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SYNTHESIS OF BICYCLO[4.3.2]UNDECA-2,4,8,10-TETRAEN-7-ONE.
I. ANIONIC ACCELERATION OF A $C_{10}H_{10}$ MULTICENTER REARRANGEMENT

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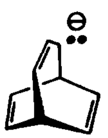
Current theoretical understanding of the stability of the 7-norbornadienyl cation[1] requires that the anions, 1 and 2, and the cation 3 also be "bicycloaromatic". Supporting evidence, albeit incomplete, is thus far available only in the case of 1[2]. Covalent derivatives of 2 have been described[3,4] but not the anion. Not even derivatives are available in the case of 3 nor, indeed, is any bicyclo[4.3.2]undecane at any level of unsaturation.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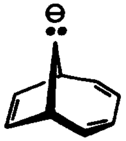
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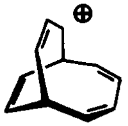
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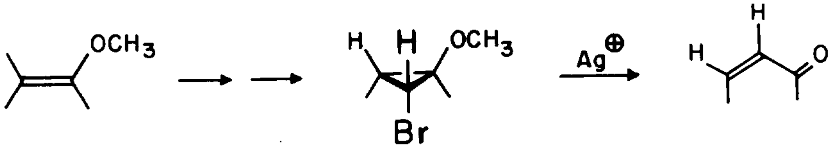
Our synthetic approach to an appropriate precursor of 3 exploits the homologative sequence



previously used to prepare homobullvalenone[5]. Although ultimately successful**, the course of

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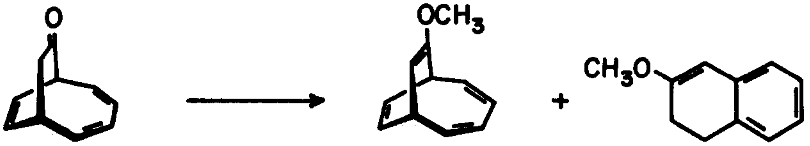
(**) Cf. accompanying communication.

these transformations was enlivened by two surprises. We here draw particular attention to one of them, an unexpectedly facile rearrangement, in part because our observations fruitfully supplement those recently reported by Press and Shechter.[6]



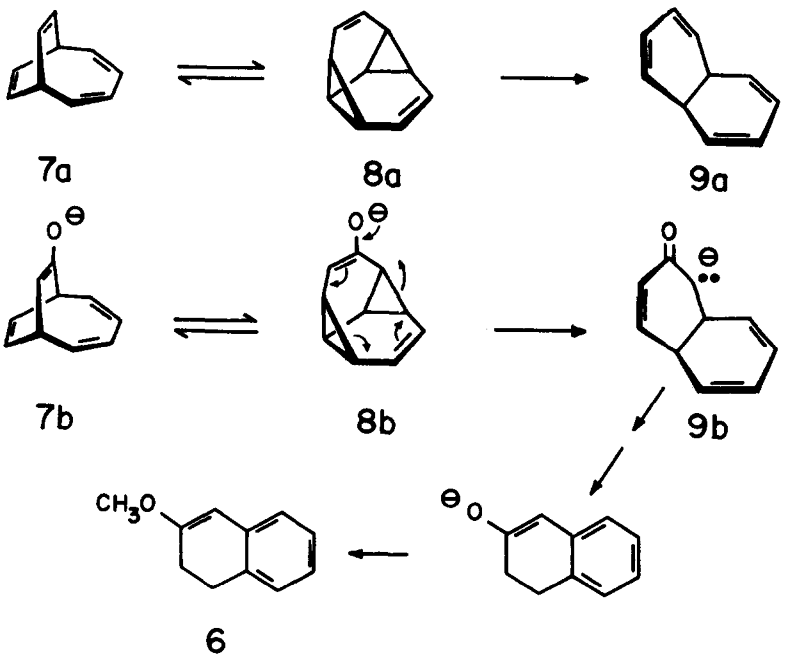
4 5 6

They report 5, the starting material of our independently developed homologative sequence[*], to be the exclusive product of conventional O-methylation (potassium *tert*-butoxide, methyl fluorosulfonate, hexamethyl phosphoramide, 5°). Unfortunately, they provide no evidence of its homogeneity nor proof of its structure. In our hands, closely similar conditions (potassium *tert*-butoxide, dimethyl sulfate, dimethyl sulfoxide or dimethyl formamide, 0-10°) produced samples of 5 that were invariably contaminated by the difficultly separable 6. Addition of dimethyl sulfate solution, almost immediately following that of the potassium *tert*-butoxide, served to minimize but never quite to eliminate such contamination. If addition were delayed for as long as 20 min, only 6 was obtained. Large scale (*ca*. 10 g) preparations of relatively pure 5 (mp 44°, 46% from bicyclo-[4.2.1]nona-2,4,7-trien-9-one[4]) were most efficiently achieved under conditions of deliberately incomplete deprotonation of 4.

There can be little doubt that the enolate anion of 4 (7b) suffers a unimolecular rearrangement whose terminus is similar to that of the parent hydrocarbon (7a→9a)[7]. But 7b does so *more rapidly by a factor of ca*. 10^{10}[**].

(*) Privately communicated to Professor Shechter 11/26/71.

(**) From $\Delta H^{\ddagger} = 34$ kcal/mol, $\Delta S^{\ddagger} = -5$ cal/mol-deg for 7a→9a.[8]



The scheme (above) rationalizes this acceleration within the context of the conventially accepted (if, superficially, thermally forbidden) ring opening of 8a to 9a.[7] The representation of a resonance stabilized intermediate (here 9b) is used to imply a diminished activation barrier to a thermodynamically attractive but otherwise quite sluggish process (8→9). Similar rationalizations have been applied to the facile anionic rearrangement of 7-norbornadienol to 7-tropyl ethers[9] as well as to the anion-promoted cleavage of cyclobutanes to dienes.[10]

These clearly serve to organize otherwise scattered experimental observations. Nevertheless, we believe that they obscure more than they reveal. In particular, they hide the inability of a first order MO approach to accommodate profound substituent effects. Nor do they recognize the critical role of the counter-ion. For such reasons, we regard the above scheme as much more a manifestation of current ignorance than as a serious mechanistic proposal.

Apart from its melting point, 5 was characterized by concordant ir (1670 cm^{-1}) and pmr spectra: τ (CCl$_4$) = 3.67 (m, 2.05), 4.25 (m, 4.01), 5.38 (d, J = 6.5 Hz, 0.98), *ca*. 6.70 (m containing s at τ = 6.58 ppm, 4.96) ppm, as well as by elemental analysis (C, 82.38; H, 7.67; Calcd: C, 82.46; H, 7.55). The spectroscopic properties of 6 (ir 1635 cm^{-1}, pmr τ = 3.08 (m, 4.08), 4.55 (s, 1.03), 6.38 (s, 2.93), 7.16 (m, 1.96), 7.75 (m, 2.00 ppm) were indistinguishable from those of an independently synthesized sample.[11]

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