Topics in Carbocyclic Chemistry

Volume one

Edited by

Douglas Lloyd
University of St Andrews

New York
Plenum Press
London
Logos Press

© LOGOS PRESS LIMITED 1969

Published in the U.S.A. by
PLENUM PRESS
a division of
PLENUM PUBLISHING CORPORATION
227 West 17th Street, New York, N.Y. 10011

Library of Congress Catalog Card Number 74-80937
SBN 306.37761.6

Printed in Great Britain by
Spottiswoode, Ballantyne & Co. Ltd., London and Colchester

TOPICS IN CARBOCYCLIC CHEMISTRY

VOLUME 1

LOGOS PRESS LIMITED
Scientific Publications

Editorial Advisory Board for Chemistry and Biochemistry

Professor D. H. Hey, F.R.S.
Professor J. I. G. Cadogan
Professor G. R. Tristram

此为试读,需要完整PDF请访问: www.ertongbook.com

FOREWORD

Professor Wilson Baker, F.R.S.

Organic compounds are classified as aliphatic, carbocyclic, or heterocyclic, though in the very many cases where two or more such characteristic groupings are present, the classification chosen will depend on the relative chemical importance of these groupings to the particular investigation in hand, and perhaps even to the outlook of the investigator. Traditionally, however, ring compounds with attached aliphatic groups are referred to as cyclic, and any heterocyclic grouping serves to categorise a molecule as heterocyclic.

In these reviews it is the intention to deal, so far as possible, with carbocyclic compounds only, as borne out by this Volume I of the series with articles on the benzidine rearrangement, the bicyclo[3,3,1]nonanes, Feist's acid, and the annulenes. The difficulty in keeping rigidly to carbocyclic substances is, however, apparent in the chapter on 'The Biosynthesis of Carbocyclic Compounds', where many heterocyclic compounds are encountered, as is inevitable in any reasonably comprehensive account of biosynthesis.

The justification for this new series is the need for reviews to enable both the specialist and the non-specialist to keep up with the accelerating expansion of original literature. This need is not wholly met by existing periodical publications, and moreover many areas of carbocyclic chemistry are ripe for review although they may not at present be under such extensive investigation as other branches of chemistry. It is the intention, as is evident from the five articles in this volume, to present the subjects with sufficient background to make them acceptable to all readers; the choice of the word 'Topics' rather than 'Advances' indicates this intention.

The standard of the articles in Volume I is uniformly very high and carries out the intention of the Editor and publishers with regard to coverage. To the individual worker the series will be of value because of the specific articles, rather than because the volumes deal essentially with carbocyclic chemistry, in the whole vast field of which he is scarcely likely to be interested. Nevertheless the series will fill a very real need and is to be warmly welcomed.

W. BAKER.

Department of Organic Chemistry
The University of Bristol
May 1969

PREFACE

The continuing expansion of original chemical literature makes it increasingly difficult for chemists to see their subject in perspective, and the accompanying spate of review publications represents an attempt to remedy this difficulty. This is indeed the justification for these secondary publications. In general it is convenient if review articles are grouped according to their subject matter, the limits of this being neither so narrow as to make them only of very specialist interest, nor so wide as to defeat the initial objective.

Various collections of reviews of the chemistry of heterocyclic compounds which have appeared in recent years have nicely exemplified this pattern, and the suggestion made to me, that a similar project dealing with the chemistry of carbocyclic compounds would be very useful, seemed a worthwhile one.

No volumes embracing carbocyclic chemistry as a whole are presently produced and it seemed to me, and to colleagues with whom I discussed the project, that this represented a very satisfactory area of chemistry to bring together. The older boundary between alicyclic chemistry and what was then called aromatic chemistry but is more precisely called the chemistry of benzene derivatives has been made obscure by the large amount of recent work on non-benzenoid aromatic compounds, and the present-day definitions of 'aromatic' make the older distinction in some ways outmoded. The present series of reviews will deal with any aspects of carbocyclic chemistry.

Review articles serve two especial purposes: to provide a non-specialist reader with a comprehensive survey of a subject for his general interest, or to provide an effective initial account of the most important information available on a particular topic as a prelude to a detailed search of the primary literature. For either of these purposes a rounded review by an expert in the field is more valuable than an article which deals only with recent advances. For this reason the present series has been entitled '*Topics* in Carbocyclic Chemistry' rather than 'Advances', and the authors have in general been asked to write their articles as overall reviews rather than as reviews of only recent work. As such it is hoped that the articles will be of much more general use and interest.

It is hoped to include articles dealing with carbocyclic chemistry from many standpoints, practical, theoretical, mechanistic and biochemical. It is also intended to include within any one volume articles of widely differing scope, from surveys of broad sections of the subject to more detailed accounts of more limited but interesting topics. All of these points are illustrated by the range of articles included in Volume I, and it is intended to maintain this breadth of approach in later volumes.

I should like to thank a number of people for their very real help to me, and especially my friends Professor Wilson Baker for writing an introduction to the series, and Professor John I. G. Cadogan for his constant helpful comments and suggestions. I am also most grateful for the co-operation and understanding of the publishers, and especially the untiring help of Mr. J. G. Mordue. Last and very far from least I must thank the authors for their kindness and hard work in contributing the articles, and their forbearance at all times with the editor.

I take no credit for the ideas put forward by the authors but I take full responsibility for any editorial errors which have crept in and apologise to authors and readers alike for them.

In conclusion may I say that I would appreciate any suggestions concerning topics which could usefully be considered for inclusion in later volumes.

St. Andrews, Fife DOUGLAS LLOYD.
January 1969

CONTRIBUTORS

D. V. Banthorpe, Department of Chemistry, University College London, Gower Street, London, W.C.1.

D. H. G. Crout, Department of Chemistry, University of Exeter, Stocker Road, Exeter, England.

G. L. Buchanan, Chemistry Department, University of Glasgow, Glasgow, W.2, Scotland.

D. M. G. Lloyd, Department of Chemistry, Purdie Building, University of St. Andrews, St, Andrews, Fife, Scotland.

H. P. Figeys, Service de Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles, Avenue F.-D. Roosevelt 50, Brussels, 5, Belgium.

CONTENTS

此为试读，需要完整PDF请访问：www.ertongbook.com

1

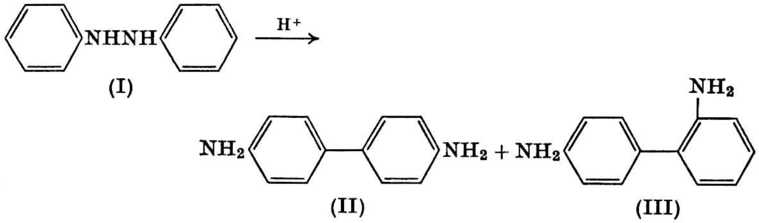
THE BENZIDINE REARRANGEMENT

D. V. Banthorpe

Chemistry Department, University College London

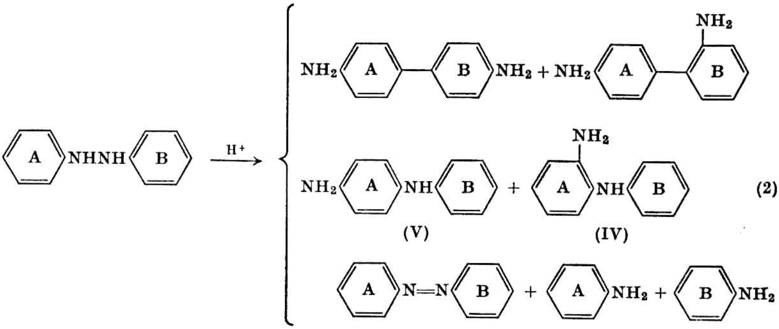
A. NATURE OF THE REACTION

The acid-catalysed conversion of hydrazobenzene (I) into benzidine (II), equation (1), was discovered by Hofmann (1863); fifteen years later a minor product, diphenyline (III) was reported and the structures of both isomers were established (Schmidt and Schultz, 1878, 1881). This reaction was the prototype of a large class of aromatic rearrangements of outstanding theoretical interest which



(1)

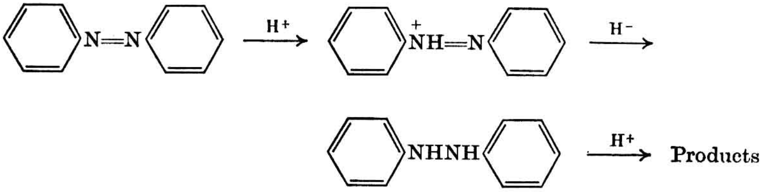
give products that are of considerable importance in the dyestuffs industry. Semi-quantitative product-studies, especially those of Jacobson over the period 1892 to 1922, showed that ring and *N*-substituted hydrazo-arenes (of both the benzene and naphthalene series) could give *o*- and *p*-semidines (IV, V) with 2,*N*′- and 4,*N*′-linking of the aryl rings respectively, in addition to the 4,4′ and 4,2′-linked products of the original example, together with oxidation and disproportionation products (azo-compounds and fission amines). The whole range of products is summarised in scheme (2); many hydrazo compounds give essentially only one or two of these types and often



(2)

ring substituents restrict the possibilities for coupling, but recent paper-chromatographic analyses of products from reaction of several substrates suggest that all the possible isomers are usually formed, albeit some in trace amounts (Vecera, Petranek and Gasparic, 1957a, b). The whole family of interconversions, the mechanism of which has remained obscure until recently, has become collectively known as the *Benzidine Rearrangement*.

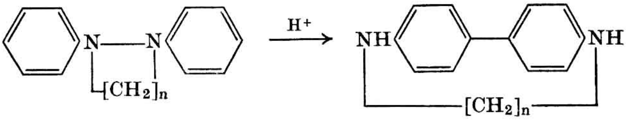
Rearrangement usually occurs readily at 0° to 20° when a solution of the hydrazo-compound in an organic solvent is treated with dilute (< 2 *N*) mineral or organic acid or with hydrogen chloride gas, but electron-withdrawing ring-substituents stabilise the substrate and stronger acid may be required to effect reaction in a convenient time. Acidic ion-exchange resins promote rearrangement and are especially convenient as the basic products are absorbed on the resin and can be filtered off (Yamada, Chichata and Tsurvi, 1954, 1955). Most of the early rearrangements were carried out under ill-defined conditions by treatment of an azo-compound with an acidic reducing agent, especially stannous chloride in hydrochloric acid often under reflux, and the transiently formed hydrazo-compound was not isolated. Although this procedure is very convenient as a preparative method, much reductive fission to amines usually occurs in competition. Direct, but little used, routes from azo-compounds to rearrangement products follow from treatment with chlorine, bromine, or hydriodic acid (Zollinger, 1961), quinol sulphonates (Reeves and Andrews, 1967) or various acids in ethanol, acetone, or other organic media (Nesmeyanov and Golovnya, 1960). Abstraction of hydride ion from the solvent probably occurs in the last method, equation (3), and the yield (10 to 80 per cent) is very sensitive to the reaction conditions. Systematic studies of catalysis by Lewis acids have not been carried out, but it is possible that under defined conditions co-ordination between metal ions (much as the stannous or titanous ion of reduction mixtures) and azo- or hydrazo-compounds could induce rearrangement. Of significance in this aspect is the rearrangement promoted by titanous chloride from azobenzene in near-neutral buffers where proton-catalysed isomerisation of any hydrazobenzene that is formed should be negligible (Veibel, 1954); but detailed kinetic investigations of the reduction of several azo-compounds with titanous chloride under more acidic conditions have shown that hydrazo-compounds accumulate during reaction to a considerable extent and are probably the rearranging species (Zollinger, 1961).



(3)

Rearrangement occurs when one or both of the hydrazo-nitrogens carry substituents such as methyl, acetoxy and phenyl groups

(Jacobson, 1922; Davies and Hammick, 1954; Holt and Hughes, 1954; Wittig *et al.*, 1957), and for *N*,*N′*-bridged species as shown in equation (4) (Wittig *et al.*, 1957; Wittig and Grolig, 1961). For the latter type of substrate, reductive scission is the sole reaction when $n = 2$ or 3, *o*-semidine and diphenylines accompany scission when $n = 4$ and 5, and *p*-benzidines are formed for $n = 10$. This progression illustrates the increasing flexibility of the structures. Heterocyclic compounds can also exhibit rearrangement: e.g. when one or both aromatic rings of the hydrazo-compound are sulphur-containing heterocycles (Beyer and Haase, 1957; Beyer and Kreutzberger, 1952; Federova and Mironova, 1962), phenylhydrazinoimidazoles (Pyl, Lahmer and Beyer, 1961) or other nitrogen-containing structures (Das-Gupta and Bose, 1929). However, 2,2′-hydrazo-pyridine and -quinoline can be recovered unchanged after refluxing for several hours with concentrated hydrochloric acid, presumably because protonation of the pyridine rings inhibits the protonation of the hydrazo-nitrogen which is necessary (see later) for rearrangement (Colonna and Risaliti, 1959; Beyer, Haase and Wildgrubbe, 1958). Phenylhydrazino-pyridines and -picolines rearrange under similar conditions in low (c. 25 per cent) yield accompanied by disproportionation and reductive chlorination (Beyer *et al.*, 1958; Colonna and Risaliti, 1956; Risaliti and Pentimalli, 1956). Reduction of azoferrocene under acid conditions gave no rearrangement product (Nesmeyanov, Perevalova and Nikitina, 1961).

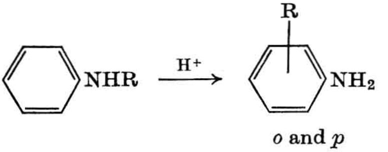


(4)

Several hundred papers have been published on the family of reactions, and three reviews are available (Jacobson, 1922; Vecera, 1958; Shine, 1967) in addition to a detailed mechanistic discussion (Banthorpe, Hughes and Ingold, 1964). This present review surveys the literature up to December 1967.

B. PROOF OF INTRAMOLECULARITY

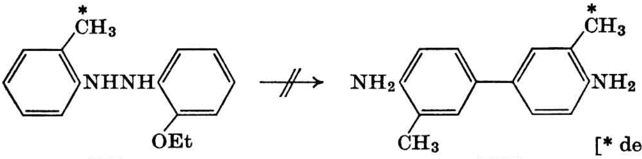
The benzidine rearrangement is one of a group of formally similar reactions in which an atom or group migrates from an amino nitrogen to the ring, equation (5), but in unique company with the rearrangement of *N*-nitroamines it is intramolecular rather than proceeding by fission and intermolecular recombination of the fragments. Early workers recognised the stereochemical restrictions to any intra-



{ R = NHPh, NO_2, NO, CH_3, OH, etc. (5)

molecular mechanism that necessitated bond-breaking and -making at sites spanning the length of the aromatic ring and apparently involved turning the molecule inside out, and they suggested intermolecular pathways. One such route (Tichwinsky, 1903), although put forward in pre-electronic concepts, is equivalent to homolytic fission of the protonated substrate to give free radicals whose radical centres become transferred to *o* or *p* positions, the precise mode of incursion of protons being an adjustable detail. Two weighty arguments were soon adduced against this view (Jacobson, 1922). First, tetraarylhydrazines, $Ph'_2NNPh''_2$, although capable of undergoing acid-catalysed rearrangement gave no such products under conditions where homolysis to radicals was detectable (Wieland, 1912; 1915). Second, a survey of the previously reported rearrangements of some 66 hydrazo-compounds carrying different substituents in each ring, i.e. of the form A—B, indicated no symmetrical products A′—A′ and B′—B′, such as would be derived from the corresponding symmetrically substituted substrates A—A and B—B, which certainly should have arisen if kinetically-free homolysis products had been formed during reaction. The power of the second argument is lessened by the impossibility, some 40 years ago, of achieving a complete material balance in products; typically less than 70 per cent of the products were accounted for. However, modern techniques have vindicated the conclusion. Paper-chromatographic analysis of the products from acid-catalysed rearrangement of 1,2′-hydrazonaphthalene shows less than 0·5 per cent, if any, cross-products (Banthorpe, 1962b) and attempts to trap such products have proved fruitless. For example, less than 0·03 per cent of the ^{14}C-containing symmetrical product (VII, equation (6)) could be isolated when the ^{14}C-labelled substrate VI was rearranged in acid and a large amount of inactive VII was added, and was reisolated for radioactive assay

(Wheland and Schwartz, 1949). The same point was made by the observation that no benzidine (II) could be isolated from rearrangement of *m*-carboxyhydrazobenzene. Similar rearrangements of the



(VI) (VII) (6)

[* denotes C14 tracer]

o and *p* isomers were complicated by decarboxylation, but when allowance was made for this side reaction no intermolecular component could be detected (Bloink and Pausacker, 1950).

Another pre-electronic theory (Stieglitz, 1903), restated in modern terms, envisaged heterolysis and intermolecular recombination (equation (7)); the disposition of protons is again adjustable. Here the

$$\text{Ph}'\text{NHNHPh}'' \xrightarrow{\text{H}^+} [\text{Ph}'\overset{+}{\text{N}}\text{H}, \text{Ph}''\overset{-}{\text{N}}\text{H}] \longrightarrow \text{Products} \qquad (7)$$

previously detailed arguments are not particularly damaging, as a substrate, A—B, containing differently substituted rings, would be predisposed to heterolyse in a particular direction, e.g. to A^+B^-, leading to exclusive recombination of counter-ions and lack of cross-over products. However, on the basis of this mechanism concurrent reaction of two symmetrical hydrazo-compounds, A—A and B—B, which individually rearrange at comparable rates, would lead to unsymmetrical cross-products of the type A′B′ in addition to a calculable proportion of non-crossed-over material. The test was first applied to the co-rearrangement of 2,2′-dimethoxy- and 2,2′-diethoxy-hydrazobenzenes which differed in rate of rearrangement under the chosen conditions by a factor of six; melting-point curves of the product indicated that less than 6 per cent, if any, cross-product was produced (Ingold and Kidd, 1933). More recently, isotopic-dilution analysis of the product of mixed rearrangement of 2,2′-dimethyl and 2-^{14}C-methylhydrazobenzene gave less than 0·03 per cent cross-product (Smith, Wheland and Schwartz, 1952) and paper chromatography of the products from the three hydrazonaphthalene isomers (Banthorpe, 1962b) and substituted hydrazobenzenes (Vecera *et al.*, 1957) have made the same point with less, but adequate, precision. All the pairs of compounds studied differed in reactivity by

此为试读，需要完整PDF请访问： www.ertongbook.com