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SYNTHESIS OF SUBSTITUTED TRIIODOALLENES

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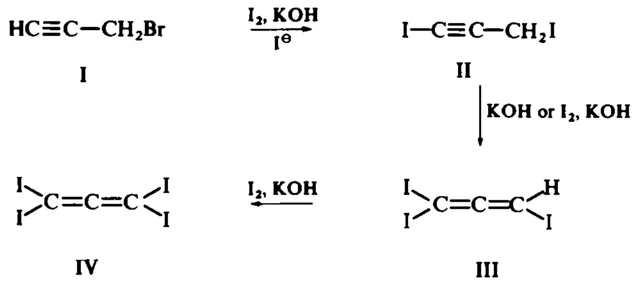
Abstract—Substituted triiodoallenes (VIa, b, c and IX) were synthesized from the corresponding substituted propynes (Va, b, c and VIII) as an extension of the acetylene-allene rearrangement of 1,3-diiodopropyne (II). A modification of the polyiodoallene synthesis using various iodoethynyl compounds (XIIa–d) such as iodinating reagents has been described.

IN THE preceding papers,[1,2] the synthesis of new haloallenes, tri- and tetraiodoallene (III and IV), from 3-bromopropyne (I) via the reaction processes in chart 1 was reported. The proposed reaction mechanism[2] which involves the intermediate allenic carbanions suggested the possibility that this reaction may be applicable to acetylenic compounds having at least one active methylene or methine group adjacent to an acetylenic linkage, and thus providing a useful method for the synthesis of substituted haloallenes.

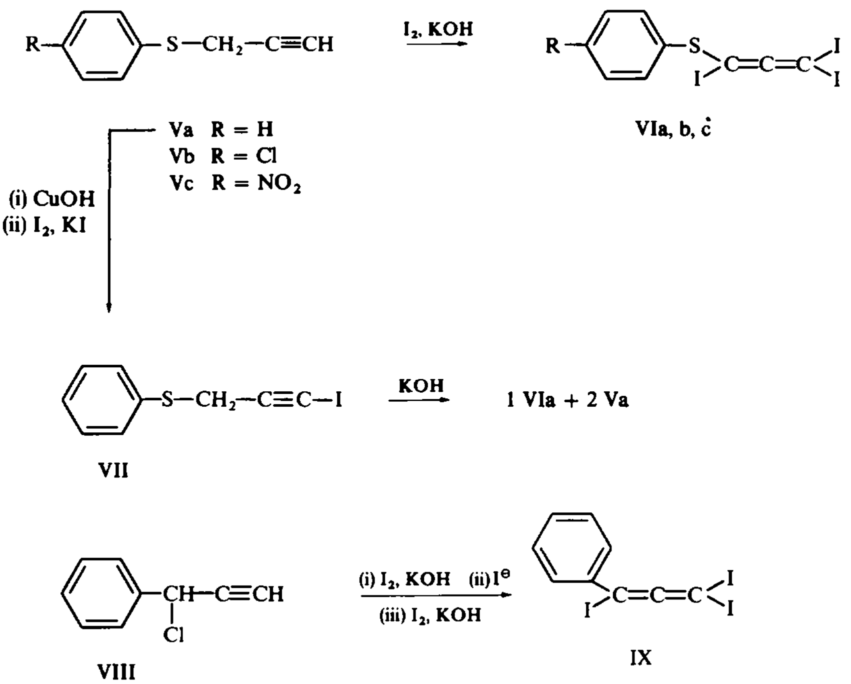
Chart 1



In this paper we show that this reaction is applicable to acetylenic compounds, such as aryl 2-propynyl sulphides (Va, b, c), 3-iodo-2-propynyl phenyl sulphide (VII) and 3-chloro-3-phenyl-1-propyne (VIII) as shown in Chart 2. When Va, b, c were treated with three mole equivalents of iodine in the presence of excess potassium hydroxide in aqueous methanol at 0–25°, corresponding substituted triiodoallenes (VIa, b, c) were obtained as yellow crystals in yields 40–56%. VIa, b, c could be recrystallized from carbon tetrachloride. Other 2-propynyl sulphides tested, e.g. *p*-tolyl, ethyl, i-butyl and benzyl 2-propynyl sulphide, however, could not be effectively converted into the corresponding substituted polyiodoallenes by employing the reaction conditions mentioned above, presumably because the formation of the intermediate 3-substituted 1-iodoallenic carbanion is thermodynamically less favourable than the corresponding carbanion (X) formation from 3-iodinated Va–c, (e.g.

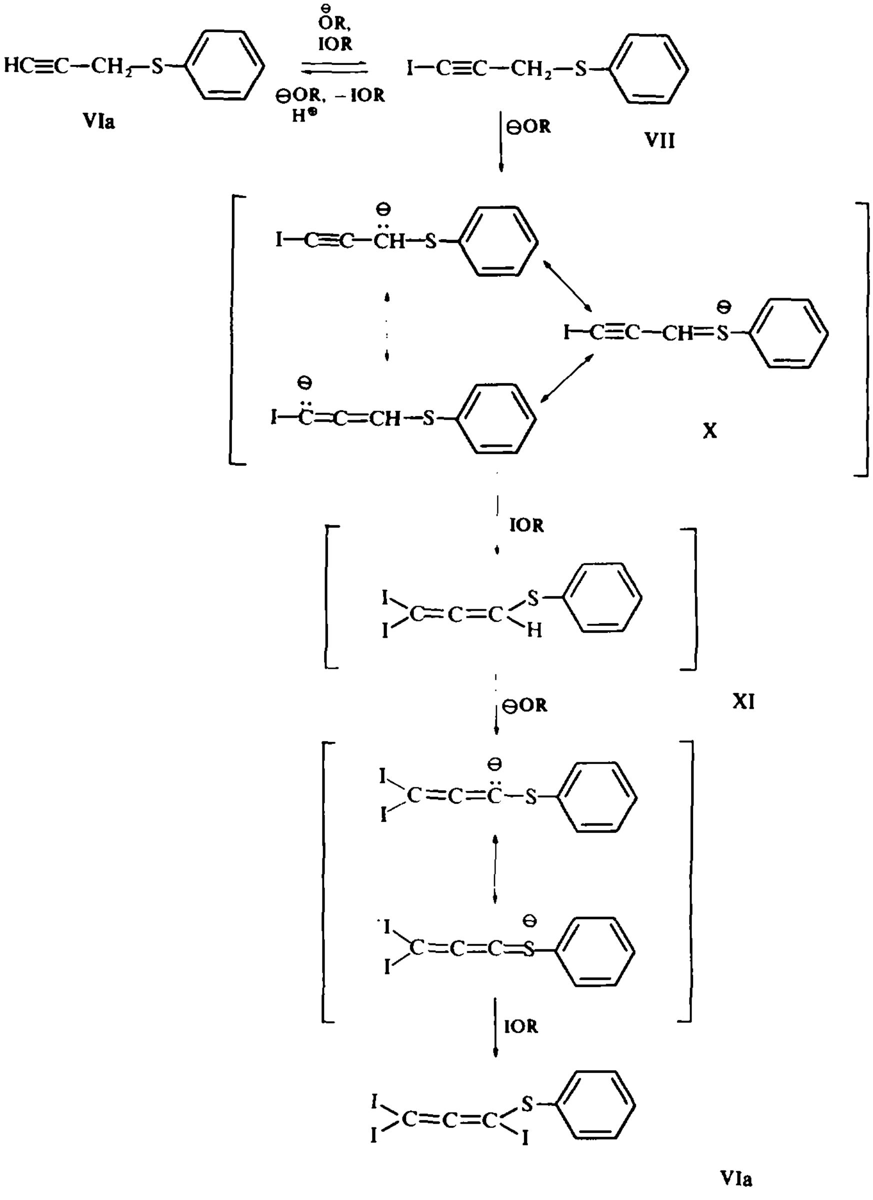
VII). Phenyltriiodoallene (IX) was obtained from VIII[6] only in poor yields (near 10%) when VIII was treated with one mole equivalent of iodine and potassium hydroxide at 20–25°, then with excess potassium iodide and finally with one mole equivalent of iodine and excess potassium hydroxide at 60° according to the procedures for the synthesis of III from I. VIa, b, c and IX show the similar properties to those of tri- and tetraiodoallene. They are unstable yellow crystals with relatively low decomposing points and are extremely susceptible to autoxidation. In the atmosphere they decomposed into black resinous materials within one day, while they could be stored unchanged for longer periods at −20° or in nitrogen. The stability against heat decreases in the order VIc > VIa > VIb > IX. The IR spectrum of each of these polyiodoallenes shows a sharp strong band characteristic of a C=C=C bond in the region 1913–1915 cm^{-1}. Elemental analyses, mol wt determinations and IR spectral analyses confirmed the structures of VIa, b, c and IX.

Chart 2



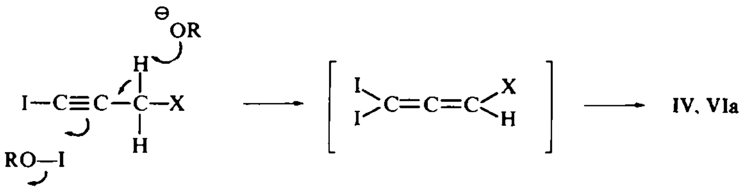
Iodination of Va through the Cu^{I}-acetylide gave VII in a yield 40%. As expected from the reaction of II, when VII was treated with a catalytic amount of potassium hydroxide in methanol at 30° for 30 min, a base-catalysed intermolecular iodine transfer reaction yielded VIa and Va in a molar ratio of 1 : 2 (isolated in 78 and 76·5% respectively calculated from the theoretical equation in Chart 2). Accordingly, the reaction can be explained by a carbanion mechanism (Chart 3) analogous to that[1,2] proposed for the reaction II → III, although in both cases the first step of the reaction could be explained also in terms of an alternative one-stage mechanism of B-S_E 2′ type[7] as shown in Chart 4.

Chart 3



R = H, Me

Chart 4

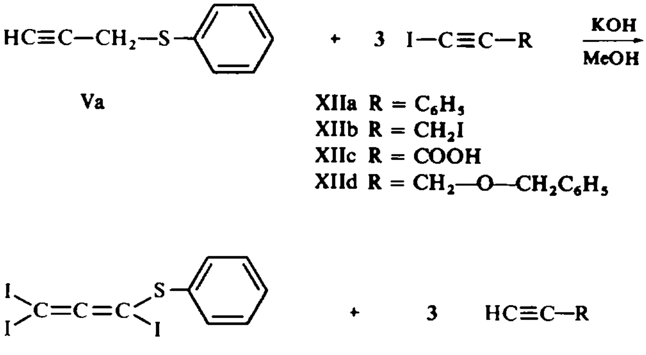


III $X = I$
XI $X = S—C_6H_5$

In every reaction, Va, b, c → VIa, b, c; VII → VIa + Va; VIII → IX, no intermediate substituted diiodoallenes were obtained. Thus, even when one mole equivalent of iodine and excess potassium hydroxide were allowed to react on Va in this reaction, the sole product isolated was the substituted triiodoallene (VIa) in 84 % yield based on the added iodine, indicating that the intermediate (probably 1,1-diiodo-3-phenylthioallene, XI) is rapidly converted into VIa under the reaction conditions.

Further, a modification of the polyiodoallene synthesis was carried out using the intermolecular iodine transfer reaction between Va and various iodoethynyl compounds (XIIa–d). As shown in chart 5, when a mixture of Va and XIIa–d (molar ratio 1:3) in methanol was treated with potassium hydroxide at 25°, VIa was obtained in yields of 32·8–64·3 %. Although quantitative isolation of the deiodinated compound (XIIIa–d) was not always easy because of the contamination of unreacted XIIa–d and unknown by-products, an approximately equivalent amount of benzyl 2-propynyl ether (XIIId) could be isolated when benzyl 3-iodo-2-propynyl ether (XIId) was used as an iodine source.

Chart 5



Va

XIIa $R = C_6H_5$
XIIb $R = CH_2I$
XIIc $R = COOH$
XIId $R = CH_2—O—CH_2C_6H_5$

VIa

XIIIa–d

EXPERIMENTAL

All m.ps were determined in capillary tubes and are uncorrected. IR spectra were taken bn a Koken Model DS 401G grating IR spectrometer. Mol. wts were determined by the method of freezing point depression of benzene.

Iodine contents of VIa, b, c, VII and IX were determined by the $NaBH_4$ reduction method.[2] Before titration of the iodide ions with a standard solution of KIO_3, organic reduction products were removed by extracting with ca $\frac{1}{3}$ volume of $CHCl_3$. Otherwise, significantly larger (10–20 %) values were obtained in the case of VIa, b, c and VII.

Arylthiotriiodoallenes (VIa, b, c)

Starting materials (Va, b, c) were prepared from 3-bromopropyne and the alkali mercaptides by the known method.[3,4] Va, b.p. 69–70°/1·3 mm, was obtained in 63 % yield (lit.[3] b.p. 104–110°/10 mm); Vb, b.p. 74–76°/0·02 mm, yield 63 %; Vc, m.p. 97–98°, yield 88 % (lit.[3] m.p. 99–100°).

(a) *Phenylthiotriiodoallene* (VIa). Powdered I_2 (10·3 g) was added in small portions, with stirring at 20–25°, during 20 min to a soln of Va (2 g) in 97 % aq. MeOH (30 ml) containing KOH (3·8 g). After stirring an additional 10 min at this temp, ice-water (10 ml) was added and the mixture was cooled at −20° for 17 hr. The product of yellow crystals (4·0 g; 56 %) were collected and washed with cold MeOH and water, m.p. 95–96° (dec). After recrystallization from CCl_4 it showed m.p. 96–97° (dec); ν_{max} (CCl_4) 1914 cm^{-1} (C=C=C). (Found: C, 20·82; H, 1·71; I, 71·90; mol. wt., 528. $C_9H_5SI_3$ (525·9) requires: C, 20·60; H, 0·96; I, 72·39 %.)

By analogous procedures, VIb and VIc were obtained from Vb and Vc, respectively.

(b) p-*Chlorophenylthiotriiodoallene* (VIb) was obtained as yellow crystals from CCl_4, m.p. 87–88° (dec), yield 49 %; ν_{max} (CCl_4) 1913 cm^{-1} (C=C=C). (Found: C, 18·75; H, 0·80; I, 67·52; mol. wt., 559. $C_9H_4SClI_3$ (560·4) requires: C, 19·29; H, 0·72; I, 67·94 %.)

(c) p-*Nitrophenylthiotriiodoallene* (VIc) was obtained as yellow crystals from CCl_4, m.p. 99–100° (dec), yield 40 %; ν_{max} (CCl_4) 1913 cm^{-1} (C=C=C). (Found: C, 19·25; H, 1·09; I, 66·90; mol. wt., 564. $C_9H_4NO_2SI_3$ (570·9) requires: C, 18·93; H, 0·71; I, 66·68 %.)

Phenyltriiodoallene (IX)

A soln of KOH (0·75 g) in 90 % aq. MeOH (3 ml) was added dropwise, at 20–25°, during 10 min, to a stirred soln of VIII[5] (1 g, b.p. 57–59°/0·5 mm, lit. b.p. 64–66°/4 mm) in MeOH (20 ml) with a suspension of powdered I_2 (1·7 g). After stirring 20 min, powdered KI (2 g) was added and stirring was continued an additional 20 min at this temp. A soln of KOH (1·5 g) in 90 % aq. MeOH (6 ml) was added at once then powdered I_2 (1·7 g) in 4 portions during 30 min to the stirred reaction mixture at 60°. MeOH was removed *in vacuo* and the residue (brown oil) was washed with ice-water (30 ml) and MeOH (10 ml) and stored overnight at −20°. The oil which crystallized was washed with cold MeOH. The yellow crystals (300 mg, 9·2 %) having a slight aromatic odour, m.p. 72–73° (dec) were recrystallized from MeOH; ν_{max} (CCl_4) 1915 cm^{-1} (C=C=C). (Found: C, 22·40; H, 1·09; I, 76·51; mol. wt., 481. $C_9H_5I_3$ (493·9) requires: C, 21·88; H, 1·02; I, 77·09 %.)

3-*Iodo-2-propynyl phenyl sulphide* (VII)

Compound Va (1 g) was shaken vigorously with CuOH[5] (prepared from 5 g of CuCl) in MeOH (50 ml) at 15–20° for 3 hr. A soln of I_2 (1·72 g) and KI (1·72 g) in water (5 ml) was added slowly to the mixture with stirring. It was stirred for 30 min and filtered. After removal of the solvent, the residue was extracted with Et_2O (50 ml). Evaporation of the Et_2O-extract left partially crystallized oily substance (crude VII, 1·34 g) which crystallized from MeOH as colourless crystals (0·74 g, 40 %), m.p. 48–49°; ν_{max} (neat) 2200 cm^{-1} (C≡C). (Found: C, 39·63; H, 2·81; I, 45·85. C_9H_7SI requires: C, 39·43; H, 2·57; I, 46·30 %.)

Compounds Va *and* VIa *from* VII

A soln of VII (400 mg) in MeOH (4 ml) containing KOH (70 mg) was allowed to stand at 30° for 30 min and then cooled at −20° overnight. The product of yellow crystals were washed with cold MeOH, m.p. 95–96° (dec), 200 mg (78 % of the theoretical amount) and found to be identical with VIa obtained from Va by the action of I_2 and KOH (mixed m.p. and IR spectra comparison). The filtrate was diluted with water (20 ml) and extracted with Et_2O (20 ml). From the Et_2O-extract a colourless oil, b.p. 70–80°/1·4 mm (bath temp), 110 mg (76·5 % of the theoretical amount), was obtained. The IR spectrum of this oil was identical with that of the authentic Va.

Compound VIa *from* Va *using iodoethynyl compounds* (XIIa–d) *as iodinating reagents*

Iodoethynylbenzene (XIIa) and XIId were prepared from XIIIa and XIIId,[10,11] respectively, by the iodination method[1,2,10] reported; XIIa, b.p. 66–68°/0·2 mm, lit.[8] b.p. 97–103°/3 mm; XIId[10], b.p. 104–105°/0·03 mm. Compound XIIb[1,2] (=II) and iodopropiolic acid[9] (XIIc) were also synthesized by the method in the literature; XIIb, b.p. 47–48°/0·025 mm; XIIc, m.p. 140–141°.

A soln of KOH (400 mg) in MeOH (2 ml) was added slowly to a mixture of Va 493 mg, (3·33 mmoles) and one of XIIa–d (10 mmoles) in MeOH (3 ml). The soln was allowed to stand at 25° for 20 min and cooled at −20° for several hr. The yellow plates (VIa) which separated were washed with cold MeOH, m.p. 96–97° (dec). The yields varied depending on XIIa–d used. 780 mg, 44·6% (from Va and XIIa); 593 mg, 32·8% (from Va and XIIb); 1025 mg, 58·6% (from Va and XIIc) and 1125 mg, 64·3% (from Va and XIId).

In an experiment in which XIId was used, XIIId was isolated as follows. MeOH was removed from the filtrate *in vacuo* and the residue was shaken with Et_2O and water. From the Et_2O-extract, by distillation, a colourless oil, b.p. 64–66°/2·0 mm (950 mg, 65% of the theoretical amount), was obtained. This oil was identical with the authentic XIIId[10, 11] prepared from 2-propyne-1-ol and benzyl chloride by the action ot NaOH. (b.p. and IR spectra comparison.)

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