

Photochemical Addition of Polyhalogenomethanes to Olefins

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THE addition of polyhalogenomethanes to olefins, commonly known as the "Kharasch Addition" may be initiated by radical initiators or by ultraviolet light.¹ The adducts are frequently formed in high yields, and the reaction has been applied to many organic syntheses.²

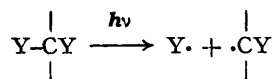
As chlorocarbene may be generated by flash photolysis of dibromochloromethane,³ and norcarane is formed in the photochemical reaction of di-iodomethane and cyclohexene,⁴ we examined the photoinduced addition of polybromomethanes and polyiodomethanes to alkenes to study the structure-reactivity relationship in these reactions.

When a solution of dibromochloromethane (0.1 mole) in cyclohexene (1 mole) was irradiated with a 450-w Hanovia Hg lamp in a quartz immersion well, 87% of dibromochloromethane was consumed after 4½ hr. The reaction mixture was resolved by fractional distillation followed by preparative v.p.c. to give isomeric 7-chloronorcaranes (4% each). The other products isolated were bromochloromethane (55%), bromocyclohexane (47%), a mixture of bromochloromethylcyclohexane and bromochloromethylcyclohexenes (16%), 1-bromo-2-bromochloromethylcyclohexane (the Kharasch-type adduct, 2.4%), dimers of cyclohexene (10%), and a high boiling residue (6.5 g). When a solution of iodoform (10%) in cyclohexene was irradiated in a Pyrex vessel, the reaction proceeds much faster than that of dibromochloromethane and most of iodoform was consumed in 1 hr. The yield of norcarane-type adduct is much higher, that isomeric 7-iodonorcaranes were

formed in 39% yield. Under similar conditions, norcarane, fluoronorcaranes, and bromonorcaranes were synthesized from the appropriate polyhalogenomethanes and cyclohexene. The isomeric products were resolved by v.p.c., and the results are summarized in the Table. The preparations of iodonorcaranes and bromonorcaranes appear to be attractive for synthetic purposes, and the reaction may also be applied to the syntheses of mono-fluorinated and monoiodinated cyclopropanes which cannot be prepared readily.

When dibromomethane which is a poor chain-carrying polyhalogenomethane was irradiated in 1-hexene which is a good chain-carrying olefin, n-butylcyclopropane was formed in 3% yield, however, no cyclopropane-type adduct was detected when both a good chain-carrying olefin, hex-1-ene, and a good chain-carrying polyhalogenomethane, dibromochloromethane, were used. Since peroxide-catalyzed addition of dibromochloromethane to cyclohexene yielded only the Kharasch-type adduct (50%) as the volatile product, and photolysis of 1-bromo-2-bromomethylcyclohexane, both in the presence and in the absence of cyclohexene, yielded no detectable amount of norcarane, we wish to suggest that photolyses of dibromomethanes and di-iodomethanes in condensed phase proceed with two primary processes:

(i) the dissociation to form a halogen atom and a radical,



TABLE

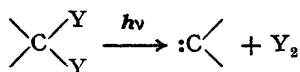
Olefin	Polyhalogenomethane	Cyclopropane (syn : anti) ^a
Cyclohexene	CH ₂ Br ₂	Norcarane, 5—14%
Hex-1-ene	CH ₂ Cr ₂	1-Butylcyclopropane, 3%
Cyclohexene	CHFBr ₂	7-Fluoronorcarane, 9% (1 : 1) ^b
Cyclohexene	CHClBr ₂	7-Chloronorcarane, 8% (1 : 1) ^c
Hex-1-ene	CHClBr ₂	non-detectable
Cyclohexene	CHBr ₃	7-Bromonorcarane, 9% (1 : 2)
Cyclohexene	CHIBr ₂	7-Bromonorcarane, 21% (3 : 4)
Cyclohexene	CHI ₃	7-Iodonorcarane, 39% (1 : 2)

^a Satisfactory analyses have been obtained for all new compounds, and u.v., i.r., n.m.r. and mass spectra data are in agreement with the structural assignments.

^b Ando and his co-workers reported the preparation of 7-fluoronorcaranes from the reduction of 7-chloro-7-fluoronorcaranes as an unresolved mixture (T. Ando, H. Yamanaka, S. Terabe, A. Horike, and W. Funasaka, *Tetrahedron Letters*, 1967, 1123).

^c G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.*, 1965, **87**, 4270; we thank Professor Closs for authentic samples of these compounds.

(ii) and the dissociation to form a bivalent carbon intermediate and molecular halogen.



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¹ For a review on "Kharasch Addition," see C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91

² For example, S. Lüsberg, W. O. Godtfredsen, and S. Vangedal, *Tetrahedron*, 1960, **9**, 149.

³ A. J. Merer and D. N. Travis, *Canad. J. Phys.*, 1966, **44**, 525.

⁴ D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, 1965, **30**, 959; D. W. G. Style and J. C. Ward, *J. Chem. Soc.*, 1952, 2125, and earlier papers; R. C. Neuman, jun., and R. G. Wolcott, *Tetrahedron Letters*, 1966, 6267.