## 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

$$\mathrm{Ar\cdot + CH_2{=}CHY \longrightarrow Ar\text{-}CH_2\text{-}CHY\cdot} \qquad (\mathrm{Y = CN\ or\ C_6H_5}) \quad (1)$$

$$\mathrm{Ar\text{-}CH_2\text{-}CHY\cdot + MX_n \longrightarrow \underset{I}{Ar\text{-}CH_2\text{-}CHYX} + MX_{n-1}} \quad (\mathrm{X = halides})$$

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<br>Styrene ($Y = C_6H_5$) | <br>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).

$$\mathrm{Ar\cdot + MX_n \longrightarrow Ar\text{-}X + MX_{n-1}} \quad (2)$$

$$\mathrm{Ar\cdot + CH_3COCH_3 \longrightarrow Ar\text{-}H + CH_3COCH_2\cdot}^{3} \quad (3)$$

$$\mathrm{CH_3COCH_2\cdot + MX_n \longrightarrow CH_3COCH_2Cl + MX_{n-1}}$$

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 $\mu$). Allene itself shows a strong carbon–carbon stretching absorption at 1950 cm.$^{-1}$ (513 $\mu$) 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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[1] This research was sponsored by the Office of Ordnance Research, U. S. Army.

[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.

peaks at mass-to-charge ratios of 112 ($C_3F_4$), 93 ($C_3F_3$), 74 ($C_3F_2$), 69 ($CF_3$), 52 ($C_2F_2$) and 31 (CF).[7] Compounds such as perfluoroethylene and perfluorocyclobutane show $CF_3$ peaks,[8] but tetrafluoroallene gave an unusually high value at 69.

Addition of chlorine to tetrafluoroallene gave 1,2,2,3-tetrachloro-1,1,3,3-tetrafluoropropane, a liquid with the same b.p., refractive index and infrared spectrum as an authentic sample.

Tetrafluoroallene polymerized even at low temperatures; at room temperature under pressure polymerization occurred in a few hours to yield first a liquid and then a white solid. The polymerization is being studied.

[7] A modified Westinghouse Model LV mass spectrometer was used. We wish to thank Mr. Robert D. Vanselow for this spectrogram.

[8] "Catalog of Mass Spectral Data," National Bureau of Standards, American Petroleum Institute Research Project 44, spectra 361 and 362.

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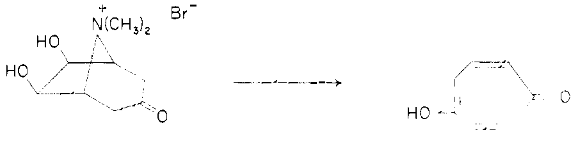
## A CONVENIENT SYNTHESIS OF γ-TROPOLONE

*Sir:*

The theoretical significance of tropone and the three isomeric tropolones (monohydroxytropones) has directed much effort toward the synthesis of these compounds. Tropone, tropolone and β-tropolone have been known for some time.[1] Recently, Nozoe and co-workers succeeded in preparing γ-tropolone (I) for the first time by acid hydrolysis of 4-bromotropone, a by-product obtained in 5–10% yield from the bromination of cycloheptanone.[2] In the same year, Johnson and co-workers reported an alternate synthesis starting from 3,6-dimethoxycycloheptatrienecarboxylic acid, obtained in quite low yield from hydroquinone dimethyl ether and diazoacetic ester.[3] As a part of a general study of the elimination reactions of bicyclic quaternary salts, we have investigated the base degradation of teloidinone methobromide (II), in the hope of developing a convenient route to γ-tropolone (I)

Teloidinone, prepared by a Robinson "biosynthesis,"[4] gave II, m.p. 218–219° (dec.), in almost quantitative yield when treated with excess methyl bromide in ethanol at room temperature. The degradation was carried out by dissolving II and two equivalents of base in distilled water and heating the solution on the steam-bath. The formation of I was followed by periodically removing aliquots from the reaction mixture and measuring the intensity of the 360 mμ absorption band exhibited by γ-tropolone in 0.1 *N* sodium hydroxide.[2,3] A variety of bases were found to produce I in yields of 45%. Sodium bicarbonate and barium hydroxide were equally effective in bringing about the desired elimination; refluxing II in anhydrous pyridine was somewhat less satisfactory. The concentration of the solution in which the degradation was carried out decidedly affected the yield of desired product. Thus, when a solution of II (66.5 mg.) and sodium bicarbonate (42.0 mg.) in 50 ml. of water was heated on a steam-bath for two hours, a 45% yield of I was obtained. However, when II (3.33 g.) and barium hydroxide (2.20 g.) were dissolved in 50 ml. of water and heated for two hours, only 24% of γ-tropolone formed. Precipitation of the barium ion by addition of Dry Ice followed by concentration of the solution to a volume of 3 to 5 ml., gave rise to I in 20% yield. After recrystallization, the product, m.p. 211–212°, showed infrared maxima (Nujol) at 6.10, 6.26, 6.60, 7.78 and 8.25 μ; its ultraviolet spectrum showed $\lambda_{\max}^{0.1\,N\,\mathrm{NaOH}}$ 360 mμ (4.33), 227 mμ (4.31) and $\lambda_{\max}^{\mathrm{CH_3OH}}$ 336 mμ (4.22), 228 mμ (4.20). These properties are in good agreement with those reported earlier for I.[2,3]



II I

**Acknowledgment.**—The authors are deeply indebted to the Research Corporation for the support of this research through a Frank Gardner Cottrell grant.

[1] For an excellent review see P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).

[2] T. Nozoe, T. Mukai, Y. Ikegama and T. Toda, *Chem. and Ind.*, 66 (1955).

[3] R. S. Coffey, R. B. Johns and A. W. Johnson, *ibid.*, 658 (1955).

[4] J. C. Sheehan and B. M. Bloom, THIS JOURNAL, **74**, 3825 (1952).

[5] American Viscose Corporation Fellow, summer 1956.

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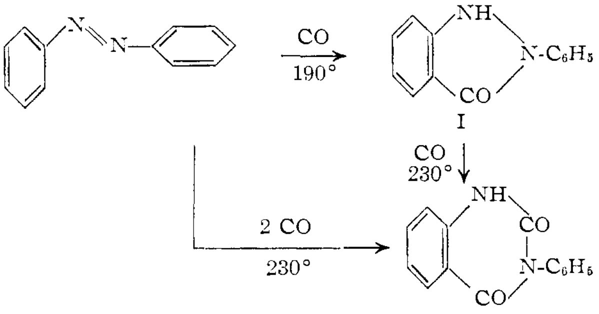
## THE REACTION OF AZOBENZENE AND CARBON MONOXIDE

*Sir:*

Previously we have shown that Schiff bases react with carbon monoxide in the presence of cobalt octacarbonyl to yield phthalimidines.[1] We have now found that azobenzene reacts similarly with one molecule of carbon monoxide (150 atmospheres pressure in all cases) to form indazolone, I, at 190° and with two molecules of carbon monoxide at 230° to yield 3-phenyl-2,4-dioxo-



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[1] S. Murahashi and S. Horiie, THIS JOURNAL, **77**, 6403 (1955).