

ON THE REORGANIZATION OF HOMOBULLVALENYL CARBONIUM IONS:

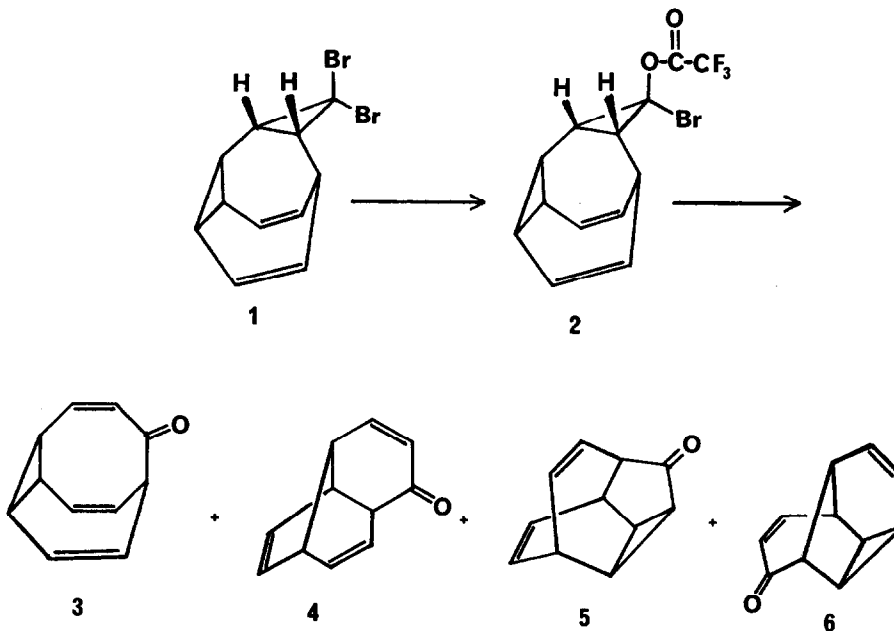
A CONVENIENT SYNTHESIS OF HOMOBULLVALENONE

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There has been continued intense interest in the reorganization of $(CH)_n$ hydrocarbons and ions particularly with regard to expectations based on theoretical grounds.¹ Toward this end we recently described the generation of enone 4 upon silver assisted solvolysis of dibromide 1.^{2a} We report here the ready conversion of dibromide 1 to the skeletally related α -bromotrifluoroacetate, 2.^{2b} Treatment of 2 with silver trifluoroacetate affords preparative quantities of homobullvalenone (3)^{3a} confirming our prior suggestion of its intermediacy on the path to 4. More importantly, the isolation of two additional isomeric ketones appears to give some additional insight into the predominant modes of rearrangement in this manifold.



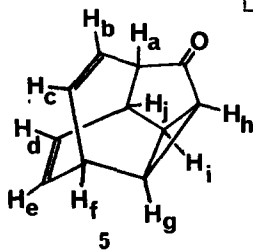
Treatment of 1 with three equivalents of anhydrous silver trifluoroacetate in benzene at reflux for 20 min lead smoothly to 2 in 80-90% yield. Bromotrifluoroacetate 2 is moderately stable to heat and could be isolated and purified by glpc but decomposed upon standing in air at room temperature. The structure of 2 was apparent from its spectral characteristics,⁴ particularly its pmr spectrum which was virtually identical to that of 1.² The singular difference, a higher-field resonance position of the two cyclopropyl protons adjacent to the annelated carbon, suggests a proximate anisotropic effect of the trifluoroacetate substituent and, accordingly, the anti-stereochemistry.

Further treatment of 2 with silver trifluoroacetate in refluxing benzene-acetic acid (1:3) and preparative column chromatography afforded 3^{3a} in 40-50% yield. Examination of the remainder of the reaction mixture revealed the presence of three additional compounds,⁵ 4,² 5, and 6.^{3b}

The structure of 5 was discerned from its spectral data.⁶ Particularly definitive was the 100 MHz pmr spectrum which was nearly first order. Spin decoupling of individual resonances allowed complete assignment of the spectrum (Table I). The vicinal olefinic couplings ($J_{b,c} = 9.5$ Hz and $J_{d,e} = 8.0$ Hz) are inconsistent with five-membered or smaller rings,⁷ the strong coupling of one bridgehead proton (H_f) to two vinyl protons (H_c and H_e) indicates a divinyl

Table I: PMR Spectrum of 5^a

δ	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i	H_j	Apparent Multiplicity	Δ_{Eu}^b
H_a	2.85	7.0						1.0		8.0	t,d	3.00
H_b		5.42	9.5								d,d	1.47
H_c			6.58			9.5					t	0.77
H_d				5.91	8.0					7.5	t	0.59
H_e					6.66	8.0					t	0.44
H_f						3.19	7.0	1.0?			q,d	0.71
H_g							1.97	8.0	7.0	2.0	q,d	0.95
H_h								2.04	5.5		d,d,m	2.67
H_i									2.50	7.0	d,t	1.02
H_j										3.51	q,m	1.16

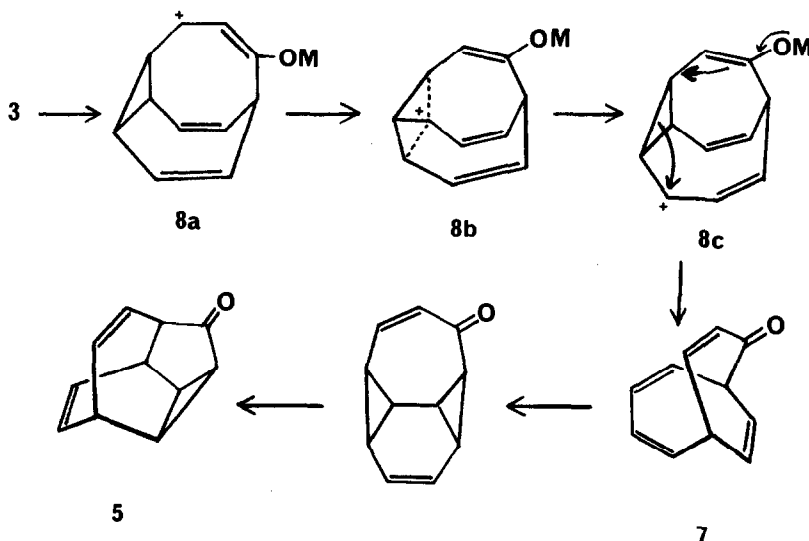


a) Diagonal elements are chemical shifts (δ) obtained in $CDCl_3$; off diagonal elements are coupling constants (Hz) assigned by decoupling; b) for $Eu(fod)_3$ in $CDCl_3$.⁹

methine structural subunit and the insulation of the three cyclopropyl protons from significant vinyl coupling eliminates several similar isomers. Further support for this structural assignment is derived from the europium (fod)₃-shifted spectrum⁸ in which two bridgehead protons (H_a and H_b) are strongly shifted to lower field while the remaining protons experience relatively modest shifts.

We have explored the possibility that 5 or 6 may derive subsequently from 3. Thus, treatment of 3 further under the reaction conditions afforded negligible amounts of these products. Also, treatment of 3 with silver trifluoroacetate in toluene at 100°C afforded only 4 in analogy to the thermal^{3c} and photochemical¹⁰ results.

Compound 5 is also related to the known ketone 7^{3d} by successive Cope Rearrangement-reverse Diels-Alder reaction. While we have not found 7 among the solvolysis products of 2, we have demonstrated that 7 is an efficient thermal precursor of 5. Thus, treatment of 3 with BF₃ afforded 7 which upon heating ($\tau_{1/2}^{80^\circ} = 4.75$ hr) or attempted glpc gave 5. Similarly, treatment of 3 with HgBr₂ at temperatures above 130° yielded 5, presumably also via 7.¹¹ That 7 arises smoothly from 3 by Lewis acid catalysis is also significant and suggestive of a relatively low-energy rearrangement path through ions of the much publicized type 8.¹² This and other facets of carbonium ion rearrangements in this manifold remain to be more fully elaborated.



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4. 3-Bromo-tetracyclo[3.3.3.0.^{2,4,8,9}]undeca-6,10-dien-3-yl trifluoroacetate (2): M/e (relative intensity) (45eV) 336(5.42), 334(5.42), 255(9.49), 254(10.85), 222(10.5), 220(10.2), 158(67.1), 140(67.1), 140(100), 130(11.9), 129(64.4), 128(100), 114(54.2), nmr ($CDCl_3$) 1.7 (2H, dd, $J = 2, 4$ Hz), 2.5(2H,m), 3.19(4H,m) 5.75(2H, t, $J = 9$ Hz); ir (CCl_4), 3060, 2060, 1790(s), 1370, 1340, 1320, 1220, 1180(vs), 1125(vs); ir (neat) 930, 895, 829, 765, 749, 730 cm^{-1} .
5. Compound, relative amount, relative glpc retention time on 3%SE-30: 3, 3.8, 2.13; 4, tr, 1.00; 5, 1.9, 1.96; 6, 1.0, 1.87.
6. Tetracyclo[5.4.0.0.^{2,11,0^{4,10}}]undeca-5,8-dien-3-one(5): m.p. 56.5-57.8°; M/e (relative intensity) (70 eV) 158 (100), 141 (37.7), 129 (82.5), 115 (56.5), 78 (60.5), 51 (14.9); ir (CCl_4) 3036, 2945, 1722, 1713, 1200, 1150, 888, 903, 850, 680, 654 cm^{-1} ; Elemental analysis was within $\pm 0.3\%$ of expected values.
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