

α -BROMOCYCLOPROPYL TRIFLUOROACETATES AS CYCLOPROPANONE PRECURSORS

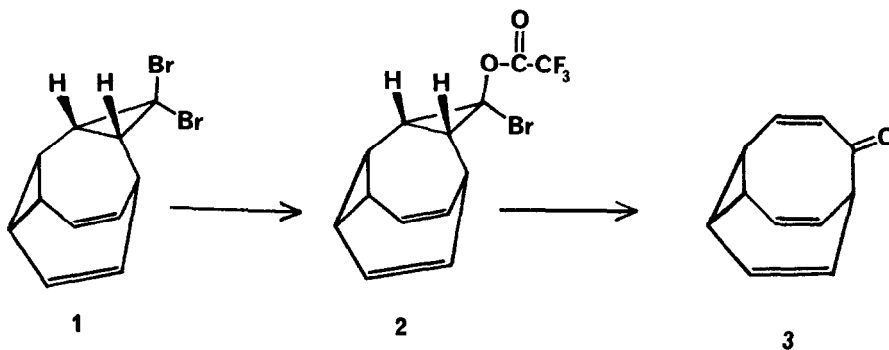
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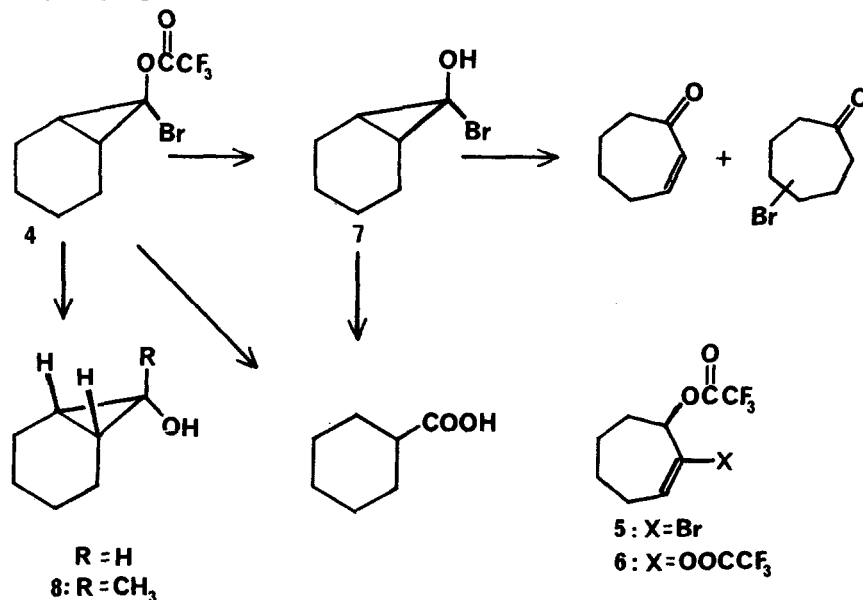
(Received in USA 24 December 1973; received in UK for publication 1 February 1974)

The use of the cyclopropanone function and its derivatives as synthetic intermediates has been limited by the inaccessibility of these compounds.¹ Dihalocyclopropanes, while generally available from simple olefins by the addition of carbenoid species², have heretofore only allowed thermal or solvolytic ring expansions.^{3,4} We have been studying ring expansion reactions of C₁₀H₁₀ hydrocarbons as a route to the family of homologous ketones and recently reported the conversion of dibromide 1 to homobullvalenone (3)⁵ via the unusual α -bromotrifluoroacetate 2. We report here that this interesting class of compounds is generally available from precursors with even a modest barrier to ring-opening and at once affords a stereospecific route for the incorporation of an angular carboxyl group, a route to ring-expanded enones, and a stereospecific cyclopropanol synthesis.



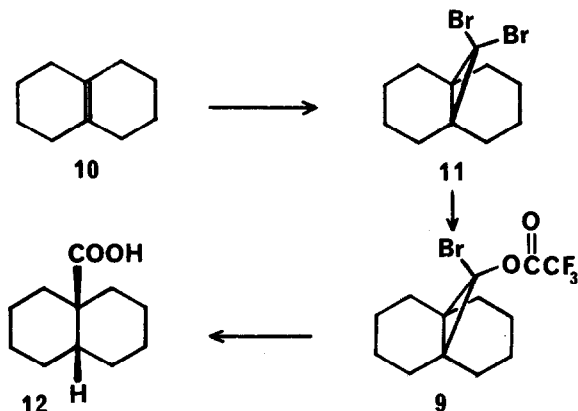
Treatment of 7,7-dibromonorcarane with silver trifluoroacetate in benzene at 80° afforded equal amounts of an α -bromocyclopropyl trifluoroacetate (**4**) and ring-opened ester **5**⁶ in 85-90% combined yield. The structure of **4** was apparent from its spectral data⁷ and subsequent chemical transformations. Compound **4** could be isolated and purified by glpc (SE-30) but it decomposed upon standing in air at room temperature. Extended treatment of **4** under the reaction conditions gave bis-trifluoroacetate **6**. The reaction of **4** with potassium hydroxide in dioxane gave a quantitative yield of cyclohexane carboxylic acid. In contrast, 9,9-dibromobicyclo[6.1.0]nonane gave a 10:1 mixture of trans and cis ring-opened allylic trifluoroacetates, the structures of which were confirmed by conversion to the known alcohols.^{4c}

With lithium aluminum hydride in ether at -78°, **4** gave an unstable hydroxybromide, **7**, which was converted to cyclohexane carboxylic acid upon treatment with mild base and afforded cycloheptenone⁸ (35%) and bromocycloheptanones^{4e} upon warming. Hydroxybromide **7** could be isolated by careful glpc but decomposed rapidly in air at room temperature. In this regard the properties of **7** were quite similar to those reported for halocyclopropanols derived from cyclopropanones.¹⁰



Reaction of $\underline{4}$ with sodium borohydride gave exclusively endo-bicyclo-[4.1.0]heptan-7-ol⁹ in ca. 60% yield. Similarly, treatment of $\underline{4}$ with methyl-lithium in ether at room temperature and aqueous boric acid work-up led to the corresponding methyl carbinol ($\underline{8}$) in 85% yield.¹¹ Upon standing in chloroform-d, $\underline{8}$ was converted to methyl cyclohexyl ketone in 85-90% yield.

The bromotrifluoroacetate $\underline{9}$, derived from octalin ($\underline{10}$), was prepared in 90% yield in the same manner as $\underline{4}$ and had similar properties.¹² The exclusive formation of cyclopropyl products in this case is in marked contrast to the behaviour of $\underline{11}$ toward other silver reagents which has been reported to produce predominantly an enone with carbon skeleton rearrangement.^{6,13} Hydrolysis of $\underline{9}$ with potassium hydroxide in dioxane gave a single carboxylic acid in near-quantitative yield which was shown to be cis-9-decalin carboxylic acid ($\underline{12}$) by comparison to the authentic material.¹⁴ This sequence, $\underline{10} \rightarrow \underline{9} \rightarrow \underline{12}$, represents a new stereospecific method for the introduction of an angular carboxyl group which is very attractive in view of the high yields and mild conditions of each step.



Acknowledgements: Financial support of this research by The University of Michigan, Research Corporation and the Merck Foundation for Faculty Development is gratefully acknowledged.

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7. λ : μ /e (relative intensity) 288(1.0), 286(1.0), 246(10), 244(10), 219(11.5), 217(11.5), 207(95), 191(20), 189(20), 174(35.5), 172(40); ir (CCl_4) 3010(w), 2944, 2860, 1802(vs), 1465, 1449, 1352, 1230(vs), 1180(vs), 1132(vs), 1092, 1056, 1017(w), 994(w), 902, 879 cm^{-1} ; nmr(CDCl_3) δ 1.41 (4H, m), 1.65 (6H, m).
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9. U. Schöllkopf, J. Paust, A. Al-Azrak and H. Schumacher, Ber., 99, 3391 (1966), we thank Professor Schöllkopf for pmr spectra.
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11. δ : ir(CCl_4) 3590, 3445(br), 2930, 2855, 1451, 1330, 1170, 1102, 1020 cm^{-1} ; nmr(CCl_4) δ 0.62(2H, t, $J=3$ Hz), 1.32 (3H, s), 1.1-1.4 (2H, m), 1.5-2.0 (6H, m), variable (1H, br s).
12. δ : ir(CCl_4) 2938, 2860, 1807, 1451, 1350, 1234, 1181, 1142, 1105, 1067, 1017, 978, 936, 916, 898 cm^{-1} ; nmr(CDCl_3) δ 1.35(8H, m), 1.65(8H, m).
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14. Spectrum #9823 from the Collection of the Institute for Organic Chemistry, Technical University of Berlin.