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THE CHEMISTRY OF 7-SUBSTITUTED NORBORNADIENES; 7-CYANONORBORNADIENE AND 7-CARBOXYNORBORNADIENE

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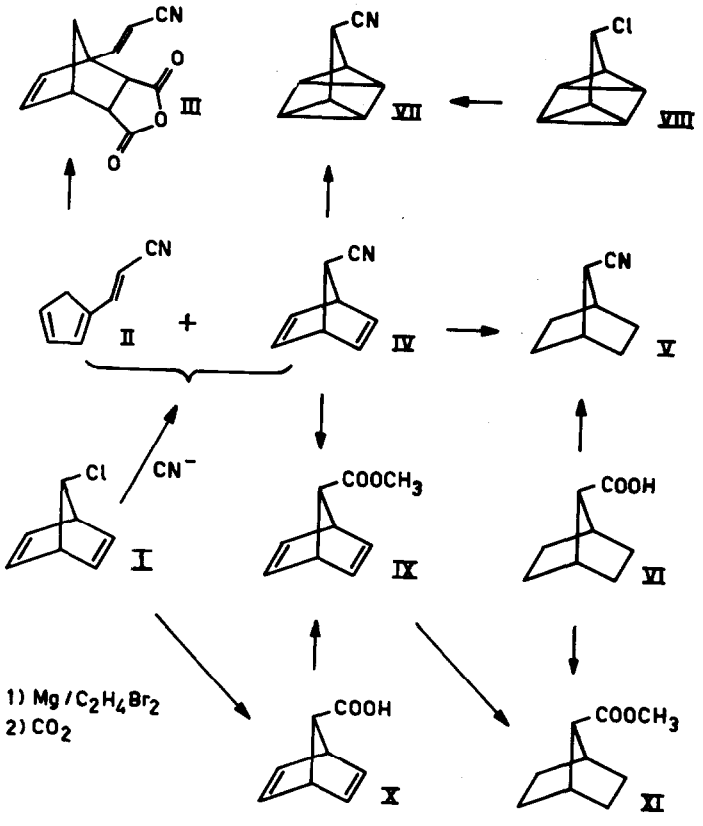
As part of another program we needed quantities of 7-carboxynorbornadiene. We therefore tried the most obvious pathways leading to this compound starting with the now easily available 7-chloronorbornadiene (I)(1,2). Two recent publications (3,4), and the continued interest in the intermediates derived from reactions at the 7-position of the norbornadiene skeleton (1-10) prompt us to report our preliminary findings on the reactions which we have carried out so far.

In aqueous dioxane or in formamide (I) reacts with sodium cyanide to give a yellow brown solution. The crude mixture of the reaction products shows strong infrared absorptions at 4,52μ and 6,20μ; the latter bas been ascribed by Tanida and Hata to the C=C stretching modes of the conjugated system of trans-β-(1-cyclopentadienyl)-acrylnitrile (II) (3). In further accordance with the results of these authors treatment of this crude mixture with maleic anhydride gave the adduct m.p. 159°, for which structure (III) has been proposed (3). However, no (II) could be monitored by gaschromatography of these mixtures, presumably because of its instability under the conditions employed. Instead, the chief product eluted in 5-15% yield appeared to be the hitherto unknown 7 cyanonorbornadiene (IV), m.p. 45°; relative retention volume

(11) 2,4; infrared 3,25, 3,33, 3,37, 4,47, 6,38, 6,50, 7,72, 8,17, 8,88, 10,90, 11,45, 12,28, 13,48, 15,00 μ. Anal. Calc. for C_8H_7N: C, 82,03, H, 6,02, N, 11,95. Found: C, 81,52, H, 5,81, N, 12,66.

The assignment of structure (IV) is based on the following evidence. Catalytic hydrogenation of (IV) led by uptake of two moles of hydrogen to 7-cyanonorbornane (V), m.p. 64°, identical in terms of mixed m.p., infrared spectrum and retention volume with an authentic sample prepared from 7-carboxynorbornane (VI) (12,13) by dehydration of the amide. Irradiation of a solution of 7-cyanonorbornadiene according to the method of Hammond (14) gave 7-cyanoquadricyclene (VII), m.p. 44°; relative retention volume 3,9; infrared in CCl_4 3,25, 3,42, 4,47, 7,43, 8,06, 8,27, 10,32, 10,86, 11,06 μ, which was shown by infrared spectroscopy, gaschromatography and mixed m.p. to be identical with the compound obtained from the reaction of 7- chloroquadricyclene (VIII) (15) with a solution of sodium cyanide in 60 % ethanolwater (16). That no rearrangement takes place under these conditions has been demonstrated by Story and Fahrenholtz (15). Saponification of (IV) with 20% alcoholic potassium hydroxide and subsequent esterification of the liberated acid with diazomethane gave 7-carbomethoxynorbornadiene (IX) which had the same infrared spectrum and retention volume as the methylester prepared from 7-carboxynorbornadiene (X) (see below).

According to infrared and gaschromatographic analysis of the crude and of the hydrogenated original mixtures of reaction products, (II) and (IV) are formed from (I) in nearly the same ratio under the conditions used by Tanida and Hata (5) and in formamide solution. Concerning the


CN
O
O
O
III
CN
VII
Cl
VIII
CN
II
+
CN
IV
CN
V
Cl
CN⁻
I
COOCH3
IX
COOH
VI
1) Mg / C2H4Br2
2) CO2
COOH
X
COOCH3
XI

controversy regarding the structure of the intermediate(s) in solvolysis of (I) (1,2,3,5,6,7,17), we find it noteworthy that in the two irreversible reactions of (I) that have been studied so far under solvolysis conditions, cyanide ion and the reactive species in hydride reductions (5), though differing in their nucleophilicity, lead to a very similar percentage of products arising from attack at the 7-position.

Carbonization of the Grignard reagent from (I) was tried as another approach to the desired acid (18). As coupling could be expected to occur to a large extent in the reaction of (I) with magnesium it was decided to conduct this reaction under heavy entrainment conditions. Ethylene dibromide was chosen for this purpose because of the known reaction between Grignard reagents and 7-t-butoxynorbornadiene (19). By use of a fivefold excess of ethylene dibromide we obtained after the usual work-up yields of 4-5 % of 7-carboxynorbornadiene (X), m.p. 87°, infrared (in CCl_4) 2,8-4,5, 5,86, 6,49, 7,05, 7,54, 7,68, 7,91, 10,60, 10,84, 11,28, 12,05, 13,90, 15,20μ , anal.calc.for $C_8H_8O_2$: C, 70,60, H, 5,92. Found: C, 70,12, H, 6,12. Besides (X) a complex mixture of neutral compounds was obtained in low yield. Reaction of (X) with diazomethane led to 7-carbomethoxynorbornadiene (IX), $n_D^{19,8}$: 1,4804, infrared 3,26, 3,33, 3,39, 3,43, 5,73, 6,50, 6,97, 7,51, 7,66, 8,17, 8,32, 9,74, 13,59, 15,10, 16,45μ , relative retention volume 1. Catalytic hydrogenation of this ester gave 7-carbomethoxynorbornane (XI) which was shown to be identical with a sample of the same compound prepared from (VI) by comparison of infrared spectra and retention volumes.

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