. Model reactions now have demonstrated that a representative highly fluorinated acetylene undergoes thermal [2 + 4], [2 + 3], and [2 + 2] cyclizations. Table II lists several new adducts from the interaction of $F$-hexyl-2-phenylacetylene and various unsaturated compounds indicative of the scope of these reaction systems.

### Table I
### Fluorinated Acetylenes

| Acetylene[a] | Bp, °C (mm) | Yield from fluoro olefin, % |
|---|---|---|
| $C_8F_{17}C{\equiv}CH$ | 132–134 | 71 |
| $C_6F_{13}C{\equiv}CPh$ | 58–61 (0.2) (bp[b] 227) | 84 |
| $(CF_2)_6(C{\equiv}CPh)_2$ | 160 (0.1) | 60 |
| $(CF_3)_2CFOCF_2CF_2C{\equiv}CPh$ | 68–71 (18) | 65 |
| $CF_3CF_2C{\equiv}CPh$ | 84–87 (50) | 92 |

[a] The acetylenes have been characterized by infrared ($R_fC{\equiv}CH$: CH, 3.0 μ, C≡C, 4.65 μ; $R_fC{\equiv}CPh$: C≡C, 4.45 μ), $^1H$ and $^{19}F$ NMR, and either mass spectroscopy or elemental analysis. [b] Reference 2.

### Table II
### Products[a] from $C_6F_{13}C{\equiv}CPh$ Cycloadditions

| Reactant | Products | Yield, % |
|---|---|---|
| $CH_2{=}CHCH{=}CH_2$ |  | 75 |
| $PhN_3$ |  (mp 134–135°) | 76 |
| $CF_2{=}CF_2$ |  (19:2 relative ratio) | 70 |

[a] The acetylene adducts have been characterized by $^1H$ and $^{19}F$ NMR, infrared, and either mass spectroscopy or elemental analysis.

The above reactions are clean; unreacted starting material accounts for the material balance (>98%).

**Acknowledgment.** We gratefully acknowledge National Aeronautics and Space Administration support under Contract NAS2-8156. Thanks are due to Dr. E. C. Stump, Jr., for his interest in this work and Mr. B. W. Cameron for his capable technical assistance.

## References and Notes

(1) R. N. Haszeldine and K. Leedham, *J. Chem. Soc.*, 3483 (1952). For recent reviews, see W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, Inc., New York, N.Y., 1969, pp 336–343; R. D. Chambers, "Fluorine in Organic Chemistry," Wiley, New York, N.Y., 1973, pp 189–199.

(2) P. L. Coe and N. E. Milner, *J. Organometal. Chem.*, **70**, 147 (1974).

(3) "F" is used in place of "perfluoro" according to recently approved fluorocarbon nomenclature; see J. A. Young, *J. Chem. Doc.*, **14** (2), 98 (1974).

(4) J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *Chem. Commun.*, 1259 (1967), *J. Chem. Soc., Perkin Trans. 1*, 639 (1972).

(5) V. C. R. McLoughlin and J. Thrower, *Tetrahedron*, **25**, 5921 (1969).

(6) R. J. De Pasquale and C. Tamborski, *J. Org. Chem.*, **34**, 1736 (1969).

(7) For examples of polymer-forming reactions between diacetylenes and bisdienes, see J. K. Stille, F. W. Hanes, R. O. Rakutus, and H. Mukamal, *J. Polymer Sci.*, **B4**, 791 (1966); C. L. Schilling, J. A. Reed, and J. K. Stille, *Macromolecules*, **2**, 85 (1969). For a similar reaction of a bis-1,3-dipolar reagent, see J. K. Stille and L. D. Gotter, *J. Polymer Sci.*, **B(6)**, 11 (1968).

*PCR, Inc.*
*Gainesville, Florida 32602*

**Ralph J. De Pasquale***
**Calvin D. Padgett**

*National Aeronautics and Space Administration*
*Moffett Field, California 94035*

**Robert W. Rosser**

*Received December 16, 1974*