

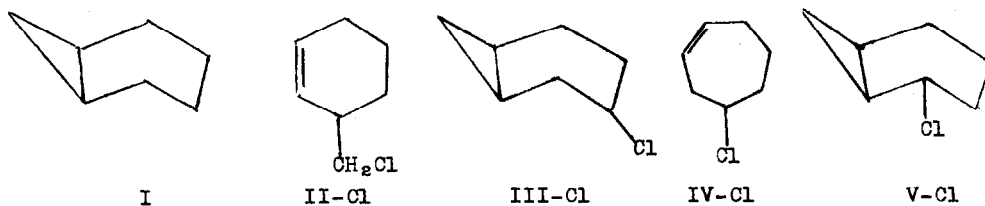
FREE RADICAL CHLORINATION OF NORCARANE¹

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The interaction between a cyclopropyl ring and an adjacent radical center has been the subject of considerable interest.² We wish to report our results on the free radical chlorination of norcarane (I) which provide evidence on the stereoelectronic requirement for the rearrangement of a cyclopropylcarbiny radical to a homoallyl one and which also provide another example of preferential formation of a cyclopropylcarbiny radical.

Reaction of norcarane (I) with chlorine in a modification of the vapor phase chlorination apparatus of Roberts and Mazur³ at 114°, maintaining a large excess of I to chlorine, yielded a complex mixture of products which were analyzed by vpc. In a typical run, carried to 46% reaction, the products consisted of 4% of olefins arising from HCl catalyzed isomerization of I;⁴ 21% of dichlorides, in the ratio 78:43:25:35, which were not further characterized and 34% of monochlorides, which arose predominantly if not exclusively from addition of HCl to I.⁴ The remaining 41% consisted of four monochlorides: 3-chloromethylcyclohexene (II-Cl) 57%, syn-3-chloronorcarane (syn-III-Cl) 19%, anti-3-chloronorcarane (anti-III-Cl) 23% and 4-chloro cycloheptene (IV-Cl) 2%, which arise from free radical chlorination.



Light initiated reaction of excess I with t-butyl hypochlorite in sealed tubes under nitrogen at 25° led to the formation of several monochlorides. The nmr spectrum of the crude reaction mixture revealed bands due to II-Cl,

III-Cl and 2-chloronorcarane (V-Cl), but no appreciable bands due to IV-Cl. When the crude reaction mixture was saturated with gaseous HCl and heated at 115°, IV-Cl formed at the expense of V-Cl, while the relative amount of II-Cl did not change. Analysis of other reaction mixtures by vpc at 70° and nmr revealed the presence of four monochlorides: II-Cl 24%, syn-III-Cl 8%, anti-III-Cl 23% and IV-Cl 45%.⁵

Products were identified by spectroscopic and vpc comparison with samples synthesized by other routes. Treatment of 3-hydroxymethylcyclohexene (II-OH)⁶ with PCl₅ in CHCl₃ yielded II-Cl, nmr (CCl₄) τ 4.24 (2H, m), 6.62 (2H, d, J=7 Hz), 7.0-8.7 (7H, m). A mixture of syn-III-Cl and anti-III-Cl, nmr (CCl₄) τ 6.23 (1H, m), 7.4-8.8 (6H, m), 9.21 (3H, m), 9.90, 10.16 (1H total, m) was prepared from Δ^3 -norcarene by hydroboration-oxidation⁷ to give a 3:1 mixture of anti-III-OH and syn-III-OH⁸ which was converted, without further isolation, to a 1:3 mixture of anti-III-Cl and syn-III-Cl by treatment with triphenylphosphine in CCl₄.¹⁰ Refluxing syn-2-norcaranol (syn-V-OH)¹¹ with excess thionyl chloride yielded¹² IV-Cl, nmr (CCl₄) τ 4.29 (2H, nonet), 6.06 (1H, m) 7.35 (2H, t, J=6Hz), 7.6-8.9 (6H, m). Reaction of syn-V-OH with thionyl chloride in anhydrous diethyl ether at 0°¹³ led to an insoluble chloride, presumably syn-V-Cl, which displayed nmr bands at τ 5.37 (1H, m) and 9.2-9.6 (2H, m) and rearranged rapidly at 60° to IV-Cl. Reaction of syn-V-OH with triphenylphosphine in CCl₄^{10a,c} led to an insoluble chloride, presumably, anti-V-Cl, which displayed nmr bands at τ 5.41 (1H, m) and 9.3-10.0 (2H, m) and rearranged rapidly at 60° to IV-Cl.

Thus, both isomers of V-Cl rearrange to IV-Cl under the conditions of the Cl₂ reaction and the vpc analysis, but not under the conditions of the *t*-butyl hypochlorite reaction. The very small amount of V-Cl formed in the vapor phase Cl₂ reaction indicates that under these conditions the 2-norcaranyl radical rearranges before it reacts to form chloride product. On the other hand, in the liquid phase *t*-butyl hypochlorite reaction formation of unrearranged V-Cl is competitive with rearrangement of the 2-norcaranyl radical. The large amount of IV-Cl revealed by vpc is formed from rearrange-

ment of V-Cl during the analysis since the nmr spectrum of the crude reaction product reveals a considerable amount of V-Cl but no appreciable amount of IV-Cl. In both reactions the major, if not exclusive product of rearrangement of the 2-norcaranyl radical is the cyclohexenylmethyl radical, leading to the formation of II-Cl.

The observed distribution of products is best accommodated by a two-step process:¹⁴ initial formation of a cyclopropylcarbinyl radical followed by formation of monochlorides or by specific external bond cleavage to a primary homoallyl radical¹⁷ which then leads to monochloride. The initially formed 2-norcaranyl radical is conformationally mobile; H-2 may swing through an arc of $\pi/2$ between two extreme boat conformations in which the radical-containing orbital is oriented virtually identically to the two adjacent cyclopropyl ring carbon-carbon bonds. In all intermediate conformations this orbital approaches or achieves coplanarity with the external cyclopropyl bond and orthogonality with the internal one, suggesting that coplanarity is best for the rearrangement. The preference for abstraction of the 2-hydrogen, which is marked in the Cl₂ reaction and increases in the milder t-butyl hypochlorite reaction is due either to resonance stabilization of the 2-norcaranyl radical or to attraction between the electrophilic attacking radical and the nucleophilic cyclopropyl ring.

We are currently examining the behavior of free radicals in related bicyclic systems containing a cyclopropane ring.

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