Photochemical Carboxymethylation of Olefins with Iodo- and Bromo-acetic Acids

By NORMAN KHARASCH,* PHILIP LEWIS, and RAM K. SHARMA
(*Department of Chemistry, University of Southern California, Los Angeles, California,* 90007)

RECENT studies[1] of the photolysis of iodo-aromatic compounds revealed diverse synthetic and mechanistic interests. In an extension of these, we have now examined the photochemical generation of carboxymethyl radicals, from iodo- and bromoacetic acid, and the interaction of the resulting carboxymethyl radicals with cyclohexene and with hex-1-ene.

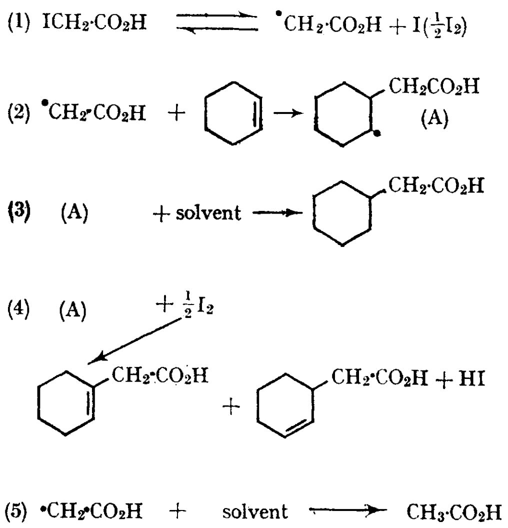
Iodoacetic acid (0·05 M) in the purified olefin was photolysed for 24 hr. under nitrogen with a low-pressure cold-cathode mercury lamp.[1] The reaction mixtures were analyzed by gas chromatography directly for carboxylic acids on columns of ethylene glycol succinate and diethylene glycol adipate polyesters, treated with phosphoric acid.[2,3] These columns gave symmetrical product peaks and were suitable for separating saturated and unsaturated carboxylic acids.

The photochemical reaction of iodoacetic acid with cyclohexene gave a mixture of cyclohexenylacetic acids (24%); cyclohexylacetic acid (3%); and acetic acid (29%)—the yields being expressed as moles % of the iodoacetic acid decomposed. The reaction was 60—80% complete in four runs, and gave consistent yields of the above products. The products were determined against known solutions of the pure reference compounds. Hydrogenation caused conversion of the cyclohexenylacetic acids into cyclohexylacetic acid. As discussed below, these results are consistent with a free-radical mechanism in which the carboxymethyl radical adds to the carbon–carbon double bond about as readily as it abstracts allylic and/or other hydrogen atoms.

Photolyses were made in a similar way in hex-1-ene. The acid fraction contained four unsaturated acids which, on hydrogenation, were all converted into n-octanoic acid. The hydrogenated acid fraction contained n-octanoic acid, and only a trace of another compound (of shorter retention time than n-octanoic acid)—possibly 3-methylheptanoic acid, resulting from attack of carboxymethyl radical at position 2 of hex-1-ene. Gas chromatographic analyses showed oct-3- and -4-enoic acids (50—60%); n-octanoic acid (5—10%); and acetic acid (*ca.* 15%), based on the iodoacetic acid decomposed. The results in hex-1-ene thus represent a higher material balance than in cyclohexene, but the high yield of unsaturated acids parallels that in cyclohexene.

The photolyses of bromoacetic acid in cyclohexene revealed an interesting difference from the reaction with iodoacetic acid. Under the same conditions, as above, in pure cyclohexene, photolysis of bromoacetic acid gave 63·5% cyclohexylacetic acid, but no cyclohexenylacetic acids were detectable. An equally high yield of cyclohexylacetic acid was found in the photolysis of bromoacetic acid in a mixture of 1 : 10 volumes of cyclohexene to acetic acid. Initial experiments showed that more than 80% of n-octanoic acid was formed by photolyses of bromoacetic acid in hex-1-ene; and that no octenoic acids are formed in this case.

Based on the evidence for dissociation of iodoacetic acid into iodine atom and carboxymethyl radical,[4] the following steps can explain the products observed in the photochemically-induced reactions of iodoacetic acid with cyclohexene, and a similar extension can be made for the reaction with hex-1-ene.



The carboxymethyl radicals produced on photolysis of iodoacetic acid[4] or bromoacetic acid can either abstract a hydrogen atom from the olefin to form acetic acid, or may add to the double bond to give the radical (A). In an excess of olefin, (A) may abstract hydrogen to give saturated alkylacetic acid, or it may transfer a hydrogen atom to iodine, to form the alkenylacetic acids. Product analysis showed that the extent of telomer formation by additions of (A) to the olefin is small.

When bromoacetic acid is used in the photochemical reaction, the bromine produced is effectively incorporated into the excess of olefin, presumably by addition to the unsaturated bond. Thus, in contrast to the case with the iodo-compound, bromine is not available to abstract hydrogen from (A). In this case, only the saturated acids are therefore formed.[5]

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[5] For a related study, leading to carboxymethylation of benzene, by photolysis of iodoacetic acid in benzene, *cf.*, N. Kharasch and L. Göthlich, *Angew. Chem. Internat. Edn.*, 1962, **1**, 459.