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SYNTHESIS OF 7-OXABICYCLO[2.2.1]HEPTANES FROM 3-CYCLOHEXENOLS INVOLVING PHOTO-INDUCED HYPOIODITE REACTION

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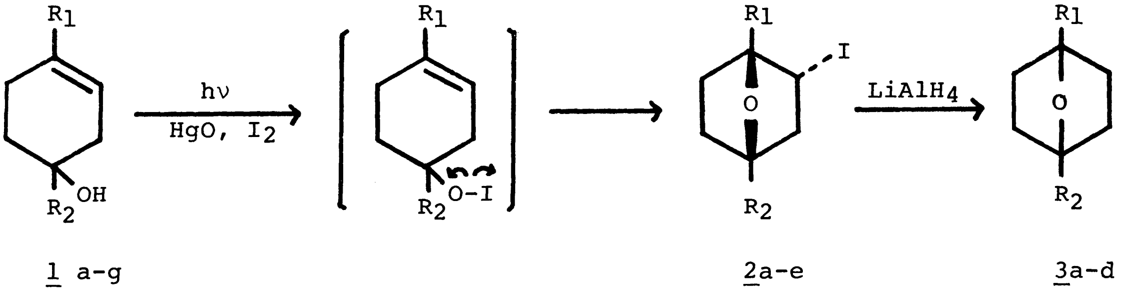
Various 7-oxabicyclo[2.2.1]heptanes were synthesized by the photo-induced hypoiodite reaction of 3-cyclohexenols, followed by reduction of 2-iodo-7-oxabicyclo[2.2.1]heptanes.

Photo-induced hypoiodite reactions have recently been reported on the steroidal six-membered homo-allylic alcohols[1)] and a terpenoidal seven-membered homo-allylic alcohol, widdrol[2)] which gave β-fission products. Interest in these reaction prompted us to communicate the relevant reaction of 3-cyclohexenols (1a-g) having substituents on the 1- and 4-carbon, which included the monoterpenoids as 1- and 4-terpineol (1d and 1e). We now found the formation of stereospicific 2-iodo-7-oxabicyclo[2.2.1]heptanes (2a-e), which were allowed to lithium aluminium hydride ($LiAlH_4$) reduction in ether giving the corresponding 7-oxabicyclo[2.2.1]-heptanes (3a-d) involving 1,4-cineole (3d).

The starting materials (1a-g) were prepared from 3-cyclohexenones by usual method. 1a-e were irradiated with iodine (1.5 mol equiv) and mercury(II) oxide (1.5 mol equiv) in cyclohexane through Pyrex with a 100W high pressure Hg arc lamp for 1 or 3 h, followed by separation with SiO_2 column chromatography affording oily products. 1a-e were converted to iodine-containing products, but 1f and 1g were not reacted under the same condition. It would be explained in terms of the difference between stabilities of sec- or tert-alkyl radicals formed as intermediate.



1a R_1=CH_3, R_2=H
1b R_1=R_2=CH_3
1c R_1=$CH(CH_3)_2$, R_2=H
1d R_1=$CH(CH_3)_2$, R_2=CH_3
1e R_1=CH_3, R_2=$CH(CH_3)_2$
1f R_1=R_2=H
1g R_1=H, R_2=CH_3

Table 1. Total yield of 3 from 1 and 60MHz-NMR [δ(ppm), $CDCl_3$] of 2 and 3

1	2	NMR of 2	3(yield)	NMR of 3
1a	2a$^+$	R_1=CH_3, 1.17 (3H, s), R_2=H, 4,42 (1H, t, J=5 Hz), C2-H, 3.80 (1H, oct, J=11, 5, 2 Hz)	3a(50%)* bp 135-137°C	R_1=CH_3, 1.50 (3H, s) R_2=H, 4.49(1H, t, J= 4 Hz)
1b	2b	R_1=R_2=CH_3, 1.44 (6H, s), C2-H, 3.88(1H, oct, J=11, 5, 2 Hz)	3b(62%)* bp 141-143°C	R_1=R_2=CH_3, 1.46 (6H, s)
1c	2c$^+$	2CH_3 of $CH(CH_3)_2$, 1.10 (6H, d, J= 7 Hz), R_2=H, 4.38 (1H, t, J=4 Hz), C2-H, 3.85 (1H, oct, J=11, 5, 2 Hz)	3c(37%)* bp 150-152°C	2CH_3 of $CH(CH_3)_2$, 0.98 (6H, d, J=7 Hz) R2=H, 4.43 (1H, t, J=4 Hz)
1d	2d	2CH_3 of $CH(CH_3)_2$, 1.18 (6H, d, J= 7 Hz), R_2=CH_3, 1.42 (3H, s), C2-H, 4.03 (1H, oct, J=11, 6, 2 Hz)	3d(76%) bp 165-167°C	2CH_3 of $CH(CH_3)_2$, 0.96 (6H, d, J=7 Hz), R_2=CH_3, 1.43 (3H, s)
1e	2e	R_1=CH_3, 1.43 (3H, s), 2CH_3 of $CH(CH_3)_2$, 0.98 (6H, d, J=7 Hz), C2-H, 3.83 (1H, oct, J=11, 6, 2 Hz)	3d(79%)	

* Yield by G.L.C. analysis. + Irradiation for 3 h.

The configurations of the iodine-containing products[3] (2a-e) were deduced from the evidence that the NMR spectra showed the same patterns concerning the signals of proton at C-2 observed as octet[4] summarized in Table 1. Reduction of 2a-e with $LiAlH_4$ in ether for 24 h afforded the 7-oxabicyclo[2.2.1]heptanes[3] in quantitative yields.

Thus, these results suggest that the extensive application of photo-induced hypoiodite reaction can be available for synthesis of 7-oxabicyclo[2.2.1]heptanes starting from 3-cyclohexenols in only two steps.

To be compared with above hypoiodite reaction, the reaction of 4-terpineol (1e) with mercury(II) acetate[5] and sodium hydroxide in 50% aq-tetrahydrofuran followed by sodium borohydride reduction was carried out affording only 1,4-terpin. This result was not expected one and different from above result.

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References and Notes

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