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ADDITION OF IODINE AZIDE TO BORNENE AND CAMPHENE

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Abstract—Addition of iodine azide to bornene and camphene has been studied. The structure of products has been established and a reaction mechanism was proposed.

In the course of our investigations on the addition of pseudohalogens to bicyclic unsaturated terpene systems,[1] the addition of iodine azide to bornene and camphene systems containing 5 and 6-membered rings has been studied.

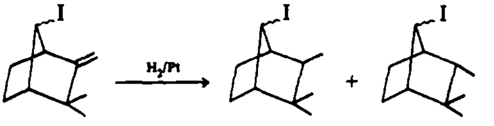
Stereochemistry of electrophilic addition of halogens and pseudohalogens to the above-mentioned hydrocarbons had been investigated by a number of authors,[2–4] who have shown that the reaction of camphene with bromine,[2] chlorine[3] or chlorine azide[4] yields mono and 2,10-disubstituted derivatives of bornene and disubstituted derivatives of isocamphene. Analogous reactions with the bornene system has not so far been fully elucidated. However, it has been demonstrated that the addition of chlorine, bromine, hypobromous and hypochlorous acids, sulphenyl chlorides, iodine chloride, "bromine fluoride" and chlorine azide to norbornene proceed stereospecifically and afford a mixture of mono-, 2,3- and 2,7-disubstituted derivatives of norbornane.[4,5] The addition of iodine azide to unsaturated bicycle compounds has been investigated by Hassner,[6] who observed that addition of iodine azide to 5,6-benzonorbornene-2 and methylenenorbornene proceeds also stereospecifically and yields 5-exo-azido-7-anti-iodo-benzonorbornane and 5-azido-1-iodo-methyl-nortricyclene, respectively.

The addition of iodine azide to bornene and camphene would be expected to afford unrearranged as well as rearranged products, according to the accepted mechanism of ionic addition to these compounds.[2–4,7] The addition was carried out at −35°, by dropwise addition of bornene or camphene dissolved in methyl cyanide to iodine azide solution prepared by the general method.[1,8] TLC of crude reaction products revealed in each case the presence of several compounds to which the structures **2**, **3**, and **4** in the case of bornene and structures **6**, **7**, and **8** in the case of camphene have been ascribed. Compounds **2**, **3**, **6**, **7**, and **8** were isolated from the respective reaction mixtures and separated by column chromatography on silica gel. Compound **4** could not be obtained in a pure state and its presence in the reaction mixture was deduced from the NMR spectra of the crude reaction product. A pure specimen of **4** was available from the reaction of **3** with $LiAlH_4$.

Drastic reduction with sodium in ethanol was applied to determine the carbon skeleton of **2–8**. Gas chromatography (GLC) analysis of the isolated hydrocarbon fractions showed that **2**, **6**, and **7** were reduced to camphene, **3** and **4** to isocamphane, and **8** to bornane.

Analysis of the NMR spectra provided further structural evidence of the addition products. Characteristic chemical shifts of some protons are recorded in Table 1.

According to Table 1, the signals of all protons of **2** are shifted downfield as compared with the analogous signals from camphene. The iodine atom in **2** could be unambiguously localized at C-7 on the basis of the above mentioned methyl protons downfield shift, as well as the appearance of –CHI signal at 3·82 ppm.[5,9] The structure of **2** was also confirmed by catalytic reduction, yielding a mixture of **9** and **10**.



2

9 and 10

The NMR spectrum of this mixture showed the presence of two signals (at 3·90 and 3·80 ppm) ascribed to protons at C-7, and the absence of olefinic proton signals (at 4·85 and 4·65 ppm) found in the NMR spectrum of the substrate. It can be assumed on these grounds that catalytic reduction of the double bond in **2** affords two isomers of 7-iodoisocamphane, with exo- and endo-methyl groups.[10,11] This conclusion is confirmed by the fact that both isomers of

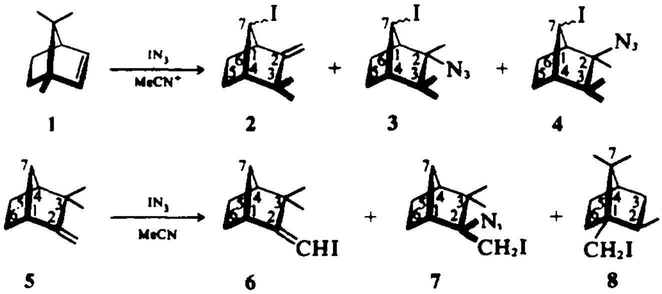


Table 1[a]. NMR spectral assignments of compounds 2–8

Compound No.	Chemical shifts (δ, ppm; J, Hz)[b]
2	4·85, 4·65 (two s, each 1H, $=CH_2$); 3·82 (broad s, 1H, CHI); 2·80, 2·18 (two m, each 1H, bridgehead protons); 1·50, 1·10 (two s, each 3H, Me).
3	3·86 (broad s, 1H, CHI); 2·68, 2·41 (two m, each 1H, bridgehead protons); 1·45, 1·39, 0·98 (three s, each 3H, Me).
4	4·6 (t, 1H, CHI, J = 1·5); 2·15, 1·88 (two m, each 1H, bridgehead protons); 1·40, 1·13, 1·05 (three s, each 3H, Me).
5	4·65, 4·45 (two s, each 1H, $=CH_2$); 2·62, 1·88 (two m, each 1H, bridghead protons); 1·05, 1·00 (two s, each 3H, Me).
6	5·50 (s, 1H, =CHI); 3·00, 2·19 (two m, each 1H, bridgehead protons); 1·10 and 1·08 (two s, each 3H, Me).
7	3·48 (dd, 2H, $-CH_2I$, J = 10); 2·48 and 2·08 (two m, each 1H, bridghead protons); 1·20, 1·03 (two s, each 3H, Me).
8	3·65 (pt, 1H, CHN_3, $W_{1/2}$ = 13); 3·22 (dd, 2H, $-CH_2I$, J = 9); 0·98, 0·90 (two s, each 3H, Me).

[a] All spectra were run in CCl_4 soln with TMS as int. ref.

[b] Abbreviations used: s, singlet; t, triplet; pt, pseudotriplet; dd, double doublet; m, multiplet.

isocamphane are formed on reduction of the mixture of 9 and 10 with $LiAlH_4$.

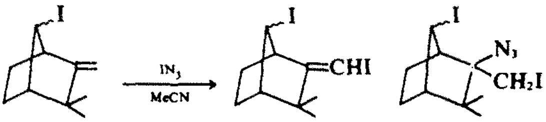
Exmaination of the NMR spectra of 3 and 4 indicates that they can be assigned the structures of endo- and exo - 2 - azido - 7 - iodoisocamphane, respectively, on the grounds of the known rules that exo substituents shift signals of C-7 protons downfield,[5,11] and that the chemical shifts of C-2 methyl protons depend upon the configuration at C-2.[5]

Addition of iodine azide to camphene in methyl cyanide afforded vinyl iodide 6, to which trans-configuration has been ascribed,[3,4] β-iodoazide 7, and 2 - exo - azido - 10 - iodobornane 8. The presence of the isocamphane carbon skeleton in 7 was confirmed by its reduction with $LiAlH_4$ yielding camphene 5. The formation of the corresponding olefins from β-iodoazides and of camphene from disubstituted isocamphane derivatives has been reported previously.[2,8] Analysis of the NMR spectrum of 7 and comparison of the methylene protons ($-CH_2I$) geminal coupling constants with those reported for analogous compounds[4] made it possible to assign the structure of 2 - azido - 2 - iodomethyl - 3,3 - dimethylnorbornane to 7. The stability of this compound, characteristic of disubstituted isocamphane derivatives with the azido group located at C-2,[4] further supports this structure. In contrast to analogous systems containing a tertiary iodine atom,[8] this compound does not undergo elimination when kept with potassium t-butoxide at 30° for 48 hr.

Similarly 8 was assigned the structure of 2-exo-azido-10-iodobornane on the basis of spectral and chemical data.[4] The position of the exo-azido group at C-2 can be deduced from characteristic splitting pattern of H-2 and H-10 NMR signals.

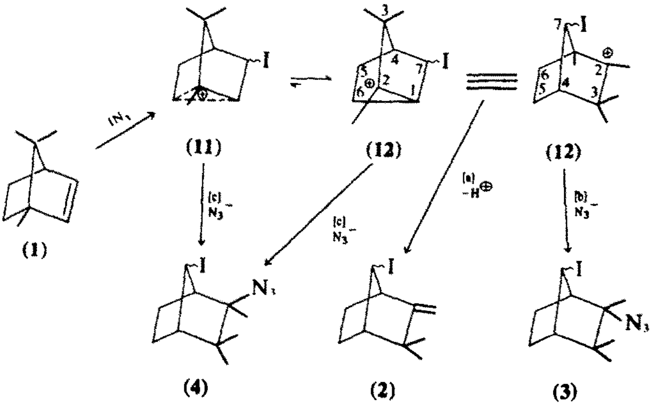
The proposed reaction pathway for the addition of iodine azide to bornene (Scheme 1) is consistent with the experimental evidence. Electrophilic attack of iodine azide on the double bond of bornene most likely results in the formation of a cation, which after Wagner-Meerwein rearrangement of the carbon skeleton can be stabilized by elimination of the H-8 proton (route a) or nucleophilic attack of an azide anion at C-2 (routes b and c). Cation 12 containing partially delocalized positive charge, similar to 2-methylnorbornyl cation,[12] is probably responsible for the formation of 2 - endo - azido - 7 - iodoisocamphane 3. Non-classical carbonium ion 11 would yield only the exo-isomer 4,[7] since nucleophilic attack is possible only from the exo side. The formation of small amounts of exo-isomer 4 may support the argument for the transient formation of cation 12 or may result from the non-classical carbonium ion 11. Steric hindrance in 12 is likewise responsible for the formation of 3 as the main reaction product.

The significant role of steric hindrance in the iodine azide addition to bicyclic unsaturated terpenes was also confirmed for 7-iodocamphene. In contrast to camphene (vide infra) no addition product 14 was formed in this case, elimination to vinyl iodide 13 being the only reaction pathway.

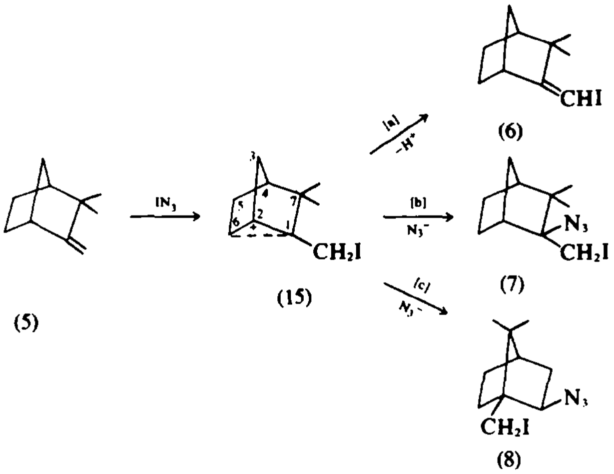


2 13 14

Iodine azide addition to camphene probably proceeds via cation 15, which can be stabilized by elimination of H-8 proton (Scheme 2, route a) or nucleophilic attack of an azido anion at C-2 (route b), yielding products 6 and 7, respectively. Nucleophilic attack of azido anion at C-6 accompanied by Wagner-Meerwein rearrangement (route c) affords compound 8, the exo-isomer being produced exclusively in accordance with the generally accepted mechanism of electrophilic addition to camphene.[2-4]

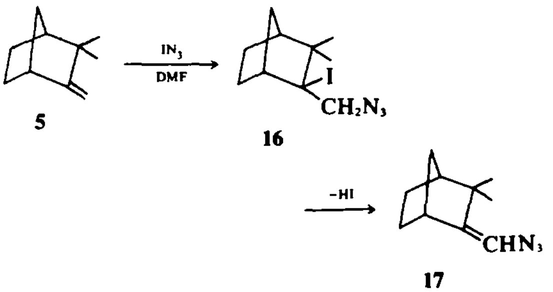


Scheme 1.



Scheme 2.

While preparing this paper, we learned of the work of Ranganathan *et al.*[13] regarding iodine azide addition to camphene. Performing the reaction at − 10°, these authors obtained only two products with physical constants similar to those of compounds **6** and **7**. The structures of 8-iodocamphene and 2 - azidomethyl - 2 - iodo - 3,3 - dimethylnorbornane have been arbitrarily assigned to them. It seems quite improbable that the structure of **7** is consistent with that proposed by Ranganathan *et al.* since this compound shows no tendency to isomerise to bornane derivatives[4] nor to elimination, yielding vinyl azide. 2 - Azidomethyl - 2 - iodo - 3,3 - dimethylnorbornane **16**, which according to Ranganathan *et al.* is one of the products of iodine azide addition to camphene in methyl cyanide, was probably obtained by us when the reaction was carried out in N,N-dimethylformamide solution. However, this compound, the NMR spectrum of which shows signals at 3·40 ppm assigned to the $-CH_2N_3$ group, is very unstable and undergoes elimination to vinyl azide **17** when purified by column chromatography.



In order to estimate the amounts of rearranged iodine azide adducts in the mixtures of crude reaction products they were reduced with sodium in ethanol. The mixture of camphene and isocamphane (1 : 1) was formed from crude IN_3-bornene adducts, whereas the reduction of IN_3-camphene adducts afforded a mixture of camphene and bornane (10 : 1). These results evidently suggest considerable contribution of Wagner-Meerwein rearrangement in the former case, but only minor involvement of it in the latter.

EXPERIMENTAL

Solvents and reagents were purified by conventional methods. All extracts were dried over $MgSO_4$ and evaporated under reduced pressure. M.ps were taken on a Kofler hot stage and were uncorrected. IR spectra were recorded using a Spectromom 2000 spectrophotometer (MOM, Budapest), NMR spectra were measured at 60 MHz with a Jeol JNM-C-60HL spectrometer in CCl_4 soln using TMS as internal standard. Gas chromatography (GLC) was performed on a 2 m column, i.d. packed with 10% reoplex on Celite 545, a V. Giede G CHF-3 gas chromatograph, was used, the column temperature was 110°, and the flow rate of the carrier gas (nitrogen) was 14 ml min^{-1}. TLC was performed using Merck silicagel and column chromatography on silicagel (E. Merck, 100–200 mesh) using light petroleum (60–80°) as eluent. Rotation measurements were carried out on a Perkin-Elmer polarimeter No. 141.

α-Pinene was obtained by fractional distillation of turpentine oil. B.p. 52°/20 mm, n_D^{20} 1·4668, $[\alpha]_D + 31{\cdot}9°$. Bornyl chloride was obtained by addition of hydrogen chloride to α-pinene.[14] M.p. 130–132°, $[\alpha]_D + 27{\cdot}1$. Bornene was obtained from bornyl chloride.[14] M.p. 108–110°, b.p. 149–150°, $[\alpha]_D - 16°$.

Addition of IN_3 *to bornene in* MeCN. To a solution of IN_3 made from ICl (18·3 g, 0·11 mol) and NaN_3 (14·8 g, 0·25 mol) in MeCN (100 ml), bornene (13·6 g, 0·1 mol) in MeCN (200 ml) was added dropwise at −35°. After heating to room temperature, the mixture was stirred for 10 hr. The reaction mixture was then worked-up as reported previously.[1,8] The resulting light-brown oil (21·2 g) was separated on a silicagel column (450 g). The separated products comprised 0·7 g of an unidentified hydrocarbon, 9·7 g of **2** and 7·0 g of **3**, as well as 2·8 g of unresolved mixture containing **4**, as shown by the NMR spectrum. Compound **2** was a colourless liquid, b.p. 40°/0·05 mm, n_D^{20} 1·5590, $[\alpha]_D + 28°$ ($CHCl_3$). IR: 1379 and 1392 cm^{-1} (Isopropyl), 3030, 1660 and 880 cm^{-1} (C=C). NMR: 4·85, 4·65 (two s, each 1H, $=CH_2$); 3·82 (broad s, 1H, CHI); 2·80, 2·18 (two m, each 1H, bridgehead protons); 1·50, 1·10 (two s, each 3H, Me) (Found: C, 45·8; H, 5·7. $C_{10}H_{15}I$ requires: C, 45·80; H, 5·73%). Compound **3** was a solid, m.p. 78·0–78·5°, b.p. 80–82°/0·06 mm, $[\alpha]_D - 56°$ (EtOH). IR (KBr): 1379 and 1392 cm^{-1} (Isopropyl), 2100 cm^{-1} (Azide). NMR: 3·86 (broad s, 1H, CHI); 2·68, 2·41 (two m, each 1H, bridgehead protons); 1·45, 1·39, 0·98 (three s, each 3H, Me). (Found: C, 39·4; H, 5·2; N, 13·8. $C_{10}H_{16}IN_3$ requires: C, 39·35; H, 5·25; N, 13·76%).

Addition of IN_3 *to camphene in* MeCN. The reaction was carried out as described above using ICl (18·3 g, 0·11 mol), NaN_3 (14·8 g, 0·25 mol) in MeCH (100 ml) and camphene (13·6 g, 0·1 mol) dissolved in MeCN (100 ml). The resulting crude product (22·0 g) was separated on a silicagel column (90 g), yielding I (1·8 g), II (13·6 g) and III (4·7 g). Fractions I and III proved to be chromatographically pure **6** and **7**, respectively. Fraction II was separated on a silicagel column (100 g), affording 5·0 g of **6**, 6·9 g of **7**, 0·8 g of **8** and 0·8 g of a mixture of identified and unidentified compounds.

Compound **6**, n_D^{20} 1·5223, $[\alpha]_D + 39{\cdot}4°$. IR: 760 and 1630 cm^{-1} (C=C), 1379 and 1392 cm^{-1} (Isopropyl). NMR: 5·50 (s, 1H, =CHI); 3·00, 2·19 (two m, each 1H, bridgehead protons); 1·10, 1·08 (two s, each 3H, Me) (Found: C, 45·4; H, 5·7. $C_{10}H_{15}I$ requires: C, 45·80; H, 5·73%).

Compound **7** was a colourless liquid, n_D^{20} 1·5480, $[\alpha]_D - 16°$ (MeOH). IR: 2100 cm^{-1} (Azide), 1379 and 1392 cm^{-1} (Isopropyl). NMR: 3·48 (dd, 2H, $-CH_2I$, J = 10); 2·48, 2·08 (two mm, each 1H, bridgehead protons); 1·20, 1·03 (two s, each 3H, Me) (Found: C, 39·9; H, 5·7; N, 14·2. $C_{10}H_{16}IN_3$ requires: C, 39·35; H, 5·25; N, 13·76%).

Compound **8** was a colourless liquid, $[\alpha]_D - 30·4°$ (CCl_4). IR: 2100 cm^{-1} (Azide). NMR: 3·65 (pt, 1H, CHN_3, $W_{1/2} = 13$); 3·22 (dd, 2H, $-CH_2I$, J = 9); 0·98, 0·90 (two s, each 3H, Me) (Found: C, 39·5; H, 5·5; N, 13·3. $C_{10}H_{16}IN_3$ requires: C, 39·35; H, 5·25; N, 13·76%).

Reduction of crude and pure IN_3 *adducts to bornene and camphene with* Na *in* EtOH. The crude mixture of IN_3-bornene adducts (10 g) was reduced with Na (10 g) in EtOH (300 ml). The resulting yellow-brown liquid (5 g) was distilled and the fraction boiling at 47–48°/7 mm (bath temp. 105–110°) collected. The isolated hydrocarbon fraction, analysed by GLC, contained 92% camphene and isocamphane (1:1), 4% bornane, 2% bornene and 2% unidentified substances.

Reduction of the crude mixture of IN_3-camphene adducts yielded a hydrocarbon fraction containing 98% camphene and bornane in the ratio 10:1.

Reduction of compounds **2, 3, 4, 6, 7** *and* **8** *with* Na *in* EtOH yielded the following hydrocarbons, camphene (90%, from **2**), isocamphane (95%, from **3** and **4**), bornane (90%, from **8**). Reduction products of **6** and **7** contained camphene (70% and 45%) contaminated with about 20% the unreacted substrates.

Reaction of **3** *with* $LiAlH_4$. To a suspension of $LiAlH_4$ (0·7 g, 0·02 mol) in Et_2O (100 ml), cooled to 0°, a solution of **3** (2·5 g, 8·2 mmol) in Et_2O (20 ml) was added dropwise with stirring. After stirring for 10 hr at room temperature the mixture was cooled in an ice-bath and excess $LiAlH_4$ decomposed with water (10 ml). The organic layer was decanted, dried and the solvent removed under reduced pressure. The resulting oil (2 g) was separated on a silicagel column (200 g). Unreacted compounds **3** (0·75 g) and **4** (0·65 g), and an unidentified substance (0·1 g) were obtained.

Compound **4** was a liquid, n_D^{20} 1·5620, $[\alpha]_D - 36·0°$ ($CHCl_3$). IR: 2100 cm^{-1} (Azide), 1379 and 1392 cm^{-1} (Isopropyl). NMR: 4·60 (t, 1H, CHI, J = 1·5); 2·15, 1·88 (two m, each 3H, bridgehead protons); 1·40, 1·13, 1·05 (three s, each 3H, Me) (Found: C, 39·9; H, 5·2; N, 13·8. $C_{10}H_{16}IN_3$ requires: C, 39·35; H, 5·25; N, 13·76%).

Catalytic reduction of **2**. Compound **2** (1·5 g, 6 mmol) was hydrogenated over platinum catalyst (0·07 g) in EtOH (150 ml) at room temperature for 28 hr. The catalyst was removed by filtration and the solvent evaporated. The resulting oil (1 g) was distilled *in vacuo* and the fraction boiling at 57–60°/0·2 mm (bath temp. 105–110°) collected. The isolated fraction was a mixture of **9** and **10**. NMR: 3·78, 3·90 (two broad s, CHI-protons of **9** and **10**; 2·12 – 1·95 (m, bridgehead protons); 1·40–0·8 (Me) (Found: C, 45·0; H, 6·1. $C_{10}H_{17}I$ requires: C, 45·45; H, 6·44%).

Reduction of **2, 9** *and* **10** *with* $LiAlH_4$. To a suspension of $LiAlH_4$ (1·0 g, mmol) in THF (90 ml) a solution of **2** (2·2 g, 8·4 mmol) in THF (20 ml) was added dropwise at room temperature and the mixture refluxed for 28 hr. The excess $LiAlH_4$ was decomposed with water (15 ml), precipitate inorganic salts were filtered off and the filtrate diluted with Et_2O and the organic layer decanted off and dried. After evaporation of the solvent an oil (1 g), identified (GLC) as camphene was obtained. A mixture of **9** and **10** (2·2 g) was reduced by the same method, using $LiAlH_4$ (1 g) and THF (100 ml). The reaction was carried out at reflux temperature for 14 hr to yield both isomers of isocamphane (0·8 g) as determined by GLC.

Reduction of **7** *with* $LiAlH_4$. The reaction was carried out as described above using 0·7 g (0·02 mol) $LiAlH_4$, 2·5 g (8·2 mmol) of **7** and Et_2O (100 ml). Excess $LiAlH_4$ was decomposed with 20% aqueous NaOH solution (10 ml). The reaction afforded camphene (40%) as detected by GLC and NMR.

Addition of IN_3 *to camphene in* DMF. To a solution of NaN_3 (14·8 g, 0·25 mol) in DMF (100 ml) ICl (18·3 g, 0·11 mol) followed by camphene (13·6 g, 0·1 mol) were added dropwise at −35°. The mixture was then stirred at room temperature for 8 hr and worked-up as previously described.[1] The NMR spectrum of the crude product (17·5 g) exhibited a double doublet at $\delta = 3·4$ ppm, J = 13 Hz, characteristic of methylene protons of the $-CH_2N_3$ group. This crude material was passed through a silica gel column (150 g). Decomposition involving elimination occured during this work-up procedure to give camphene (3·0 g), **17** (trans isomer,[4] 4·5 g) and an unidentified mixture (3·2 g).

Compound **17**, n_D^{20} 1·5271, $[\alpha]_D + 32·2°$ (MeOH). IR: 2100 cm^{-1} (Azide), 1670 cm^{-1} (C=C). NMR: 5·7 (s, 1H, $=CHN_3$); 3·0 (m, 1H, bridgehead proton); 1·0, 0·98 (two s, each 3H, Me) (Found: C, 67·6; H, 8·6; N, 23·6. $C_{10}H_{15}N_3$ requires: C, 67·80; H, 8·47; N, 23·73%).

Addition of IN_3 *to 7-iodocamphene in* MeCN. The reaction was carried out as previously described, using compound **2** (2·0 g, 7·6 mmol) ICl (1·2 g, 7·4 mmol) and NaN_3 (0·5 g, 7·7 mmol). The resulting crude product (2·0 g) was purified on a silicagel column (20 g), yielding **13** (1·8 g), m.p. 74·0–74.5°, $[\alpha]_D - 63°$ (benzene). IR: 780 and 1660 cm^{-1} (=C).

NMR: 5·76 (s, 1H, =CHI); 3·85 (broad s, 1H, CHI); 3·3, 2·45 (two m, each 1H, bridgehead protons); 1·62, 1·22 (two s, each 3H, Me) (Found: C, 30·5; H, 3·8. $C_{10}H_{14}I_2$ requires: C, 30·93; H, 3·60%).

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