A NEW REACTION OF 1-ALKENES WITH IODINE

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The direct substitution of hydrogen by iodine does not proceed in alkanes, and alkyl iodides are obtained by the substitution of functional groups by iodine or the addition of HI at a double bond. We have found that iodoalkanes with an iodine atom at a secondary carbon atom are readily obtained upon heating iodine with excess 1-alkene at reflux. Heating 1-heptene and 1-octene with iodine at reflux with a 1:2 iodine/alkene ratio gave a mixture of 2-, 3-, and 4-iodoheptanes and 2-, 3-, and 4-iodooctanes, respectively, is greater than 80% yield relative to iodine consumed. Skell and Palvis [1] have reported that iodine adds to 1-alkenes at from −20 to −40°C to form unstable 1,2-diiodoalkanes, while Adel'son et al. [2] have reported that iodine dehydrogenates 1-alkenes above 200°C to give dienes. This new reaction proceeds in an intermediate temperature range (120-130°C) which has not been studied previously. A sample of 180 mmoles 1-octene was added dropwise with stirring over 3 h to 92 mmoles iodine at 125-130°C bath temperature. After cooling of the reaction mass and the separation of iodine, the organic portion was distilled at 81-82°C (15 mm) to yield 80 mmoles (85%) iodooctane. Found, %: C 39.93; H 6.79; I 52.86. $C_8H_{17}I$. Calculated, %: C 40.01; H 7.14; I 52.85. ^{13}C NMR spectroscopy indicates that the product is a mixture of approximately equal amounts of 2-, 3-, and 4-iodooctanes, judging from the CHI group signals ($CHCl_3$, δ, ppm): 29.13 (2-CHI), 41.10 (3-CHI), 38.68 (4-CHI). The conversion of iodine was 51%. The nondistillable residue was shown by ^{13}C NMR spectroscopy to consist of octene oligomers.

The reaction of iodine with 1-heptene proceeds by analogy. Normal alkanes do not react with iodine under these conditions. The addition of small amounts of iodoform may be directed toward the formation of 2-iodoalkanes.

LITERATURE CITED

1. P. S. Skell and R. R. Palvis, J. Am. Chem. Soc., 86, 2956 (1964).
2. S. V. Adel'son, I. G. Levitina, V. I. Nikonov, and A. V. Sakovich, Kinet. Katal., 13, 1327 (1972).

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