ysis of acetone at low temperatures tends to yield low values for the activation energies.[4]

With slight modifications this method can be adapted to the study of many other chlorine atom reactions. The results will be reported in full when the program of work is complete.

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[4] A. J. C. Nicholson, THIS JOURNAL, **73**, 3981 (1951).

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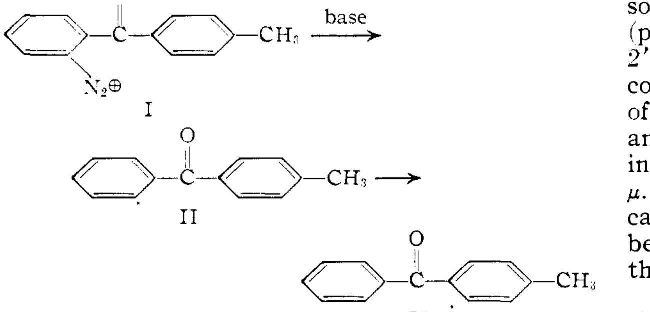
A NEW TYPE OF CHAIN TRANSFER REACTION[1]

Sir:

In the course of studies on the intramolecular reactions of free radical intermediates we have been investigating the reactions of diazotized 2′-amino-4-methylbenzophenone (I). Evidence has already been presented[2] which indicates that the C–N cleavage of the diazonium group can occur by either a heterolytic or by a homolytic process, the former under acidic conditions, the latter under alkaline conditions.

We have been successful in obtaining evidence for the intramolecular chain transfer step (II → III)



and believe this to be the first actual demonstration of this type of reaction between an aryl radical and an aromatic ring. Decomposition of a stirred mixture of the diazonium fluoborate (I), carbon tetrachloride and sodium hydroxide led to a complex reaction mixture from which could be isolated by chromatography an oily fraction containing 3-methylfluorenone (10% based on the diazonium salt), 2′-chloro-4-methylbenzophenone (10%) and 2-chloro-4-methylbenzophenone (10%). The last named product is the one expected from reaction of the radical III with carbon tetrachloride. The products were identified and determined quantitatively by means of the infrared spectra of solutions in carbon disulfide. The melting points and the analytical infrared peaks of the model compounds were as follows: 3-methylfluorenone[3] 66.0–66.5° (10.88, 9.02), 2′-chloro-4-methylbenzophenone[4] 98.5–99.5° (10.78, 13.43), 2-chloro-4-methylbenzophenone 51.0–52.0° (10.69, 12.20).

We have applied this technique to several other reactions with most encouraging results. As reported elsewhere[2] the reaction of the diazonium salt I in aqueous sodium chloride under acidic conditions leads to a mixture of 2′-hydroxy-4-methylbenzophenone (21%), 2′-chloro-4-methylbenzophenone (14%) and 3-methylfluorenone (60%). This heterolytic reaction is not expected to lead to any of the "wrong" 2-chloro-4-methylbenzophenone, and we found this "wrong" chloro compound was absent within the experimental error (no 10.69 peak). Similarly with sodium bromide the expected 2′-bromo-4-methylbenzophenone was the only halogen-containing compound found (no 10.71 peak). In contrast to the above reactions, the Sandmeyer reaction of I with cuprous bromide gives a mixture of 2′-dromo-4 methylbenzophenone and 2-bromo-4-methylbenzophenone. This seems to be a clear demonstration that this Sandmeyer reaction proceeds at least in part by a free radical mechanism in which the radical is free enough to undergo the chain transfer step II → III. The melting points and the analytical infrared peaks of the model compounds were as follows: 2′-bromo-4-methylbenzophenone[5] 89.0–90.0° (10.79); 2-bromo-4-methylbenzophenone, b.p. 171–172° (3 mm.) (10.71). Reaction of the diazonium salt I with sodium iodide in aqueous solution proceeded as follows: at a *p*H of 1 and of 7 (phosphate) only one iodo compound was produced, 2′-iodo-4-methylbenzophenone; m.p. of model compound 52–53° (10.80). At a *p*H of 11 the yield of iodo compounds was smaller, but both the 2′,4- and the 2,4-isomers appear to be present since the infrared spectra had peaks at 10.69, 10.80 and 10.88 μ. The spectra of a series of benzophenones indicates that a 10.70 peak is characteristic of the benzoyl group and a 10.80 peak is characteristic of the *p*-toluyl group.

These results are of some importance in planning the use of the Sandmeyer and related reactions for synthetic purposes. We expect the reactions to be of great help in a study of several of the diazonium salt reactions and in a study of free radical reactions.

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[1] Supported by a Rohm & Haas research assistantship (DIR) and by a National Science Foundation Grant.

[2] D. F. DeTar and S. V. Sagmanli, THIS JOURNAL, **72**, 965 (1950); D. F. DeTar and D. I. Relyea, THIS JOURNAL, in press.

[3] F. Ullmann, *Ber.*, **31**, 1694 (1898).

[4] W. D. Cohen, *Rec. trav. chim.*, **38**, 117 (1918).

[5] A. Heidenreich, *Ber.*, **27**, 1452 (1894).

A NEW METHOD FOR DETERMINING ADSORPTION SEPARATION FACTORS AND ADSORBENT CAPACITIES

Sir:

In a recent publication[1] we reported an equation for determining adsorption separation factors of liquids in static systems. Use of the equation as given there is only possible if the adsorbent capacities are determined by some independent method, and if these values are assumed to equal the "selective" adsorbent capacities.

In more recent studies we have found that the selective adsorbent capacity need not be deter-

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[1] R. W. Schiessler and C. N. Rowe, THIS JOURNAL, **76**, 4611 (1953).