tiated dimers, which are likely formed by the internal scavenging reactions mentioned above. Usually, however, boiling points of parent and dimer products are so far apart that the removal of the latter poses no problem. When this step is taken, mercury-sensitized photolysis in paraffin–tritium systems provides a simple, rapid, and highly selective method for tritiating gaseous paraffins.

RADIATION LABORATORY   PRESTON L. GANT
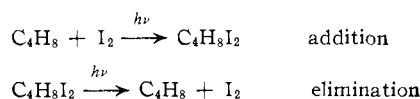CONTINENTAL OIL COMPANY   KANG YANG
PONCA CITY, OKLAHOMA

Stereospecific *trans* Photoaddition of Elementary Iodine to Aliphatic Olefins. Bridged Iodoalkyl Radicals

Sir:

The literature contains few references to the synthesis of aliphatic vicinal diiodides and it is the general impression that these substances are both difficult to synthesize and are unstable, decomposing to elementary iodine and the corresponding olefin.[1] We can report that elementary iodine adds readily under illumination to 1-butene,[2] the 2-butenes, and isobutene at $-40°$ to produce colorless crystalline diiodides. Decomposition of these diiodides to starting materials occurs at room temperature.

Additions are conveniently carried out in refluxing propane $(-42°)$ with illumination from a tungsten filament lamp. With reactive olefins, decolorization of a mixture of 1 g. of iodine and 10 g. of olefin in 50 ml. of propane usually occurs within 30 min. under illumination, although occasionally the reaction is slower, suggesting that oxygen or perhaps other substances can inhibit the additions. A comparable dark reaction for several hours does not result in extensive loss of iodine. The colorless diiodides are isolated in quantitative yield by pumping off solvent and unreacted olefin. Samples have been kept in the dark at $-78°$ for days without decomposition. At room temperature the iodides decompose rapidly to the original reactants in a reaction which is accelerated by illumination. The olefin can be isolated by pumping under high vacuum through a $-78°$ trap which stops the iodine but allows the olefin to pass through. In each case pure olefin was recovered in yields greater than 90%, and in one case the trapped iodine was weighed and found to be 88.5% of the original.

$$C_4H_8 + I_2 \xrightarrow{h\nu} C_4H_8I_2 \qquad \text{addition}$$

$$C_4H_8I_2 \xrightarrow{h\nu} C_4H_8 + I_2 \qquad \text{elimination}$$

The addition–elimination cycle applied to *cis*- and *trans*-2-butenes yielded colorless diastereomeric 2,3-diiodobutanes, m.p. -24 to $-23°$, and $-11°$ dec. Decomposition at room temperature converted the diiodides to the respective starting olefins in better than 90% yields and purities identical with the original. Thus, both addition and elimination reactions are stereospecific.

(1) T. S. Paterson and J. Robertson, *J. Chem. Soc.*, **125**, 526 (1924); A. Fairbourne and D. W. Stevens, *ibid.*, 1973 (1932); M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957); F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958); S. J. Cristol, L. K. Gaston, and T. Tiedeman, *J. Am. Chem. Soc.*, in press.

Two lines of evidence indicate these stereospecific addition reactions occur with a *trans* geometric requirement. (a) Dehalogenation of the diiodides with zinc dust in methanol at $-78°$ regenerates the olefin from which it had been prepared. A similar procedure, applied to the known 2,3-dibromobutanes, generates olefins by a stereoselective *trans* elimination.[3] (b) The *dl*- and *meso*-2,3-dichloro- and -dibromobutane isomer pairs show similar characteristic differences in δ for the proton magnetic resonance absorptions of the CH_3 and the CH groups. The same differences occur in the spectra of the diastereomeric diiodides. If the analogy is applicable, the *meso*- and *dl*- forms are identified. Methods (a) and (b) are in agreement, thus identifying the diiodides, *meso*, m.p. $-11°$ dec., and *dl*, m.p. -24 to $-23°$.

The slow dark reaction, photoacceleration of *trans* additions, erratic rates of reaction, and *trans* photodecompositions are best explained by the hypothesis of a radical chain mechanism.

$$C_4H_8 + I\cdot \rightleftharpoons \cdot C_4H_8I$$

$$\cdot C_4H_8I + I_2 \rightleftharpoons C_4H_8I_2 + I\cdot$$
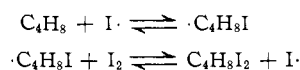
Evidence has been presented[3-5] which requires a bridged radical structure for β-bromo and β-chloroalkyl radicals. Unpublished work has established the order of bridge stabilities, $F \ll Cl < Br$, and this suggests that the most effective bridging halogen in β-haloalkyl radicals should be iodine, just as for β-bridging in carbonium ions.

The observations reported here are best rationalized by assigning bridge structures to the radical intermediates.
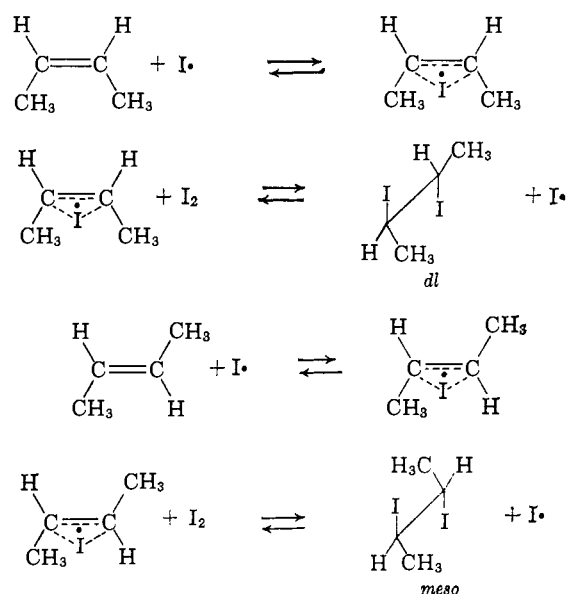
(2) G. S. Forbes and A. F. Nelson, *ibid.*, **59**, 693 (1937).
(3) W. M. Schubert, B. S. Rabinowitch, N. R. Larson, and V. A. Sims, *ibid.*, **74**, 4590 (1952).
(4) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).
(5) P. S. Skell and P. D. Readio, *ibid.*, in press.

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