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RADICAL ADDITION OF t-BUTYL MERCAPTAN TO 1,2,3,4,7,7-HEXAMETHYLBICYCLO[2.2.1]HEPTADIENE[x)]

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In the course of free-radical additions to norbornadiene derivatives possessing bulky substituents with -I effect (Cl, OR, etc.) the endo- or exo-direction of the radical attack is determined by the positions and number of these substituents, the reaction becoming practically endo-stereospecific in the case of hexasubstituted compounds (1,2). There is also a possibility of a parallel free-radical Wagner-Meerwein isomerization (1,2). The study of such reactions for the case of bicyclodiene systems having electron-donating substituents of sufficient steric size is of considerable interest.

In this communication is reported the study of free-radical thiylation of hexamethylnorbornadiene-2,5 (I) by tert-butyl mercaptan - i.e. the combination of reagents which makes the steric effects more perceptible. The reagents (in the ratio I: tert-BuSH = 1:10) in hexane with azobisisobutyronitrile as initiator were kept for 15 hrs at 75-80° in a sealed glass tube and gave a 70% overall yield of the reaction product. The latter consisted mainly of two compounds (II,III) and a third one (IV) present in minor quantity. On the basis of the chemical and spectral evidence now available the following structures could be assigned to these compounds: 1,2,3,4,7,7 - hexamethyl-endo-5-tert-butylthionorbornene-2 (II); 1,2,3-endo-5,6,6-hexamethyl-syn-7-tert-butylthionorbornene-2 (III); 1,2,3,4,7,7-hexamethyl-exo-5-tert-butylthionorbornene-2 (IV):

[x)] Named hexamethylnorbornadiene in the text for shortness.

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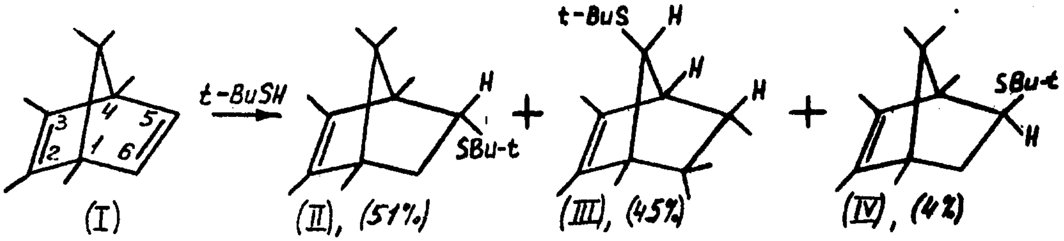
Scheme 1



The authentic sulphides II and IV have been prepared by Diels-Alder condensation of hexamethylcyclopentadiene (V) with tert-butylvinylsulphide (180°, 9 hrs, overall yield ~ 70%, ratio II:IV ≈ 13:1).

For the sulphide II the n.m.r. spectra[x] showed three characteristic multiplets $6H_{endo}$ ($\delta = 1.21$ ppm), $6H_{exo}$ (2.10 ppm) and 5H (2.87 ppm) with coupling constants $^2J_{gem} = 12.65$ c/s, $^3J_{cis} = 7.86$ c/s, $^3J_{trans} = 3.47$ c/s; the sulphide IV showed the multiplets $6H_{exo}$ (1.20 ppm), $6H_{endo}$ (1.75 ppm) and 5H (2.28 ppm) with coupling constants $^2J_{gem} = 13$ c/s, $^3J_{cis} = 7.85$ c/s and $^3J_{trans} = 5.32$ c/s. The sulphide III was isolated by preparative thin-layer chromatography on Al_2O_3; its n.m.r. spectra comprised multiplets $5H_{exo}$ (1.81 ppm), 4H (2.33 ppm) and $7H_{anti}$ (2.74 ppm) with $^3J_{4,7anti} = 1.05$ c/s and $^3J_{5exo,4} = 2.93$ c/s. The value of the last constant is indicative of exo-5H-configuration whereas the shift of the 3-CH_3-signal towards the lower field in comparison with the spectra of (II) and (IV) affirms the syn-position of the tert-butylthio-group in III.

The hitherto undescribed hexamethylnorbornadiene (I) was obtained by decarboxylation of the diacid (VI) over Cu-chromite (in quinoline, at 200-210°, in a nitrogen flow) giving a 25% overall yield of a mixture of hydrocarbons I,VII-IX (scheme 2), containing (by g.l.c.) about 60% of I:

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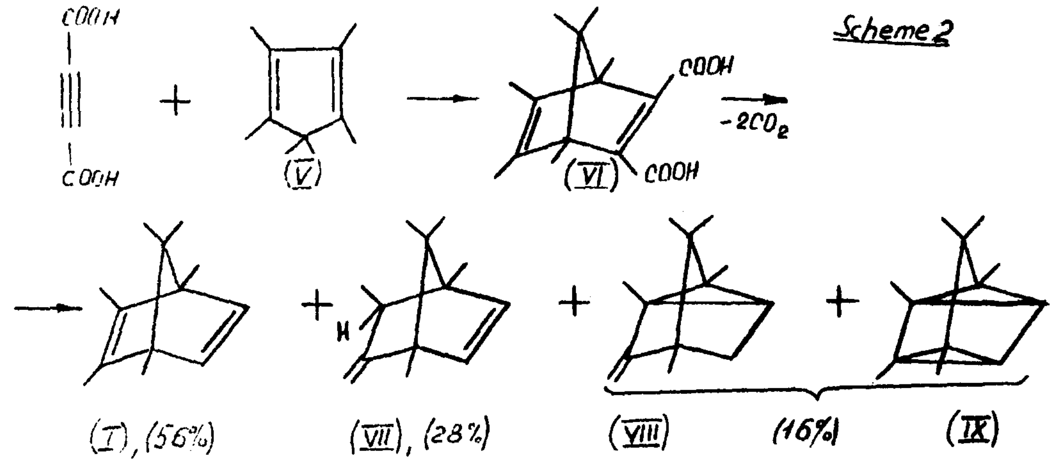
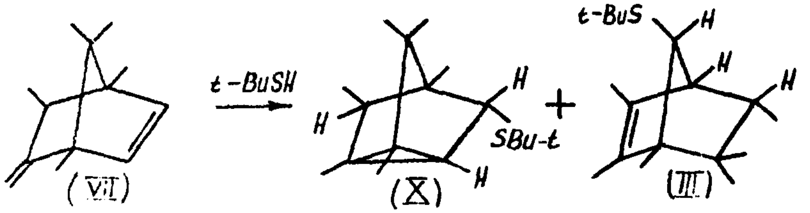
[x] The n.m.r. spectra were obtained with a Varian HA-100 instrument.


Scheme 2

Pure I was isolated by preparative g.l.c. It was also possible to carry out the addition reaction without isolation of I from the mixture of the hydrocarbons due to its very high reactivity in comparison with VII-IX. Besides II-IV nortricyclene X was formed in this case in minor quantity (8-9%). The relatively slow reaction of the VII-IX mixture with butanthiol yields only the sulphides X and III in a 2.5:1 ratio. We believe this fact to be the result of thiylation of the diene VII (scheme 3), the reactivity whereof should be sufficiently higher than that of VIII by analogy with unsubstituted methylene-norbornene systems (3).

Scheme 3



The n.m.r. spectra of X showed the multiplets 3H (1.68 ppm), 6H (2.36 ppm), 5H (2.91 ppm) and $^3J_{5,6}$ = 11.25 c/s.

In the reaction of tert-butyl mercaptan with diene I (scheme 1) the low transfer constant of the former leads to a high percentage of the isomerized sulphide III. The driving force in this Wagner-Meerwein type free-radical isomerization is probably the secondary-to-tertiary radical-center shift in the intermediate endo-radical[x], the syn-configuration of the product III confirming its relation to primary endo-attack. Thus for the reaction studied the endo-to-exo ratio in the radical attack is as high as 20:1.

On account of the structure of the reaction products (scheme 3) diene VII seems to add the thiyl radicals solely to its endo-cyclic bond and from the endo-side. The possibility is assumed for the radicals thus formed[xx] to undergo a 1,3-hydrogen migration followed by a radical-center shift which may give an additional route to the isomerized product III.

Comparison of our results with those of British chemists (4) who recently demonstrated an exclusive exo-addition of thiophenol to bornylene and apobornylene leads to a conclusion that the stereochemistry of free-radical attack on the substituted norbornene (and norbornadiene) systems is controlled by both electronic and steric factors. In the case studied by the present authors the latter factors are prevailing and lead to a close analogy with hexachloronorbornadiene thiylation reactions in spite of the electron-donating nature of the methyl groups.

All the compounds obtained were characterised by elemental analyses, n.m.r. and IR spectra; their purity and the percentage in the reaction mixtures were determined by t.l. and g.l. chromatography.

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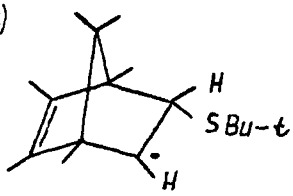

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