

FREE RADICAL ADDITION OF CARBON TETRAHALIDES
TO THE 3,7-DIMETHYLENEBICYCLO[3.3.1]NONANE

A.G.Yurchenko*, L.A.Zosim, N.L.Dovgan', N.S.Verpovsky

Department of Chemical Technology, Kiev Polytechnic
Institute, Kiev, 252056, USSR

(Received in UK 28 October 1976; accepted for publication 8 November 1976)

The attractive idea to synthesize adamantane derivatives starting from substituted bicyclo[3.3.1]nonanes by introducing a methylene group between C-3 and C-7 of the latter was developed in numerous studies of the electrophilic addition to unsaturated derivatives of bicyclo[3.3.1]nonane (1-5). In some cases formation of noradamantane derivatives could be expected due to the difference in nucleophilicity of the reaction centers (2,5). Nevertheless the structure of the resulting compounds shows the noradamantane nucleus cannot be formed via intramolecular interaction of π - electrons with the carbonium center (6). In all cases the conversion proceeds via the thermodynamically most favorable pathway, deprived of the additional increase in molecular strain.

In this paper we report a new approach to the formation of the noradamantane nucleus based on the detailed study of the free radical addition of carbon tetrachloride to 3,7-dimethylenebicyclo[3.3.1]nonane.

The addition of carbon tetrachloride to 3,7-dimethylenebicyclo[3.3.1]-nonane in the presence of azobisisobutyronitrile results in the formation of two adducts in the ratio of about 1:3.

The major component of the mixture was separated by crystallisation [47% yield, m.p. 73-74° (propanol), δ 3.67 s (2H), 3.08 s (2H), 1.3-2.4 (12H), m/e 300 (M^+)] (7).

The minor component of the mixture was separated as a liquid by chromatography on alumina column [17% yield, b.p. 137-138° (0.75mm Hg), n_D^{20} 1.5496, δ 2.75 s (2H), 1.5-2.3 (14H), m/e 300 (M^+)] .

The tetrachlorides appeared to be extremely stable to hydrolysis both in alkaline and in acidic media and also in the presence of silver sulfate.

Dehalogenative hydrogenation of the liquid isomer over Raney nickel under basic conditions gave 80% of 1-ethyladamantane (III). It was reduced with zinc in abs. ethanol to 1-ethyl-3-chloroadamantane (IV) in 86% yield. This proves the liquid isomer to be 1-chloro-3-(2,2,2-trichloroethyl)adamantane (I).

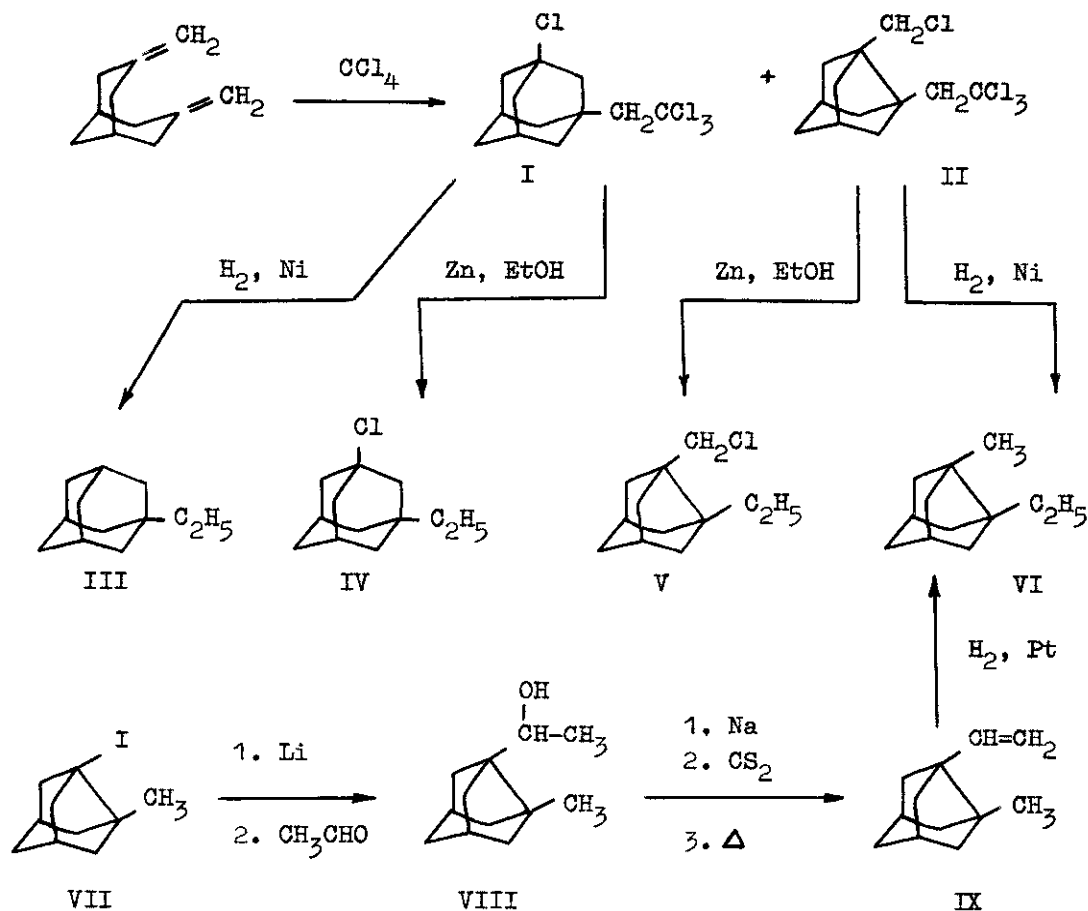
Hydrogenation of the tetrachloride mixture gave 1-ethyladamantane and an unknown hydrocarbon in a 1:3 ratio. This hydrocarbon was also formed by hydrogenation of the crystalline tetrachloride in 75% yield. The structure of 3-methyl-7-ethylnoradamantane (VI) was postulated for this compound on the basis of its spectral data. Reduction of the crystalline tetrachloride with zinc in abs. ethanol yielded a substance containing ethyl and chloromethyl groups. The spectroscopic and chemical data were consistent with the crystalline tetrachloride to have the structure 3-chloromethyl-7-(2,2,2-trichloroethyl)noradamantane (II).

The hydrocarbon obtained by exhaustive hydrogenation of the tetrachloride (II) was synthesized from 3-methyl-7-hydroxynoradamantane (8). This was heated in an excess of 47% aqueous HI to give 3-methyl-7-iodonoradamantane (VII) [55% yield, b.p. 89° (1mm Hg), m.p. 46°, δ 1.33 s (3H), 1.67 m (6H), 2.01 m (2H), 2.48 m (4H)] . Treatment of the iodide (VII)

with excess tert.butyl lithium at -70° followed by acetaldehyde addition gave 3-methyl-7-(1-hydroxyethyl)noradamantane (VIII) [47% yield, b.p. $72-73^{\circ}$ (0.5 mm Hg), m.p. 38° , δ 1.08 d (3H, $J=6.3$ cps), 1.15 s (3H), 1.52 m (10H), 2.01 m (2H), 3.73 q (1H, $J=6.3$ cps)].

The hydroxyethyl derivative (VIII) was converted by Tschugaev's method into 3-methyl-7-vinylnoradamantane (IX) [15% yield, b.p. $69-70^{\circ}$ (15 mm Hg), δ 1.02 c (3H), 1.4-2.4 m (12H), 4.77-5.35 m (3H, vinyl)], which on hydrogenation over Adams catalyst gave the hydrocarbon identical to that obtained from the crystalline tetrachloride.

Scheme 1.

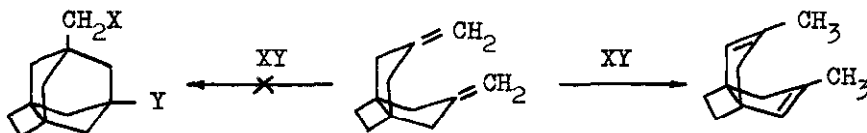


Attempts to synthesize this hydrocarbon from both 3-methyl-7-bromonoradamantane and 3-methyl-7-iodonoradamantane under Wurtz conditions with ethyl iodide yielded mixtures of 3-methylnoradamantane and the desired substance in a 7:1 ratio.

The addition of carbon tetrabromide to the 3,7-dimethylenebicyclo[3.3.1]nonane is even more selective, the ratio of 3-bromomethyl-7-(2,2,2-tribromoethyl)noradamantane [48% yield, m.p. 100-101° (hexane), δ 1.30 m (2H), 1.47 broad s (4H), 1.97 (6H), 3.20 s (4H)] to 1-bromo-3-(2,2,2-tribromoethyl)adamantane was found to be 9:1 (determined by glc of the hydrocarbon mixture obtained by hydrogenation of the crude tetrabromide mixture).

References and footnotes

1. H. Stetter, J. Gärtner, *Chem. Ber.*, **99**, 925 (1966); J. G. Korsloof, V. G. Keizer, *Tetrahedron Lett.*, **1969**, 3517; F. Blaney, D. Faulkner, M. A. McKerverey, G. Step, *J. Chem. Soc., Perkin Trans.*, **1972**, 2697.
2. A. G. Yurchenko, Z. N. Moorzinova, T. G. Fedorenko, *Zh. Org. Khim.*, **10**, 1125 (1974).
3. A. G. Yurchenko, Z. N. Moorzinova, F. N. Stepanov, *Zh. Org. Khim.*, **8**, 2332 (1972).
4. A. G. Yurchenko, Z. N. Moorzinova, S. D. Isaev, *Zh. Org. Khim.*, **11**, 1427 (1975).
5. F. N. Stepanov, T. N. Utochka, A. G. Yurchenko, S. D. Isaev, *Zh. Org. Khim.*, **10**, 59 (1974).
6. According to unpublished data of this laboratory (A. G. Yurchenko et al.), 3,7-dimethylenetricyclo 3.3.2.0 decane on treatment with iodine or hydrogen bromide does not yield a 3,6-dehydrohomoadamantane derivative, but isomerises to 3,7-dimethyltricyclo 3.3.2.0 deca-2,6-diene.



7. All new substances gave satisfactory elemental analysis. NMR Spectra were recorded on a Varian A-60A spectrometer in carbon tetrachloride solution using TMS as internal standard. Mass Spectra were measured on Varian CH-4 spectrometer at 70eV and 20°C.

8. M. A. Eakin, J. Martin, W. Parker, *Chem. Commun.*, **1965**, 206.