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PHOTOREDUCTIVE DEHALOGENATION OF 5-BROMOMETHYL- 1,2,3,4,7,7-HEXACHLORO-2-nor-BORNENE (BROMODAN) -A CYCLODIENE INSECTICIDE

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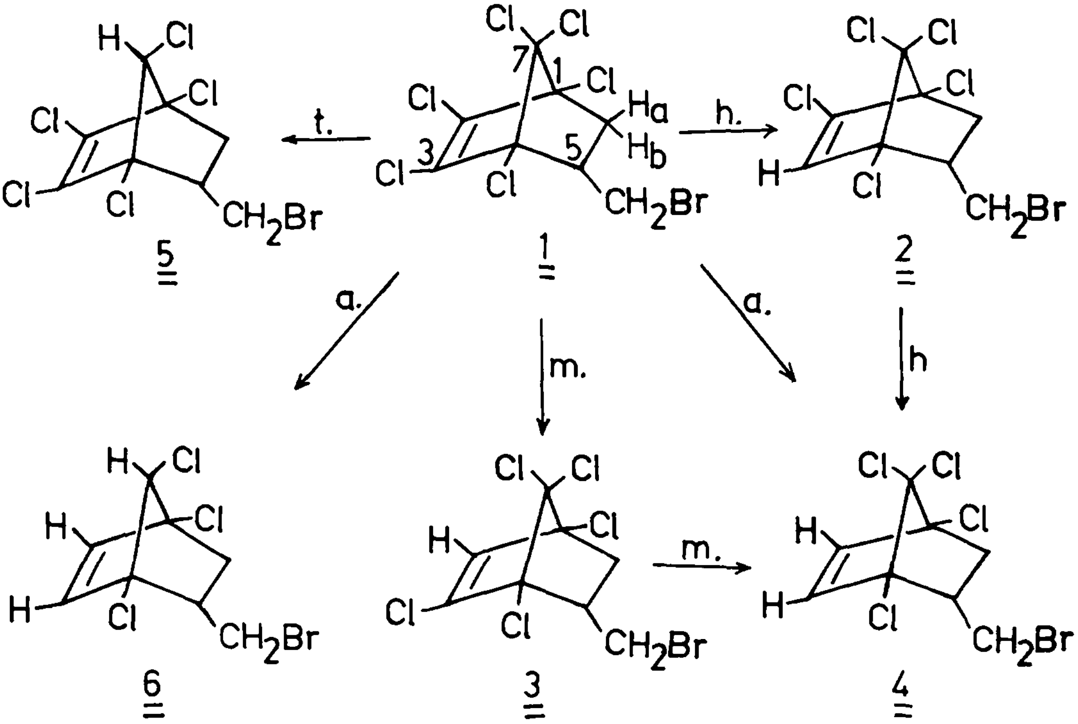
Abstract- Photoirradiation of bromodan in hexane and methanol gave mono and di-dehalogenated photoproducts by replacement of chlorine atoms from the double bond. Whereas on photolysis in triethylamine there was stereo-selective removal of syn-chlorine atom from the methanobridge carbon.

Selective dehalogenation in the cyclodiene insecticides is an interesting chemical exercise both from the point of view of mechanism as well as for providing authentic materials needed for identification of metabolites arising out of photochemical and microbial changes during their metabolism. A combination of various chemical and photochemical techniques have been employed earlier to prepare reductively dechlorinated metabolites of organochlorine insecticides.[1-3] Recently amine-induced stereo-selective photodehalogenation of cyclodiene insecticides and their photoisomers have also been reported.[4-5] Since halogenated metabolites are more prone to further biodegradation, it is essential to study their formation under different photochemical conditions. Such an exercise should be particularly interesting with bromodan (1)(5-bromomethyl-1,2,3,4,7,7-hexachloro-2-norbornene)- a safe older generation insecticide for which there is no information available on its photochemical degradation. This paper deals with the photochemical dehalogenation of bromodan under different conditions.

RESULTS AND DISCUSSION

Irradiation of bromodan (1)in n-hexane with UV-light filtered through quartz gave a mixture of two closely related products which were separated by column chromatography. The mass spectrum of the first photoproduct showed a molecular ion peak at m/z 357 alongwith a characteristic RDA fragment ion at m/z 236. Besides the usual peaks present as in bromodan 1 , its 'HNMR spectrum exhibited a new one proton singlet at δ 6.28. This new singlet can probably arise by the displacement of C_3-ethylenic chlorine. On this basis it was assigned the structure 5-bromomethyl-1,2,4,7,7-pentachloro-2-norbornene (2). The mass spectrum of the second photoproduct gave a parent ion peak at m/z 323 alongwith a characteristic RDA fragment at m/z 202 corresponding to $C_5Cl_4H_2$ unit indicating loss of two chlorine atoms. Its 'HNMR spectrum exhibited two doublets located at δ 6.05 and 6.35(J=7.0 Hz) corresponding to two ethylenic protons indicating loss of ethylenic chlorines. These findings were consistent with the proposed structure 5-bromomethyl-1,4,7,7-tetrachloro-2-norbornene(4).

Irradiation of bromodan (1) in methanol with UV-light also gave two photoproducts. The first photoproduct was characterised by its 'HNMR spectrum in which a new singlet peak appeared at δ 5.98 corresponding to loss of chlorine substituents from C_2 position. Its structural similarity with hexane photoproduct 2 was evident from almost similar mass fragmentation pattern. A comparison of the NMR spectrum of the photoproducts 2 and 3 revealed that C-2 ethylenic proton in 3 appeared at δ 5.98 whereas C-3 proton in 2 appeared at δ 6.28 because of deshielding effect of bromomethyl moiety. It was therefore assigned the structure 1,3,4,7,7- pentachloro-2-norbornene (3). When irradiation in methanol was continued for longer duration, another photoproduct was isolated which was found to be identical with 4 (NMR & MS).



a Acetone ; h Hexane m Methanol t Triethylamine

Irradiation of bromodan in hexane containing acetone as sensitizer enhanced the rate of phototransformation and besides usual products 2, 3 (minor) and 4 (major) a new photoproduct was isolated whose mass spectrum (M^+, 289) indicated loss of three chlorine atoms from the parent 1. This photoproduct was assigned the structure 6 as its 'HNMR spectrum exhibited a singlet at δ 4.25 corresponding to syn proton at geminal carbon atom and a multiplet centred at δ 6.05-6.35 corresponding to two ethylenic protons.

When bromodan was photolysed in triethylamine using pyrex filter, it gave a new photoproduct. The 'HNMR spectrum of this photoproduct displayed one additional one-proton singlet at δ 4.15 indicating loss of syn-chlorine atom from C-7 hydrogen is based on the fact that it absorbs slightly upfield as compared to anti-oriented hydrogen as observed earlier during stereospecific dehalogenation of some cyclodiene insecticides.[4,5] Its structure was further supported by mass spectroscopy which showed a molecular ion peak at m/e 357 which is typical of a monodehalogenated product. On the basis of spectroscopic evidences the photoproduct was assigned the structure 5-bromomethyl-1,2,3,4,7 (anti) - pentachloro-2-norbornene (6). No other product could be detected when irradiation in triethylamine was continued for longer duration.

It is interesting to note that during photoirradiation in hexane, C-3 chlorine is preferentially dechlorinated whereas when methanol was used as a solvent, C-2 chlorine atom was preferentially removed. It is also worth mentioning that bromomethyl moiety and chlorine atoms situated at methano-bridge position remained unaffected under these conditions. However, photoirradiation in presence of triethylamine gave a product resulting in stereoselective loss of C_7-syn chlorine atom.

EXPERIMENTAL PROCEDURES

Melting points are uncorrected. 'HNMR spectra were recorded in ppm δ scale relative to TMS as internal standard. Mass spectra were obtained on a Zeol JMS-D300 mass spectrometer. Gas liquid chromatography was carried out on Hewlett Packard GLC equipped with EC detector using OV-210+OV-17 column.

Photoirradiation of Bromodan in Hexane

Bromodan (1) (5-bromomethyl-1,2,3,4,7,7-hexachloro-2-norbornene) in hexane (0.1%, 500 ml) was irradiated in a quartz vessel with light from a high pressure Hg-lamp for 48 hours. The irradiated solution was concentrated under reduced pressure at room temperature and fractionated by column chromatography over silica gel. The first fraction (75 ml) eluted with hexane was identified as unreacted bromodan.

The second fraction (200 ml) eluted with hexane (R_f 0.65, hexane) was obtained as a viscous liquid which was further purified by preparative TLC as 2 (220 mg). NMR (CCl_4): δ 2.0 (1H, dd, J=3.5 Hz Hb), 2.65 (1H, d, J= 8.0 Hz - $C\underline{H}_2Br$), 2.95 (1H, dd J=2.5 Hz, Ha). 3.05 (1H, m, $-\dot{C}\underline{H}-CH_2Br$), 3.70 (1H, dd J=2.5 Hz, Ha), 6.28 (1H, s, $-CH=\dot{C}-$). MS, m/z (rel. int): 357 (M^+, 3.7%), 322 (M^+-Cl, 100%), 287 (M^+-2Cl, 2.5%), 277 (M^+-Br, 2%), 242 (322-Br, 17.5%), 236 (C_5Cl_5H, 5%), 207 (281-Br, 25%), 201 (25), 181 (27). GLC (retention time): 2.74'.

Further elution with hexane (300 ml) gave a photoproduct 4 (R_f 0.55, hexane) which was crystallised from methanol as colourless crystals (85 mg) mp 117-18°. NMR (CCl_4): δ 2.0 (1H, dd, J=3.5 Hz, Hb), 2.65 (1H, J = 8.0 Hz, $-CH_2Br$), 2.95 (1H, dd, J=8.0 Hz, $-CH_2Br$), 3.10 (1H, m, $-\dot{C}\underline{H}-CH_2Br$), 3.70 (1H, d, J=2.5 Hz Ha), 6.05 (1H, d, J=6 Hz, $-CH=CH-$), 6.35 (1H, d, J= 6 Hz, $-CH=CH-$). MS, m/z (rel. int.): 323 (M^+, 2.5%), 288 (M^+-35, 100%), 253 (M^+-2Cl, 10%), 202 ($C_5Cl_4H_2$, 12%), 207 (288-HBr, 22.5%) 172 (253-HBr, 27%), 137 (172-Cl, 16%), 202 (12%), 181 (17.5%). GLC (retention time) 2.32'.

Photoirradiation of Bromodan in Methanol

Bromodan in methanol (0.1%, 500 ml) was irradiated in a quartz vessel and worked up as above to give a mixture which was subjected to column chromatography. The first compound eluted with hexane (R_f 0.65, hexane) was identified as unreacted promodan (mp, Co-TLC).

The second photoproduct (R_f 0.70, hexane) eluted with hexane (100 ml) was further purified by preparative TLC to afford 3 (185 mg) as viscous liquid. NMR (CCl_4): δ 1.75, 1.95 (1H, dd, J=3.5 Hz, Hb), 2.60 (1H, d, J =8.0

Hz,-CH_2Br), 2.95 (1H, d, J=8.0 Hz,-CH_2Br), 3.05(1H, m,-$\overset{|}{C}\underline{H}$-$CH_2Br$) 3.60, 3.70 (1H, dd, J=2.5 Hz, Ha), 5.98 (1H, s,-CH = C-Cl). MS, m/z (rel. int.): 357 (M^+, 2.4%), 323 (M^+-Cl, 100%), 287 (M^+-2Cl, 5%), 277 (M^+-Br, 2.5%), 243 (323-Br, 12.5%), 236 (C_5Cl_5H, 10%), 201 (C_5Cl_4H, 2.5%), 193(10). GLC (Ret. time): Rt, 2.80'.

The third photoproduct (R_f 0.55, hexane) eluted with hexane (200 ml) was crystallised from methanol as colourless crystals (135 mg) mp 117-18° and was identified as 4 on the basis of NMR & Mass spectral analysis.

Photoirradiation of Bromodan in hexane/acetone

Bromodan in hexane/acetone (0.1% 500 ml) was irradiated in a quartz vessel with UV light for 48 hours. The irradiated solution was concentrated under reduced pressure and subjected to column chromatography over silica gel. The first three products eluted with hexane were identified as dechlorinated analogues 2, 3 and 4. The fourth compound (R_f 0.30, hexane) isolated as a viscous liquid could not be crystallised and was purified by preparative TLC to give 5 (55 mg). 'HNMR (CCl_4): δ 1.2-1.7 (1H, m, Hb), 2.55 (1H, m,-CH_2-Br), 3.0 (1H, m,-CH_2Br); 3.2 (1H, m,-$\overset{|}{C}\underline{H}$-$CH_2Br$). 3.65 (1H, m, Ha), 4.25 (1H, s, -$\overset{|}{C}$H-Cl (anti), 6.2 (2H, m,-CH=CH-). MS (Rel. int): 289 (M^+, 2.5%), 254 (M^+-CL, 100%). 168 ($C_5Cl_3H_3$, 45%).

Photoirradiation of Bromodan in presence of Triethylamine

Bromodan (500 mg) in dry and distilled triethylamine (50 ml) was irradiated for 24 hours using a high pressure mercury lamp and quartz filter at room temperature. After 24 hours the reaction mixture was diluted with solvent ether (500 ml) and extracted with dil HCl to remove triethylamine. The organic layer was washed with water and dried over anh.sodium sulphate. After distilling off the solvent, the reaction mixture was chromatographed over silica gel column. The first fraction (200 ml) eluted with hexane was identified as unreacted bromodan (Co-TLC & NMR).

The second fraction (100 ml) gave a new photoproduct (R_f 0.75, hexane) which was purified as before to furnish 5 (135 mg) as viscous liquid. 'HNMR (CCl_4): δ 1.85-2.05(1H, m, Hb), 2.75 (1H, m,-CH_2Br), 3.25 (1H, m,-$\overset{|}{C}\underline{H}$-$CH_2Br$), 3.7 (1H, m, Ha), 4.15 (1H, s,-$\overset{|}{C}$HCl), MS, m/z (rel. int.): 357 (M^+, 30.0%), 323 (M^+-Cl, 2.5%), 287 (M^+-2Cl, 9.5%), 277 (M^+-Br, 1.9%), 242 (15%), 236 (C_5Cl_5H, 35%), 238 (100%), 207 (22%) 201 (40%), GLC (ret. time) 2.47'.

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