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SYNTHESIS AND SOME REACTIONS OF 7-HALO- AND 7,7-DIHALONORCARANES

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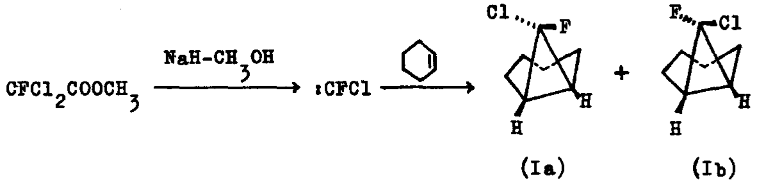
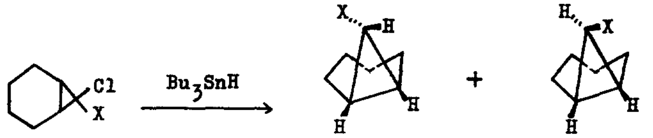
Here we wish to report on the preparation of 7-chloro-7-fluoronorcarane (I), 7-chloronorcarane (II) and 7-fluoronorcarane (III), as well as on their ring expansion reaction in quinoline at elevated temperature.

7-Chloro-7-fluoronorcarane (I) was prepared by adding 0.6 mole of methanol gradually to a mixture of 0.75 mole of cyclohexene, 0.6 mole of sodium hydride and 0.6 mole of methyl dichlorofluoroacetate at room temperature.$^{(1)}$ The yield of the adduct was 60%, being the highest one ever reported in the literature.



Analysis of the product by vpc showed the ratio of the isomers formed (Ia/Ib) to be in the range of 1.2 to 1.5. The configuration of each isomer was determined by their ^{1}H and ^{19}F nmr spectra,$^{(2)}$ based on the assumption that in fluorocyclopropanes the coupling constant between vicinal H and F is generally larger when H and F are cis to each other than when they are trans.$^{(3)}$ From the ^{19}F nmr spectrum J_{HF}^{cis} in Ia and J_{HF}^{trans} in Ib were found to be 19 cps and 5 cps, respectively. A chemical shift of 34.5 ppm was observed between the F's in Ia and Ib, the former resonating at a lower field.

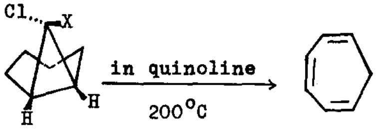
7-Chloronorcarane (II) was prepared by partial reduction of 7,7-dichloronorcarane (IV), which was obtained in a 65% yield from methyl trichloroacetate in a similar way as above. The reduction proceeded most satisfactorily when an equimolar amount of tributyltin hydride was used at 140°C without solvent.$^{(4)}$ The yield was 80%, and the ratio of the isomers formed (IIa/IIb) was 2.5 to 3.0. There was no sign of norcarane being formed.



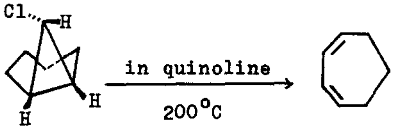
(IV, X = Cl) (IIa, X = Cl) (IIb, X = Cl)
(I, X = F) (IIIa, X = F) (IIIb, X = F)

Reduction of 7-chloro-7-fluoronorcarane (I) by the same procedure resulted in a 61% yield of a new compound, 7-fluoronorcarane (III). The product was a mixture of IIIa and IIIb (IIIa/IIIb = 0.67 to 0.77), b.p. 133°C, n_D^{20} 1.4400, C% 73.42 (calcd. 73.65), H% 9.73 (calcd. 9.71), ir (cm^{-1}) 3010m, 2924vs, 2880s, 1455s, 1435s, 1093vs, 1080vs, 1020m, 858m. Its ^1H and ^{19}F nmr spectra are shown in FIG. 1 and FIG. 2, respectively. The parameters of the spectra are listed in TABLE I. The assignment of the structure is based on the well-established fact that J_{HH}^{vic} in cyclopropanes is generally larger when the two hydrogens are cis to each other than when they are trans.(5) Neither chloronorcarane nor norcarane was detected in the reduction product.

Treatment of dichloronorcarane (IV) with a large excess of quinoline at 200°C for 10 hours followed by distillation of the reaction mixture gave 1,3,5-cycloheptatriene (61%).(6) Vpc analysis proved the absence of toluene in the product.



(IV, X = Cl)
(Ia, X = F)



(IIa)

A mixture of Ia and Ib also gave cycloheptatriene (50%, based on Ia) when heated in quinoline at 200°C for 10 hours, but Ib was nearly completely recovered. Similarly, a mixture of IIa and IIb gave 1,3-cycloheptadiene (80%, based on IIa) with recovery of IIb.(7) Both Ib and IIb were stable in quinoline at 200°C for 30 hours. The first-order rate constants of the ring expansion of Ia, IIa and IV were 4×10^{-5}, 7×10^{-5} and 2×10^{-5} sec^{-1} at 200°C, respectively.

It seems to deserve further discussion that the isomers of I and II showed a distinct difference in reactivity, since they possess no hetero atom that might exert an

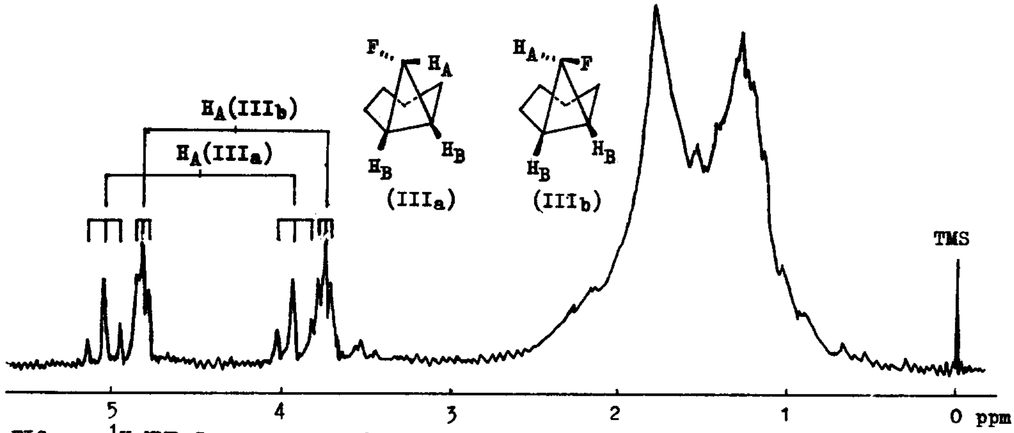


FIG. 1. ^1H NMR Spectrum of a Mixture of IIIa and IIIb at 60Mc (Varian A-60) in $CDCl_3$ with TMS as Internal Reference.

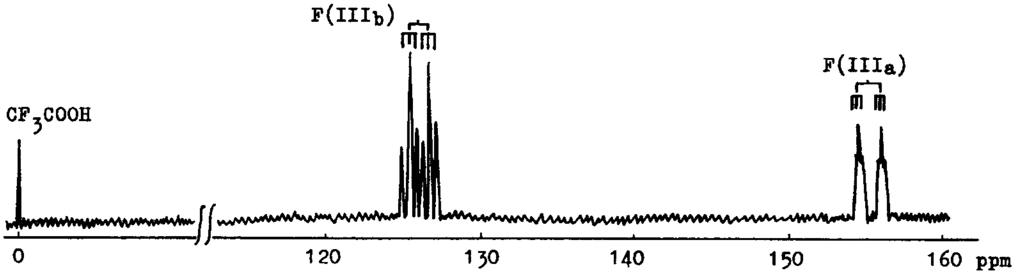


FIG. 2. ^{19}F NMR Spectrum of a Mixture of IIIa and IIIb at 56.4 Mc (Hitachi High-Resolution NMR Spectrometer H-60) in CCl_4 with CF_3COOH as External Reference.

TABLE I

Parameters of the NMR Spectra Shown in FIGS. 1 and 2

Compound	Chem. Shift of H_A (ppm)*	Chem. Shift of F (ppm)**	Coupling Constant		
			J_{HH}^{vic}***	J_{HF}^{vic}****	J_{HF}^{gem}*****
IIIa	4.47	156.0	6.3	9.0	68
IIIb	4.25	126.2	2.0	18.0	65

* downfield from TMS. ** upfield from CF_3COOH.

*** between H_A and H_B. **** between H_B and F. ***** between H_A and F.

anchimeric assistance as was proposed by Parham, et al.,(8) for explaining the different behaviors of the two isomers of 7-chloro-2-oxanorcarane.

There are several papers dealing with a similar difference in reactivity between isomers of norcarane derivatives in hydrolysis or acetolysis:(9-12) an empirical rule has recently been advanced, based on the theoretical treatment of electrocyclic transformations,(13) that in disrotatory ring opening of cyclopropanes the group trans to the leaving group rotates outward, and the group cis, inward.(11) The observed relative reactivities of IIa and IIb are in good agreement with this rule, which predicts that the transition state formed from IIb should be sterically much less favored than the one from IIa.

Under the reaction conditions, the C-F bond was far more resistant than C-Cl, as is evident from the greater stability of Ib compared with Ia. In accord with this, a mixture of IIIa and IIIb did not show any appreciable change even when heated at 200°C for 50 hours in quinoline. Probably more drastic conditions are necessary to effect ring expansion of Ib, IIb or III.

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