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CYCLOBUTYL NEIGHBORING GROUP EFFECT ON THE STABILITY OF BICYCLO-[2.2.2]OCTYL BRIDGEHEAD CARBENIUM IONS [**]

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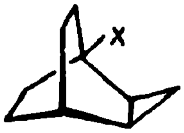
Summary: Solvolysis of the novel bridgehead cyclobutyl methyl chloride 4b proceeds without skeletal rearrangement. Its relative rate is the first unequivocal proof for a small, but significant ability of the cyclobutyl group to stabilize an adjacent positively charged center.

The unique stabilizing power of cyclopropyl groups on neighboring cationic centers is well documented [1]. Although the molecular orbital description of the cyclobutane ring [2] renders a similar electron donating effect possible, the literature records no examples which unequivocally confirm this expectation. The significant rate enhancements previously reported for the solvolysis of cyclobutyl methyl derivatives have to be attributed, at least in part, to strain release in the transition state, because these reactions were accompanied by ring enlargements to cyclopentyl systems [3, 4]. Therefore, with our succesful investigations on polycyclic cyclopropyl carbinyl systems [5] in mind, we chose to study the solvolysis kinetics of the bridgehead cyclobutyl methyl derivative 4 in comparison to the known reference data for 1, 2 and 3.

1



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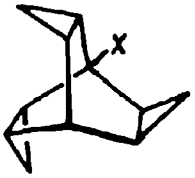

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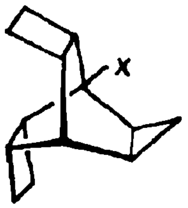
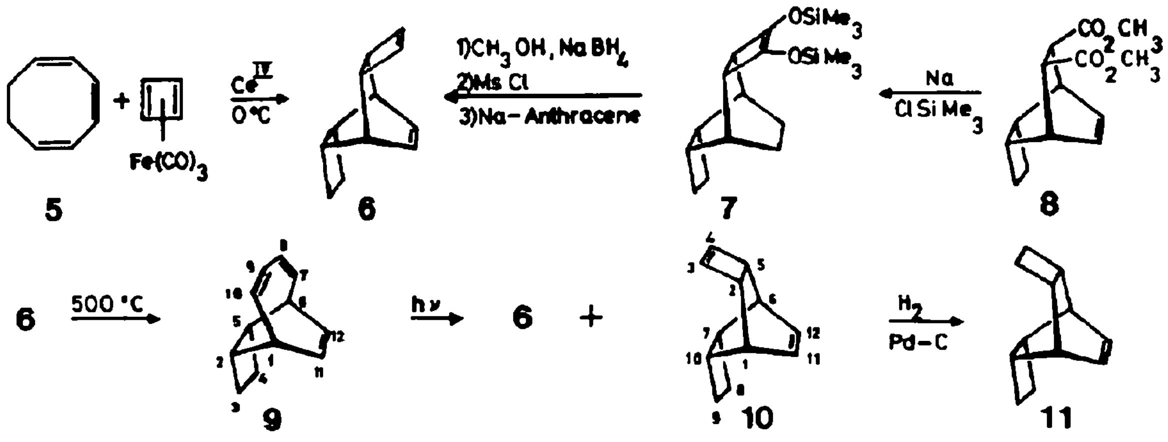


4

a) X = H b) X = Cl c) X = OH d) X = OEt

The key precursor exo,exo-tetracyclo[4.4.2.0^{2,5}.0^{7,10}]dodeca-3,11-diene (**6**) to the hydrocarbon **4a** was prepared either by the cycloaddition of cyclobutadiene, generated in situ from its iron tricarbonyl complex, to 1,3,5-cyclooctatriene (**5**) (95 % yield) or starting with the Diels-Alder adduct of maleic anhydride to **5** [6]. Acyloin condensation of the dimethyl ester **8**, obtained in 82 % yield from this adduct, in the presence of trimethylsilyl chloride [7] gave **7** (78 %). **7** was reduced with sodium borohydride in methanol, the resulting diol was transformed to the corresponding dimesylate, which upon reductive elimination with anthracene sodium led to **6** (overall yield 69 %). Gas-phase pyrolysis (flow system, 500 °C, 1 torr) of **6** yielded the exo-tricyclo[4.4.2.0^{2,5}]-dodeca-7,9,11-triene (**9**) (35 %, gc-isolated) along with 40 % unreacted **6** and traces of dihydronaphthalene (1.5 %) and naphthalene (1 %).



Irradiation of **9** (1 % in pentane, r.t.) through quartz afforded the two stereoisomeric dienes **6** and **10** in a ratio of 2 : 1 (80 % total) which were separated by column chromatography on silver nitrate impregnated silicagel.

Catalytic hydrogenation of **10** proceeded in two steps, thus the monoene **11** could be isolated from **10** after take-up of 1 equivalent of hydrogen. **11** was cyclopropanated with methylene iodide/diethylzink to the endo,exo,syn-pentacyclo-[4.4.3.0^{2,5}.0^{7,10}.0^{11,13}]tridecane (**4a**) (32 % gc-isolated).

Photochlorination of 4a with t-butyl hypochlorite [5] gave the bridgehead chloride 4b[8] as the major product along with isomeric chlorides. In 80 % aqueous dioxane 4b solvolyzed without skeletal rearrangement to the corresponding alcohol 4c [8].

The solvolysis rate of 4b (see table 1), which was determined conductometrically[9], is substantially larger than those of the reference compounds 1b and 2b [5]. Any interpretation of this result has to take into account, that the inductive effect of a cyclobutyl group [10] must be intermediate between the large negative value for a cyclopropyl and the positive one for the cyclopentyl group. A reasonable estimate of the cyclopentyl effect in bicyclo[2.2.2]octane anellated systems can be made from the solvolysis rate of 1-chloro-tricyclo[5.2.2.$0^{2,6}$]undecane 14b [8], synthesized from the cycloadduct 13 of ethyl 1-cyclohexa-1,3-diencarboxylate (12) by catalytic hydrogenation, ester hydrolysis and lead tetraacetate decarboxylation in the presence of N-chlorosuccinimide (44 % overall yield). 14b solvolyzes about 95 times faster than 1b (see table 1).

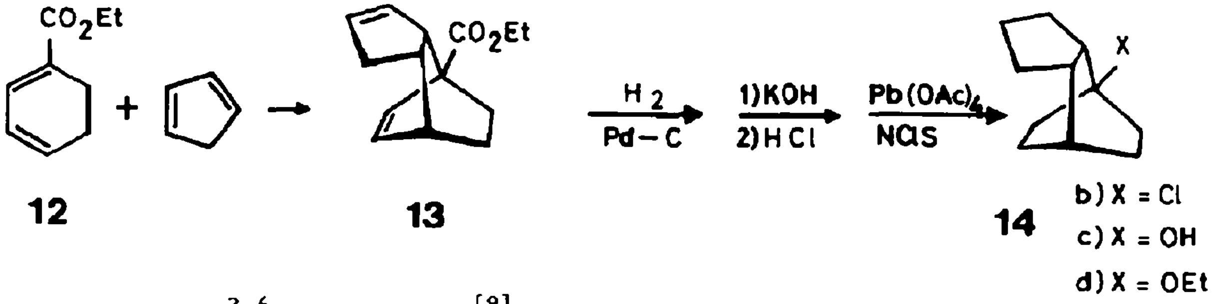


Table 1. Rates of solvolysis of the bridgehead chlorides 1b - 4b and 14b in 80 % aqueous ethanol

Compd	$k_{25}[sec^{-1}]$	k_{rel}	$\Delta H^{\ddagger}$[kcal/mol	$\Delta S^{\ddagger}$[Clausius]
1b [a]	$2.1 \cdot 10^{-12}$	$\boxed{1.0}$	-	-
2b [b]	$6.1 \cdot 10^{-8}$	$2.9 \cdot 10^{4}$	20.6	-19
3b [b, c]	$5.8 \cdot 10^{-4}$	$2.8 \cdot 10^{8}$	20.2 [c]	-10 [c]
4b [c]	$1.5 \cdot 10^{-5}$	$7.1 \cdot 10^{6}$	22.3 [c]	-10 [c]
14b [d]	$2.0 \cdot 10^{-10}$	$9.5 \cdot 10^{1}$	25.8 [d]	-11 [d]

[a] Cf. ref.[5]. [b] From ref. [5b]. [c] Determined in 80 % aqueous dioxane [11].
[d] Determined in 60 % aqueous ethanol [11].

A second difficulty in interpreting the observed rate ratio arises from the fact, that cyclobutane anellation onto a bicyclo[2.2.2]octane skeleton increases its rigidity to an unknown extent[12]. Therefore, it can only be assumed that the rate enhancement due to the α-cyclopropyl group in **4b** is somewhere intermediate between that in **2b** ($2.9 \cdot 10^4$) and that of a single cyclopropyl group in 1-chlorotrishomobarrelene (**3b**) ($6.5 \cdot 10^2$) [5b]. With these limiting factors the rate enhancing effect of a single cyclobutyl group in **4b** amounts to a value between 15.6 and 104. The pure conjugative effect should be somewhat larger corresponding to the slightly negative inductive effect of the cyclobutyl group[10].

References and footnotes

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[8] Spectroscopic and elemental analysis data for all new compounds are in full accord with the proposed structures.

[9] Cf. R.N. McDonald, G.E. Davis, *J. Org. Chem.* **38**, 138 (1973).

[10] Cf. J.D. Roberts, V.C. Chambers, *J. Am. Chem. Soc.* **73**, 5030 (1951).

[11] k_{25} and k_{rel} for 80 % aqueous ethanol were calculated using the Grundwald-Winstein equation with $m = 1.11$, E. Grunwald, S. Winstein, *J. Am. Chem. Soc.* **70**, 846 (1948).

[12] For the corresponding cyclopropane anellated systems this effect could be corrected for by observing the rate changes in the complete series including the symmetrical trishomobarrelene derivative[5].

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