Reaction of Propylene with a Mixture of Iodine and Iodosobenzene or Phenyl Iodine Diacetate*[1]

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In our kinetic study of iodination by a mixture of iodine and peracetic acid, it has been postulated that acetyl hypoiodite, CH_3COOI, is a probable attacking species.[1] Recently, our further study has revealed that iodosobenzene or phenyl iodine diacetate is a more effective oxidizing agent than peracetic acid for iodinating aromatic compounds, but here again acetyl hypoiodite can be postulated as the attacking species[2]:

$$I_2 + PhI(OCOCH_3)_2 \rightarrow 2CH_3COOI + PhI \quad (1)$$

$$ArH + CH_3COOI \rightarrow ArI + CH_3COOH \quad (2)$$

The addition of the acetyl hypohalite formed by the reaction of silver acetate with elementary halogen to olefin has been called the "Prévost reaction."[3] Prévost products have also been observed in the reaction of cyclohexene[4] or propylene[5] with a mixture of iodine and peracetic acid, *e. g.*,

$$2CH_3CH{=}CH_2 + I_2 + CH_3CO_3H + CH_3CO_2H \rightarrow 2CH_3CH(OCOCH_3)CH_2I + H_2O \quad (3)$$

Therefore, we reacted olefin with a mixture of iodine and phenyl iodine diacetate or iodosobenzene.

The reaction of propylene with a mixture of iodine and phenyl iodine diacetate in a mixed solvent of acetic acid and ethyl ether at 21—27°C was found to give 1-iodo-2-acetoxypropane in a yield of 56%:

$$2CH_3CH{=}CH_2 + I_2 + PhI(OCOCH_3)_2 \rightarrow 2CH_3CH(OCOCH_3)CH_2I + PhI \quad (4)$$

Also, the reaction of propylene with a mixture of iodine and iodosobenzene in acetic acid-ethyl ether at 22—28°C was found to give a lower yield (37%) of 1-iodo-2-acetoxypropane:

$$2CH_3CH{=}CH_2 + I_2 + PhIO + 2CH_3CO_2H \rightarrow 2CH_3CH(OCOCH_3)CH_2I + PhI + H_2O \quad (5)$$

The reaction of propylene with a mixture of iodine and peracetic acid in a similar method gave 1-iodo-2-acetoxypropane in a 56% yield.

Although the reaction of phenyl iodine diacetate with olefin alone is known to give *vic*-diacetoxy alkane,[6] 1,2-diacetoxypropane was not detected in the present reaction products.

These results suggest that iodine is converted by phenyl iodine diacetate to acetyl hypoiodite, which then adds to propylene to give an iodoacetoxy compound.

Experimental

Materials. The iodobenzene was prepared by the reaction of benzene with a mixture of iodine and peracetic acid, bp 182—185°C.[1] The phenyl iodine diacetate was prepared by the peracetic acid oxidation of iodobenzene, mp 157—159°C (lit., mp 158°C[7] and 161.1—162.2°C[8]). The iodosobenzene was prepared from iodobenzene *via* iodobenzene dichloride.[9] Ethyl ether and iodine were reagent-grade. 99.5% acetic acid and 99.5% propylene were used. The peracetic acid solution was prepared by stirring acetic anhydride (407 g) drop by drop into a solution of 60% hydrogen peroxide (100 g) and concentrated sulfuric acid (1 m*l*) as a catalyst at 30—40°C over a period of 3 hr.[10] The 1,2-diacetoxypropane was prepared by the reaction of propylene and peracetic acid in a mixture of ether and acetic acid, bp 51—52°C/1.3 mmHg.[5]

Analysis of the Products. The infrared spectra were determined by a Perkin-Elmer Model 333 spectrophotometer. The products were analyzed by means of gas chromatography employing a Yanagimoto Model GCG 550 F apparatus equipped with a flame ionization detector operated with a 2 m×3 mm column packed with Apiezon grease L 15% on Celite 545 (80—100 mesh), using nitrogen as a carrier (18—12.5 m*l*/min) at 80—200°C (6°C/min); hydrogen flow rate 25 m*l*/min, injection temperature 255°C, detector temperature 250°C. The retention times of 1-iodo-2-acetoxypropane, iodobenzene, and 1,2-diacetoxypropane were 9.7, 12.5, and 7.1 min respectively.

Reaction of Propylene with a Mixture of Iodine and Phenyl Iodine Diacetate. Into a stirred ethereal solution (100 m*l*) of iodine (2.54 g, 0.01 mol), phenyl

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iodine diacetate (3.22 g, 0.01 mol) was added. Propylene was passed into the solution, but apparently no reaction occurred, because phenyl iodine diacetate is virtually insoluble in ether. Therefore, acetic acid (50 m*l*) was added to the solution to dissolve it, and propylene was passed into the solution at 21—27°C over a period of 35 min. The mixture was then kept standing for additional 1 hr. Finally, the solution became transparent. The mixture was transferred into a separatory funnel containing ether (50 m*l*) and water (100 m*l*). The ether layer was washed three times with a 5% sodium hydroxide solution (each 50 m*l*) to remove the acetic acid, and finally washed with 5% sodium thiosulfate (50 m*l*) and dried over anhydrous sodium sulfate. The ether was evaporated under reduced pressure (42 mmHg) at 17°C. The residual liquid (4.01 g) was analyzed by gas chromatography in order to estimate the yields of 1-iodo-2-acetoxypropane (56% on the basis of the iodine) and iodobenzene (72% on the basis of the phenyl iodine diacetate). The infrared spectrum of the liquid is consistent with a binary mixture of the corresponding authentic samples. The absorption bands at 2970, 1740, 1370, 1240, 1023, and 600 cm^{-1} are characteristic of 1-iodo-2-acetoxypropane, and while those at 3050, 1570, 1470, 1440, 730, 685, and 655 cm^{-1} are characteristic of iodobenzene. Gas chromatography shows that the products do not contain 1,2-diacetoxypropane.

Reaction of Propylene with a Mixture of Iodine and Iodosobenzene. Iodosobenzene (2.20 g, 0.01 mol) was added to a stirred ethereal solution (100 m*l*) of iodine (2.54 g, 0.01 mol). The iodosobenzene was insoluble in ether. Acetic acid (50 m*l*) was then added to the mixture, and propylene was passed into the solution at 22 —28°C over a period of 30 min, and the mixture was left standing overnight. The solution gradually turned pale yellow and transparent, and some unreacted iodosobenzene settled at the bottom of the flask. The reaction mixture was then worked up as above, giving a residual liquid (2.89 g). The yields of 1-iodo-2-acetoxypropane (37%) and iodobenzene (60%) were estimated by gas chromatography.

Reaction of Propylene with a Mixture of Iodine and Peracetic Acid. Into a stirred ethereal solution (100 m*l*) of iodine (2.54 g, 0.01 mol) there was added, drop by drop, an acetic acid solution of 1.79 M peracetic acid (30 m*l*, 0.0537 mol). Propylene was passed into the solution at 16—25°C over a period of 110 min. The product was worked up as above, giving 1-iodo-2-acetoxypropane (2.56 g, 56%), bp 33.5—35.5°C/0.7—0.8 mmHg.[5] This was used as the authentic sample for the infrared spectrum study and for the gas chromatography.