α-BROMOCYCLOPROPYL TRIFLUOROACETATES AS CYCLOPROPANONE PRECURSORS

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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) 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 (5) and ring-opened ester 6 in 85–90% combined yield. The structure of 5 was apparent from its spectral data and subsequent chemical transformations. Compound 5 could be isolated and purified by glpc (SE-30) but it decomposed upon standing in air at room temperature. Extended treatment of 5 under the reaction conditions gave bis-trifluoroacetate 7. The reaction of 5 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.

With lithium aluminum hydride in ether at -78°, 5 gave an unstable hydroxybromide, 7, which was converted to cyclohexane carboxylic acid upon treatment with mild base and afforded cycloheptenone (35%) and bromocycloheptanones 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.

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

The bromotrifluoroacetate 2, derived from octalin (10), was prepared in 90% yield in the same manner as 11 and had similar properties. The exclusive formation of cyclopropyl products in this case is in marked contrast to the behaviour of 11 toward other silver reagents which has been reported to produce predominantly an enone with carbon skeleton rearrangement. Hydrolysis of 2 with potassium hydroxide in dioxane gave a single carboxylic acid in near-quantitative yield which was shown to be cis-9-decalin carboxylic acid (12) by comparison to the authentic material. This sequence, 10→2→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.

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REFERENCES


7. M/e (relative intensity) 288(1.0), 286(1.0), 284(1.0), 283(1.0), 219 (11.5), 217(11.5), 207(95), 191(20), 189(20), 174(35.5), 172(40); ir (CCl4) 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(CDC13) δ 1.41 (4H, m), 1.65 (6H, m).


11. δ: ir(CCl4) 3590, 3455(br), 2930, 2855, 1451, 1330, 1170, 1102, 1020 cm⁻¹; nmr(CDC13) 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 a).

12. δ: ir(CCl4) 2938, 2860, 1807, 1451, 1350, 1234, 1181, 1142, 1105, 1067, 1017, 975, 936, 916, 898 cm⁻¹; nmr(CDC13) δ 1.35(8H,m), 1.65(8H, m).
