In the 157 pages devoted to air there are described its composition, mechanical and thermal properties, solubility in various media, and the acoustical, magnetic and electrical behavior. The chapter on active oxygen required only 8 pages to review the formation and the chemical reactions of this substance.

The final chapter of 200 pages on ozone lists review literature up to 1959, including the American Chemical Society publication, "Ozone Chemistry and Technology," 1959. The topics covered include the formation and decomposition of ozone, thermodynamic data, the physical properties, the electrochemical behavior and the chemical reactions of ozone with other substances. The description of the methods of formation and decomposition is very thorough, as is the discussion of the reactions of ozone with inorganic substances. Only a brief paragraph is devoted to the reactions with organic compounds. However, pertinent literature references to the latter subject are given; these refer to books and review articles published as late as 1958.

This book conforms to the high standard set by previous volumes of this edition of Gmelin's Handbuch, and it includes German and English tables of contents as well as English headings and subheadings in the margins.

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International Series of Monographs on Organic Chemistry Volume 4. Homolytic Aromatic Substitution. By G. H. WILLIAMS, Reader in Organic Chemistry, Birkbeck College, London. Pergamon Press Inc., 122 East 55th Street, New York 22, N. Y. 1960. vii + 133 pp. 17 × 25.5 cm. Price, $7.50.

Reactions involving free radical intermediates commonly yield complex reaction mixtures. Careful and critical interpretations of product and rate date have, nevertheless, led to considerable information about the mechanisms. The pace has accelerated markedly with the increasingly accurate data derived through use of infrared spectrophotometry and gas phase chromatography. Yet critical reasoning remains an indispensable ingredient.

The present book emphasizes (according to the preface) the theoretical aspects of homolytic substitution, although preparative aspects are also considered. There is an introduction followed by four chapters on arylation, one on alkylation and one on miscellaneous reactions.

Superficially the book has an authoritative appearance. The style is attractive and so is the typography. Beyond these there are few features to praise.

There are glaring oversights in the coverage of the literature. Thus, in the brief summary of electrophilic substitution there is no mention of the important recent studies by H. C. Brown and his students. Again the old radical mechanism is given on page 39 for the reaction between phenols and diacyl peroxides in spite of recent work of Walling which indicates that it is largely ionic.

However, the most serious deficiency of this work is the confused and non-critical reasoning employed throughout. One example will have to suffice. The key step in the arylation reaction is written as follows: R'· + ArH → ArR' + (H·) (page 38).

The meaning of this equation is clarified in these words: "It therefore follows that the only chain-termination reaction which is consistent with the above observations is the reaction between R'· and ArH, producing the unsymmetrical diaryl ArR', and not an inactive solvent radical, *but the highly reactive hydrogen atom*" (the italics are mine).
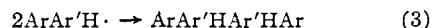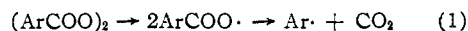
This should suffice to explain the author's intent, but he has some second thoughts which he offers the reader in a footnote. Here he suggests that biphenyls are produced by reaction of a "σ- complex" (nature undefined) written as [Ar'-Ar-H]· with a *peroxide molecule*. Much later on (page 49) he tosses out yet another suggestion: [R-Ar-H]· is now an intermediate "following the suggestion of Waters." And among the reactions proposed for this intermediate is the conventional disproportionation in which a hydrogen atom is abstracted by some other radical.

Regarding the above there is an interesting and significant bit of by-play in the literature. A few years ago Williams

co-authored a review article covering much the same ground as the present book (D. R. Augood and G. H. Williams, *Chem. Revs.*, 57, 123 (1957)). In the review the hydrogen ejection step is clearly presented in eq. 14, p. 131, and also in Scheme III on p. 133. I would definitely interpret these as the mechanisms preferred by the authors. Now it is well known that such a step must be endothermic by the difference in relevant C–C and C–H bond dissociation energies. Thus such a step cannot be important in the arylation process. Mention of this deficiency was made by E. S. Lewis and M. C. R. Symons (*Quart. Revs.*, 12, 230 (1958)). This prompted an indignant rejoinder (*J. Chem. Soc.*, 1871 (1959)) that Williams had never advocated hydrogen ejection but that Lewis and Symons had not read the review carefully. It is difficult to know just which statements of Williams we are to accept as official.

It is possible to discover reasons why it might be hazardous to examine the mechanisms of arylation too closely. Considerable effort has been spent in determining isomer ratios and relative reactivities in arylation reactions. From these Williams has calculated partial rate factors and has written at length on the theoretical bases for the results. It would be unpleasant if it should turn out that the actual mechanisms do in fact invalidate this whole approach. It is, nevertheless, desirable to analyze the rationale briefly to show what theoretical significance such results may be expected to have, apart from their obvious empirical practical significance.

Present studies of the reaction of benzoyl peroxide and benzene can be summarized by the mechanistic steps

$$(ArCOO)_2 \rightarrow 2ArCOO\cdot \rightarrow Ar\cdot + CO_2 \qquad (1)$$

$$Ar\cdot + Ar'H \rightarrow ArAr'H\cdot \qquad (2)$$

$$2ArAr'H\cdot \rightarrow ArAr'HAr'HAr \qquad (3)$$

$$2ArAr'H\cdot \rightarrow ArAr'H_2 + ArAr' \qquad (4)$$

Although these are the major primary reactions occurring in dilute solutions, it must be emphasized that other reactions also occur, the number and variety increasing with increasing peroxide concentrations. Thus dihydrobiphenyl produced by reaction 4 is a product at low peroxide concentration (0.01 M) but is not readily found at conventional concentration (0.1 M). Presumably this is the result of radical attack leading to dehydrogenation of the dihydrobiphenyl, though radical addition remains a possibility.

Now a major premise must be made by those who seek to base partial rate factors on a determination of the isomer distribution among, say, the chlorobiphenyls obtained from the decomposition of benzoyl peroxide in chlorobenzene. This premise is that the isomer distribution is determined by step 2. Obviously the calculations can be run through without any assumption at all, but then the whole procedure is merely a numbers game. Consideration of the implications of steps 3 and 4 and their counterparts with other radicals affords little justification for the required tacit assumption that exactly the same fraction of every one of the isomers of ArAr'H· will ultimately give the same ratio of biphenyl to other products. Yet without this or its equivalent assumption, what useful theoretical conclusions are possible?

Nevertheless, from the practical point of view it is reasonable to predict that detailed studies will tend to substantiate the so-called partial rate factors for homolytic arylation. Of the fifty numbers quoted in the table on page 73, more than half are between 0.6 and 1.5. Only one is larger than 10. For comparison, nitration, a typical electrophilic reaction, exhibits a range of partial rate factors of over 10⁶. Correcting a 3 to a 2 or even a 1 will not constitute a very significant change. Such numbers as these do not make serious demands on theory.

In conclusion it should be noted that the monographs in these series are not very long. At a price of almost 6 cents a page and with a virtual captive market in the world's technical libraries, the venture should prove highly profitable to the publisher.

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