HOMOLYTIC ADDITION TO OLEFINS: CHAIN TERMINATION BY METAL HALIDES

Sir:

We wish to give evidence for the efficiency and the mechanism of the termination of radical chain processes by metal halides,[1] and to demonstrate its preparative use in homolytic additions to olefins. Aryl radicals were generated from four independent sources and allowed to react with either acrylonitrile or styrene in essentially anhydrous acetone solutions containing ferric chloride or cupric chloride. The process can be formulated as

$$\text{Ar}\cdot + \text{CH}_2{=}\text{CHY} \longrightarrow \text{Ar-CH}_2\text{-CHY}\cdot \qquad (\text{Y} = \text{CN or C}_6\text{H}_5) \quad (1)$$

$$\text{Ar-CH}_2\text{-CHY}\cdot + \text{MX}_n \longrightarrow \underset{\text{I}}{\text{Ar-CH}_2\text{-CHYX}} + \text{MX}_{n-1}\ (\text{X} = \text{halides})$$

In most cases we studied, substances corresponding to vinyl polymers could not be detected; the aryl radicals could be accounted for in good yields as shown in Table I. Ferrous and cuprous chlorides were isolated or determined titrimetrically.

TABLE I

Radical source	Per cent. yield of product I Styrene ($Y = C_6H_5$)	 Acrylonitrile ($Y = CN$)
Benzenediazonium chloride	49	63
p-Chlorobenzenediazonium chloride	71	52
p-Nitrobenzenediazonium chloride	78	65
N-Nitroso-*p*-nitroacetanilide	67	25[a]
Phenylazotriphenylmethane	54[b]	. . .
Benzoyl peroxide	68[c]	. . .

[a] 50% yield of *p*-nitrochlorobenzene. [b] Trityl radical did not add to olefin under these conditions. Trityl chloride isolated as triphenylcarbinol in 90% yield. [c] Based on CO_2 liberated; yield based on benzoyloxy radicals is 5.5%.

The alternate routes for the destruction of the aryl radicals are represented by equations (2)[2] and (3).

$$\text{Ar}\cdot + \text{MX}_n \longrightarrow \text{Ar-X} + \text{MX}_{n-1} \qquad (2)$$

$$\text{Ar}\cdot + \text{CH}_3\text{COCH}_3 \longrightarrow \text{Ar-H} + \text{CH}_3\text{COCH}_2\cdot^{3} \qquad (3)$$

$$\text{CH}_3\text{COCH}_2\cdot + \text{MX}_n \longrightarrow \text{CH}_3\text{COCH}_2\text{Cl} + \text{MX}_{n-1}$$

A detailed study of the decomposition of diazonium salts in acetone with cuprous chloride[4] showed that the ratio of chloroacetone (or Ar-H) to Ar–X formed as in equations (2) and (3) is inversely proportional to the cupric chloride concentration. In the presence of olefin, however, no or little chloroacetone is formed; the reaction occurred predominantly by equation (1), the extent of reaction (2) depending on the relative concentrations of cupric chloride and olefin. When molecular iodine was used to trap the radicals, the product was exclusively Ar-I even in the presence of a large excess of chloride ion. With added olefin the same reaction yielded significant amounts of product I (Y = CN, X = I). When *p*-nitrobenzenediazonium bisulfate was decomposed at −25° in aqueous acetone with cuprous chloride, approximately 30% of 4,4′-dinitrobiphenyl was formed. In the presence of oxygen, this reaction yielded 35% of *p*-nitrophenol. The addition of styrene to the cuprous chloride induced decomposition of *p*-nitrobenzenediazonium bisulfate in aqueous acetone at −30° with bubbling oxygen yielded a product which decomposed[6] to give 4-nitrodesoxybenzoin in 30% yield.

Experiments with *n*-butyl mercaptan were unsuccessful.

Acknowledgment.—I am indebted to Professor G. Hammond for kindly placing laboratory facilities at my disposal, and to Mr. J. Garst for generous amounts of tritylazobenzene.

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[1] C. Bamford, A. Jenkins and R. Johnston, *Nature*, **177**, 992 (1956); E. Collinson and F. Dainton, *ibid.*, **177**, 1224 (1956); R. Haines and W. Waters, *J. Chem. Soc.*, 4256 (1955).

[2] Further evidence for the reaction of radicals with metal halides is obtained from the good yields of cuprous chloride resulting from the decomposition of azobisisobutyronitrile in the presence of cupric chloride in anhydrous *t* butyl alcohol (with R. Keys).

[3] W. Waters, *J. Chem. Soc.*, 2007 (1937); 864, 1805 (1939).

[4] Aryl radicals arise from the process:[5] $ArN_2^+ + CuCl_2^- \rightarrow ArN_2CuCl_2 \rightarrow Ar\cdot + N_2 + CuCl_2$.

[5] W. Waters, "Chemistry of Free Radicals," Oxford University Press, London, 1948 (second edition), p. 164; S. Dickerman, K. Weiss and A. Ingberman, *J. Org. Chem.*, **21**, 380 (1956).

[6] C. Walling and S. Buckler. THIS JOURNAL, **77**, 6032 (1955).

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TETRAFLUOROALLENE[1]

Sir:

Tetrafluoroallene is of special interest as a monomer that might yield useful polymers. Miller[2] reported its synthesis by the reaction of 2-chloro-3-iodo-1,1,3,3-tetrafluoro-1-propene with zinc in dioxane. No experimental details were given and we have been unable to make the compound by this reaction, obtaining instead good yields of the coupled product, 2,5-dichloroperfluoro-1,5-hexadiene.

We have obtained tetrafluoroallene in moderate yield by dehydrobromination of 3-bromo-1,1,3,3-tetrafluoro-1-propene with powdered potassium hydroxide. The starting material[3] was prepared by dehydrobromination of 1,3-dibromo-1,1,3,3-tetrafluoropropane which was readily made from dibromodifluoromethane[4] and 1,1-difluoroethylene. Tetrafluoroallene is a colorless gas, b.p. −38 ± 0.5° (Miller[2] gives −28°).

Anal.[5] Calcd. for C_3F_4: C, 32.16; molecular weight, 112.0. Found: C, 31.80; molecular weight (vapor density method), 114.

The infrared spectrum of this compound was characterized by a strong band at 2065 cm.$^{-1}$ (4.87 μ). Allene itself shows a strong carbon–carbon stretching absorption at 1950 cm.$^{-1}$ (513 μ) and replacement of hydrogen by fluorine would be expected to shift the absorption to higher frequencies.[6] The mass spectrum showed large

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[2] W. T. Miller, U. S. Patent 2,668,182 (Feb. 2, 1954); *Chem. Abstr.*, **49**, 2478 (1955).

[3] P. Tarrant, A. M. Lovelace and M. R. Lilyquist, THIS JOURNAL, **77**, 2783 (1955).

[4] We wish to thank the Dow Chemical Co. for the gift of a generous supply of dibromodifluoromethane.

[5] The combustion analysis was carried out by Dr. Adalbert Elek.

[6] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 37.