[Chem. Pharm. Bull.
13(11)1374~1376(1965)]

UDC 547.315.1.07

Formation of Tri- and Tetraiodoallene from 1,3-Diiodopropyne

It is known that various three-carbon acetylenic systems rearrange to allenic systems through anionotropic[1] or prototropic[2] mechanisms. In the case of 3-halopropynes or their 3-alkyl derivatives whose rearrangement reactions have been studied most extensively,[1] it is noticeable that while 3-halopropynes or their derivatives rearrange to the corresponding mono-haloallenes by the action of acids anionotropically, their reactions with bases on the other hand give the ordinary displacement products, 2-propynyl-alcohols, -ethers,[1b,d,f] or -amines.[3] However, no works on the related reactions of 1,3-dihalopropynes have been reported.

This communication is concerned with the formation of tri- and tetraiodoallene from 1,3-diiodopropyne by the action of potassium hydroxide through at least two reaction steps, a possible prototropic acetylene-allene rearrangement being accompanied by an intermoleculer transfer of iodine. An oxygenolytic alcoholysis of tetraiodoallene to the formation of alkyl triiodoacrylate is also described as a characteristic reaction of poly-haloallene.

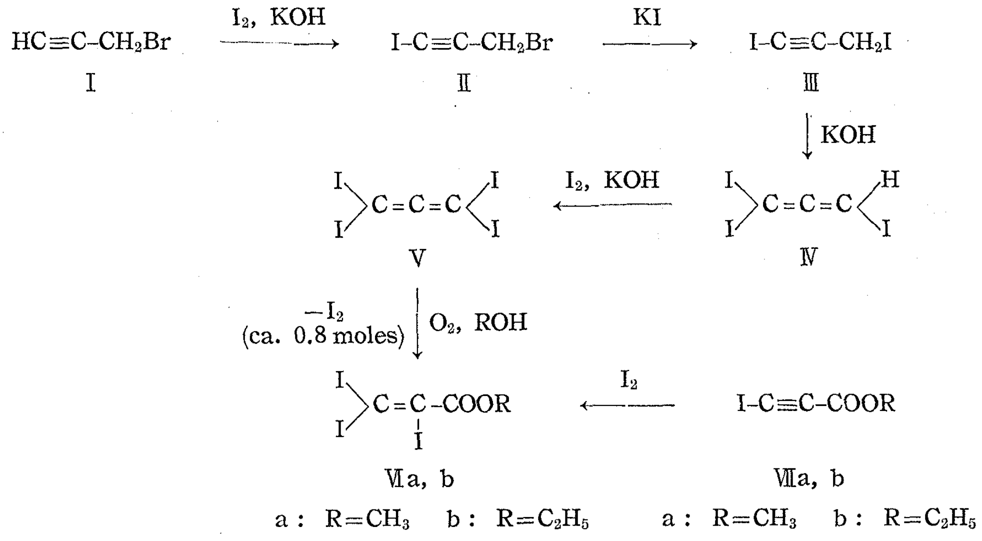

Chart 1.

Iodination of 3-bromopropyne (I) with one mole equivalent of iodine and potassium hydroxide in methanol at 5~20° gave 1,3-diiodopropyne (Ⅲ), colorless liquid, b.p$_{0.014}$ 44.5~45.0°. *Anal.* Calcd. for $C_3H_2I_2$: C, 12.35; H, 0.69; I, 86.96. Found : C, 11.92; H, 1.16; I, 86.90. The yield (11%) of Ⅲ was low because of contamination of the inter-

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1) *a*) A. Favorsky, T.A. Favorskaya : Compt. rend., **200**, 839 (1935). *b*) G.H. Hennion, J.J. Sheehan, D.E. Maloney : J. Am. Chem. Soc., **72**, 3542 (1950). G.F. Hennion, D.E. Maloney : *Ibid.*, **73**, 4735 (1951). *c*) T.L. Jacobs, W.F. Brill : *Ibid.*, **75**, 1314 (1953). *d*) A. Burawoy, E. Spinner : J. Chem. Soc., **1954**, 3752. *e*) T.L. Jacobs, E.G. Teach, D. Weiss : J. Am. Chem. Soc., **77**, 6254 (1955). *f*) V.J. Shiner, Jr., J.W. Wilson : *Ibid.*, **84**, 2402 (1962). *g*) J.H. Wotiz : *Ibid.*, **72**, 1639 (1950). *h*) Y.R. Bhatia, P.D. Landor, S.R. Landor : J. Chem. Soc., **1959**, 154.

2) *a*) A. Favorsky : J. prakt. Chem., **37**, 382 (1888). *b*) T.L. Jacobs, R. Akawie, R.G. Cooper : J. Am. Chem. Soc., **73**, 1273 (1951). *c*) E.R.H. Jones, G.H. Whitham, M.C. Whiting : J. Chem. Soc., **1954**, 3201. *d*) T.L. Jacobs, S. Singer : J. Org. Chem., **17**, 475 (1952). *e*) L. Crombie, A.G. Jacklin : J. Chem. Soc., **1955**, 1740. *f*) G. Pourcelot, P. Cadiot, A. Willemart : Compt. rend., **252**, 1630 (1961).

3) *a*) G.F. Hennion, K.W. Nelson : J. Am. Chem. Soc., **79**, 2142 (1957). *b*) G. F. Hennion, R. S. Hanzel : *Ibid.*, **82**, 4908 (1960).

mediate compound, 3-bromo-1-iodo-1-propyne[4] and a by-product, methyl 3-iodo-2-propynyl ether. III is comparatively stable and could be stored at 15∼20° for a few weeks without remarkable decomposition. A strong band at 2220 cm^{-1} (-C≡C-) and the absence of bands in the region of 1900∼1950 cm^{-1} which indicate allenic structures[1c,4,5] in the infrared absorption spectrum of III (liquid film) indicate that III exists stable as the acetylenic form in contrast with the case of 3-iodopropyne[1c,4] in which an equilibrium between acetylenic and allenic tautomer is observed. Treatment of III with one mole equivalent of potassium hydroxide in methanol at 15∼20° for seventeen hours and dilution with ice-water gave pale yellow plates (IV), m.p. 80∼82° (decomp.), *Anal.* Calcd. for C_3HI_3 : C, 8.63; H, 0.24; I, 91.13. Found: C, 8.97; H, 0.16; I, 91.40. IV is very unstable and on standing in the atmosphere for a few hours decomposed oxygenolytically to black resinous materials. In a vacuum desiccator at 20∼25° IV could be stored for about a week almost unchanged. The infrared absorption spectrum of IV (CCl_4, or $CHCl_3$) shows a typical allenic absorption band[5] at 1928 cm^{-1}. The nuclear magnetic resonance spectrum of IV shows one[*1] singlet proton at 4.55 τ (CCl_4). Reduction of IV with excess sodium borohydride in ethanol at 50° for ten minutes gave quantitative amount of iodide anion (three moles from one mole of IV) which was titrated with a standard solution of potassium iodate in conc. hydrochloric acid. Molecular weight determination of IV by the method of freezing point depression of benzene gave the values 410∼435 (Calcd. 417.8). IV was also obtained in ca. 50% yield from I by treatment of the iodinated reaction mixtures containing crude III with one mole equivalent of potassium hydroxide at 55° for five minutes. From the above experimental data the structure triiodoallene (IV) was confirmed.

Iodination of I with three moles of iodine and six∼seven moles of potassium hydroxide in 90∼95% aqueous methanol at 15∼20° for seventeen hours and dilution with ice-water gave yellow prisms (V), m.p. 93∼94° (decomp.),[*2] yield 26%, *Anal.* Calcd. for C_3I_4 : C, 6.63; I, 93.37. Found : C, 6.89; H, 0.51; I, 93.00. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} : 1905[*3] (s C=C=C), 723 (w), 700 (s). The nuclear magnetic resonance spectrum of V showed no proton resonances. Molecular weight determination of V gave the values 530∼550 from the freezing point depression of benzene (Calcd. 543.8). V could be also derived from IV by the action of one mole of iodine and two moles of potassium hydroxide in 70% yield or otherwise from III by the action of potassium hydroxide in 20% yield. Therefore a route in the formation of V proved to be I→III→IV→V.

As shown in Chart 2, the intermediate formation of hypoiodite anion[*4] can be suggested for the interpretation of the iodine transfer reaction in the formation of IV and V from III.

V is more stable than IV in its crystalline form and could be stored for a few weeks in a vacuum desiccator without decomposition. But in solutions (methanol, carbon tetrachloride or benzene) V is very unstable and decomposes releasing iodine in the presence of air. Thus, when a methanolic solution of V was stirred at 20∼25° in an open flask for seventeen hours then poured into a large amount of water, ca.

[*1] The number of hydrogen was determined from the integrated intensity of the signal comparing with that of a standard compound, methyl triiodoacrylate (VIa) (CH_3, 6.12 τ, CCl_4). The spectrum was taken on Varian Associates A-60 recording spectrometer.

[*2] A lower melting point was observed near 90° when temperature was raised very slowly.

[*3] The allenic band shifted to 1915 cm. when measured in CCl_4.

[*4] Of course, which of the conceivable iodinating reagents, *e.g.* $OI^{\ominus}$, HOI or $I^{\oplus}$ should be written most correctly in place of $OI^{\ominus}$ in Chart 2 is a point to be discussed, but in such a strong alkaline solution as used here, dominant existence of $OI^{\ominus}$ can be assumed, so we regard the anion as the iodinating reagent tentatively.

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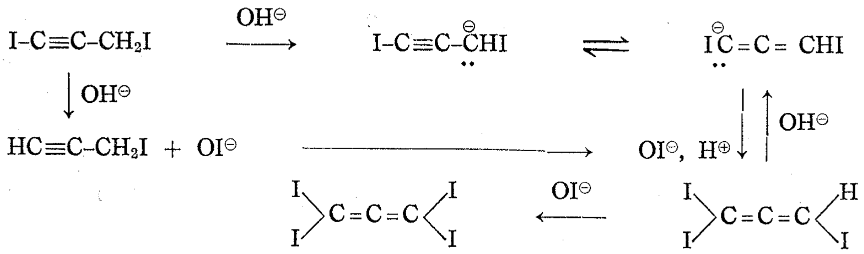

Chart 2. A Possible Reaction Route in the Formation of Tri- and Tetraiodoallene from 1,3-Diiodopropyne

0.8 moles of iodine and colorless plates (Ⅵa) of m.p. 85～86° (yield 76%) were obtained. *Anal.* Calcd. for $C_4H_3O_2I_3$: C, 10.35; H, 0.65. Found: C, 10.29; H, 0.53. When the above reaction was carried out in the nitrogen atmosphere, only the starting material (Ⅴ) was recovered. The structure of Ⅵa, methyl triiodoacrylate was confirmed through direct comparison with the authentic specimen synthesized from methyl iodopropiolate (Ⅶa) by addition of iodine. From an ethanolic solution of Ⅴ, by the same procedure described above there was obtained ethyl triiodoacrylate (Ⅵb), colorless prisms of m.p. 65.5～66.5°, which was also identical with the authentic specimen synthesized from ethyl iodopropiolate (Ⅶb).

Tetrachloro- and tetrabromoethylene are known to be oxidized similarly to the corresponding trihaloacetyl halide in conc. nitric acid.[6] Therefore the intermediate formation of triiodoacryloyl iodide can be suggested in this reaction and the fact that all iodine removed from Ⅴ is not ionic but elemental is explainable suggesting that the primarily generated hydroiodic acid through the alcoholysis of the acid iodide was oxidized to elemental iodine in the course of the reaction. Further elucidations are in progress in connection with the reaction of Ⅳ and in various solvents.

The authors express their gratitude to Dr. T. Nishida, Kobayashi Institute of Physical Research, for NMR spectral measurements, and to Dr. H. Honma, the Institute of Physical and Chemical Research, for elemental analyses. The authors are also grateful to Dr. H. Ogawa, Director of these Laboratories, for his encouragement throughout this work, and to Miss M. Takei and Miss Y. Sekiya of these Labolatories, for elemental analyses.

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Received July 24, 1965

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