syn- and *anti*-7-Chloro-7-azabenzonorbornadiene

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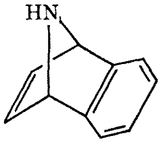
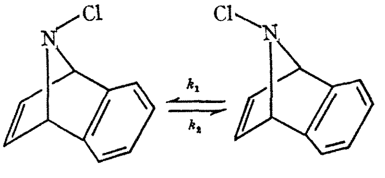
Summary The strained compounds in the title undergo slow nitrogen inversion (*cf.* aziridines, especially those with electronegative substituents on nitrogen[1]).

7-AZABENZONORBORNADIENE (I)[2] reacts with *N*-chlorosuccinimide to form a mixture of *ca.* 35% of *syn*-7-chloro-7-azabenzonorbornadiene (II) and *ca.* 65% of *anti*-7-chloro-7-azabenzonorbornadiene (III).[†]

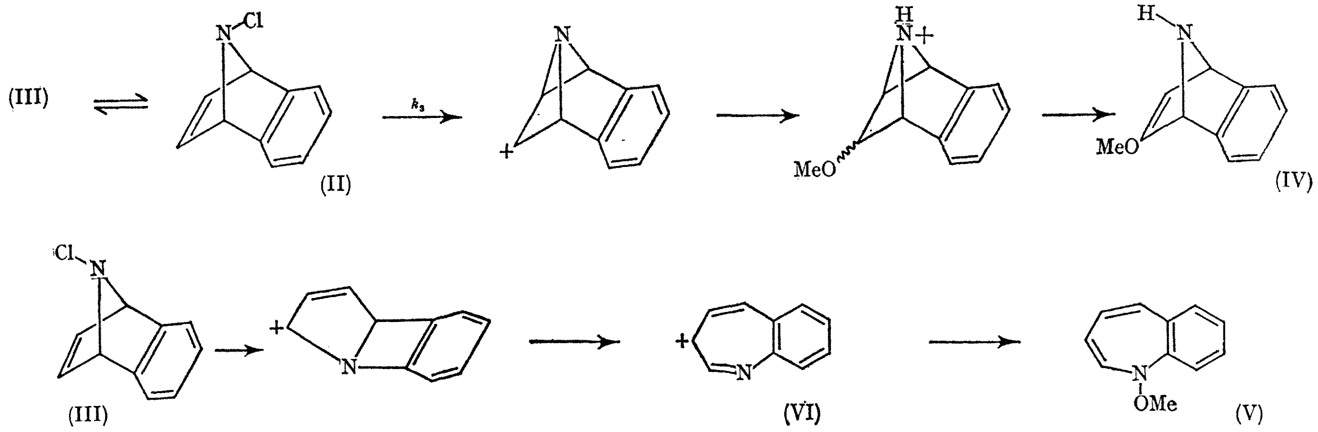
Equilibration of the initially formed mixture, or of pure (III), in carbon tetrachloride solution at room temperature (+23°) can be conveniently monitored by n.m.r. spectrometry[‡]: it leads[§] to a mixture of *ca.* 60% of (II) and *ca.* 40% of (III) with a rate constant k_1 of *ca.* 2·5 × 10^{-5} sec.$^{-1}$ ($\Delta F^{\ddagger}$ = 23·5 kcal/mole).



(I)



(II) (III)



The *syn*-chloride (II) is much more reactive in solvolysis than the *anti*-isomer (III); when the mixture of chlorides initially obtained is dissolved in methanol at room temperature and the solution allowed to stand for *ca.* 40 min., (II) completely solvolyses to form the hydrochloride of an amine (IV), while (III) is not appreciably affected. This fact can be used to prepare pure (III); it is convenient to solvolyse the mixture of (II) and (III) in methanol in the presence of silver carbonate on celite.[3] Compound (II) solvolyses to form (IV) carbonate which is retained on the celite. Filtration and evaporation of the solvent gives pure (III). The structural assignment of (III) [m.p. (uncorrected) 65—66°, decomp.) is based on the n.m.r.[‡] [δ 6·95 (A_2B_2, 4ArH), 6·65 (t, *J* 1·1 Hz, 2 Vinyl-H), and 4·87 p.p.m. (t, *J* 1·1 Hz, 2 bridgehead H)] and mass spectrum[¶] [$(M + 1)^+$ = 178, 180]. Pure (II) was not isolated but readily recognized in the mixtures of (II) and (III) by its n.m.r. spectrum[‡] [δ *ca.* 6·9 (A_2B_2, 4 ArH), 6·75 (t, 1·6 Hz, 2 vinyl H), and 4·67 p.p.m. (t, 1·6 Hz, 2 bridgehead H)].

The configurational assignment of (II) and (III) is based on three arguments. The chemical shifts of the vinyl and bridgehead protons of (II) and (III) correlate with those of the corresponding protons in *syn*- and *anti*-7-chlorobenzonorbornadiene.[4] In analogy with this system, one would expect the *syn*-isomer (II) to be more reactive in solvolysis than the *anti*-isomer (III).[5] The kinetically controlled chlorination of (I) should lead to (III) preferentially by approach of the reagent from the less hindered side.

When the initially formed mixture of (II) and (III) is dissolved in methanol at room temperature and the solution left for *ca.* 36 hr. both (II) and (III) disappear. Crystalline (IV) hydrochloride can be isolated in *ca.* 40% yield as the only product, apart from a small amount of (I) hydrochloride, and can be converted to the free amine (IV). The structure of the amine (IV) is assigned on the basis of the n.m.r.[‡] [δ 7·10 (m, 4 ArH), 6·76 (m, 1 vinyl H), 4·19, 3·77 and (br t, 2 bridgehead H), 3·11 (3 methyl H), and 2·38 p.p.m. (1 N-H)], i.r. (1200 cm^{-1}), and mass spectrum[¶] [$(M + 1)^+$ = 174].

Compound (IV) is presumably derived from (II) by heterolysis of the N–Cl bond[6] with participation of the double bond, reaction with the solvent, cleavage of the aziridine thus formed and elimination of a proton as indicated. Compound (III), present in the mixture, reacts by prior nitrogen inversion to (II).

[†] Heterogeneous reaction in ether at +5° for 2 hr. The crystalline mixture, m.p. (uncorrected) 57—63° (decomp.) is light- and air-sensitive but stable in carbon tetrachloride or ether solution at or below room temperature for several days.[§]

[‡] Varian A-60, CCl_4 solution with TMS as internal standard.

[§] Equilibration is accompanied by decomposition (*ca.* 50% in 48 hr.).

[¶] Atlas CH4, inlet temperature *ca.* 150°, 70 ev electrons; extensive decomposition of (III).

The rate constant k_3 of the methanolysis of (II) at room temperature can be estimated as at least *ca.* 3×10^{-3} sec^{-1}.

When (III) is treated with silver nitrate in methanol for 20 minutes at +5°, a rapid heterogenous reaction takes place. One crystalline compound (m.p. 61—62°) can be isolated in *ca.* 50% yield, which is tentatively assigned structure (V) on the basis of the n.m.r.‡ [δ 6·6—7·3 (m, 4 ArH), 6·21 (m, 1 vinyl H), 5·58 (m, 2 vinyl H), 4·97 (m, 1 vinyl H), and 3·36 p.p.m. (3 methyl H)], u.v. [λ_{max} (hexane) 215 (ϵ = 6,300), 232 (6,500), 285 nm (2,600)] and mass spectrum¶ (M^+ = 173).

Compound (V) probably arises from (III) directly, without prior rearrangement to (II), by silver ion-assisted heterolysis of the N–Cl bond,[6] 1,2-shift of the benzene ring, and ring opening to an azatropylium ion (VI). This sequence is formally analogous to the norbornadien-7-yl—tropylium cation rearrangement observed by Winstein and his co-workers in PSO_3H medium.[7]

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