

extinction coefficients for pure I and II agrees with the prior determinations. The mass spectrum of II is qualitatively similar to that of I; in particular, the parent peak of each is at m/e 58.⁹ Confirmation of the mass spectral value of the molecular weight of II was obtained by a micro Regnault vapor density determination.

The close structural kinship of II to I is evidenced by their base-catalyzed isomerization to the same product, formaldehyde methylhydrazone (III).¹⁰ This substance is identified directly in the aqueous reaction solution by its proton resonance spectrum, comprising an AB quartet ($\delta_A - 1.88$ p.p.m., $\delta_B - 1.52$ p.p.m., $J_{AB} = 10.6 \pm 0.3$ c.p.s.) arising from the methylene group and a singlet ($\delta + 2.12$ p.p.m.) arising from the methyl group.¹¹

Thus II is bound by the requirements that it is isomeric with I, has all protons identical, shows near-ultraviolet absorption, is formed in photochemical equilibrium with I, and suffers, with I, base-catalyzed isomerization to the same product (III). We conclude that II is *cis*-azomethane.

(9) We are indebted to Dr. G. O. Dudek (Harvard University) for aid in obtaining the mass spectra.

(10) This reaction, together with the stability of II, argues strongly against 1,1-dimethyldiazine ($(CH_3)_2N^+=N^-$) as a structure for II. Further evidence is the lack of a significant peak at m/e 44.

(11) These data agree with those for formaldehyde N,N-dimethylhydrazone, $J_{AB} = 10.3 \pm 0.2$ c.p.s.; private communication from Dr. Shapiro, from work by B. L. Shapiro, G. J. Karabatsos, and S. L. Manatt. *J. Am. Chem. Soc.*, **85**, 4041 (1963).

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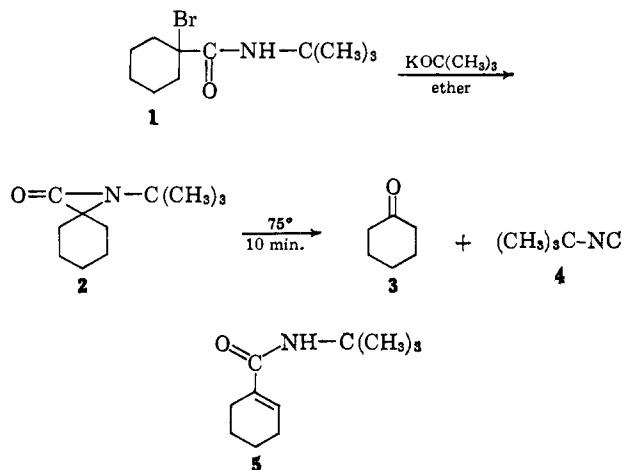
ROBERT F. HUTTON
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RECEIVED DECEMBER 16, 1963

The Formation of an Isocyanide and a Ketone from an α -Haloamide

Sir:

We have found that the reaction of 1-bromo-1-N-*t*-butylcarboxamidocyclohexane (1) with potassium *t*-butoxide and subsequent warming produces cyclohexanone (3) and *t*-butyl isocyanide (4) as the major products, together with a small amount of 1-cyclohexene-1-N-*t*-butylcarboxamide (5).¹ This reaction ap-



(1) Recently, we noted the formation of small amounts of acetone and *t*-butyl isocyanide in the isomerization of 1-*t*-butyl-3,3-dimethylaziridinone to *N*-*t*-butylmethacrylamide [J. C. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, in press.

parently first produces a relatively stable α -lactam, 1-*t*-butyl-3,3-pentamethyleneaziridinone (2), which decomposes on warming (75°). We are unaware of any close analogy to this reaction.

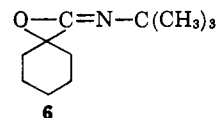
1-Bromo-1-N-*t*-butylcarboxamidocyclohexane (1), m.p. 82–83°, was prepared from 1-bromocyclohexanecarbonyl chloride² and *t*-butylamine in 92% yield. *Anal.* Found: C, 50.33; H, 7.61; N, 5.31; Br, 30.73. A mixture of potassium *t*-butoxide (1.12 g., 10 mmoles) in a solution of 2.62 g. (10 mmoles) of 1 in 100 ml. of absolute ether was stirred for 1 hr. at –15°, the suspension was cleared by centrifugation, and the supernatant solution was concentrated at 0° (reduced pressure, finally at 1 mm.). The residual colorless liquid, which crystallized promptly in an ice bath, showed the strong band in the infrared (CCl_4) at 1835 cm^{-1} characteristic of an α -lactam and a weak one at 1675 cm^{-1} . On the basis of the infrared spectrum it was estimated that α -lactam 2 constituted about 80% of the product.

Without further purification this product was warmed at 75° for 10 min.; at the end of this period the α -lactam-type band in the infrared at 1835 cm^{-1} had disappeared completely. The volatile components were removed at 25° (2 mm.) and trapped in a receiver cooled with Dry Ice–acetone. V.p.c. revealed only two components, which were separated by fractional distillation. The first fraction (0.52 g., 63%), b.p. 89–91°, infrared 2135 cm^{-1} , was identified as *t*-butyl isocyanide by direct comparison with an authentic sample.³

The second fraction, b.p. 155°, infrared 1715 cm^{-1} , gave a 2,4-dinitrophenylhydrazone (1.84 g., 66%), m.p. 161–162°. A mixture melting point with an authentic sample of cyclohexanone-2,4-dinitrophenylhydrazone was undepressed.

The crystalline residue after the removal of the volatile portion showed two major components on thin layer chromatography (Silica Gel G with 96% benzene–4% ethyl acetate or 95% benzene–5% ether). These were separated by column chromatography (silicic acid with benzene–ether eluent). The first fraction eluted (0.45 g., 17%), m.p. 81–82°, was unchanged starting material (1). The second fraction (0.20 g., 11%), m.p. 113–114°, was identified as 1-cyclohexene-1-N-*t*-butylcarboxamide (5). *Anal.* Found: C, 72.85; H, 10.77; N, 7.95. The infrared spectrum (CCl_4) showed 3420 (NH), 2930 (aliphatic CH), 1670 (amide carbonyl), 1640 (C=C bond), and 1505 (amide 2) cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 211 $\text{m}\mu$ ($\log \epsilon$ 4.06). A mixture melting point with an authentic sample, prepared from 1-cyclohexenecarbonyl chloride^{4,5} and *t*-butylamine, was undepressed. The present experiments do not permit a decision as to whether product 5 arose from α -lactam 2 or from 1 by direct dehydrobromination. However, the observation that 1-*t*-butyl-3,3-dimethylaziridinone isomerized to *N*-*t*-butylmethacrylamide¹ on warming supports the first alternative.

Recent evidence⁶ indicates that in the normal state α -lactams have the true lactam structure (as represented by formula 2). However it seems likely that the



(2) J. von Braun, *Ber.*, **67B**, 218 (1934).

(3) *t*-Butyl isocyanide, which can easily be recognized by its repulsive, bitter odor, was synthesized for comparison by the method of I. Ugi and R. Meyr [*Ber.*, **93**, 239 (1960)].

(4) J. Kenner and R. L. Wain, *ibid.*, **72**, 456 (1939).

(5) G. Baddeley, H. T. Taylor, and W. Pickles, *J. Chem. Soc.*, 124 (1952).

(6) H. E. Baumgarten, *et al.*, *J. Am. Chem. Soc.*, **85**, 3303 (1963).

observed major products (3 and 4) did not arise directly from 2, but rather from an isomer, the oxirane 6. We suggest that warming first transforms the α -lactam into oxirane 6, which species fragments into cyclohexanone and *t*-butyl isocyanide. The nature of the transformation of 2 to 6 (free-radical, ionic, or carbene) is not obvious on the basis of the evidence at hand.

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BOOK REVIEWS

Organische Chemie in Einzeldarstellungen. Band 7. Die Photochemie der Organischen Farbstoffe. By HANS MEIER, Dr. rer. nat., Diplomchemiker, Staatliches Forschungsinstitut für Geochemie, Bamberg. Springer-Verlag, Abteilung VI, 1 Berlin 31 (Wilmersdorf) Heidelbergerplatz 3, West Berlin, Germany. 1963. xvi + 471 pp. 16 × 24 cm. Price, ganzleinen, DM 79.

The photochemistry of organic compounds is a field having many different aspects; this subject is primarily of interest to physical chemists. The fading of dyed textiles and other substrates, however, is a problem which has been investigated mainly by dye chemists and technologists. Investigations of light-catalyzed organic reactions have increased appreciably in recent years and the importance of photochemical processes in biology has been clearly recognized.

There is no previous monograph which discusses the photochemistry of organic compounds with visible light. This book covers this topic and is therefore most welcome.

The author opens with a general survey of the theory of light absorption by organic compounds in relation to their constitution and their states of aggregation. Two chapters are devoted to fluorescence and phosphorescence. A discussion of photochemical reactions of dyes then follows. The central and largest part of the book contains five chapters on the photoconductivity of dyes. In the later chapters some specific effects are discussed, namely the sensitization of photographic layers and of inorganic semiconductors by dyes, the photodynamic damage of biological substrates, the nature of human vision, the photosynthesis of organic compounds in plants, and a short discussion of the problem of energy transportation in biological materials.

In the preface the author states that he wishes to review the whole field of the photochemistry of dyes by discussing as many literature references as possible. Indeed, the number of papers cited (some 1200) is extremely high. One therefore expects comprehensive coverage of the whole subject. This is not always true. For example, from our own files on the fading of dyes on textiles, which is by no means comprehensive but contains 107 references, we found only six in this monograph. The name of C. H. Giles, an author who has made substantial contributions to the fundamental understanding of the lightfastness of dyeings, does not appear in the context; some of his papers are mentioned by the name of the first author with the appendix, *et al.* Whereas the photodynamic effect of dyes on the degradation of biological systems is discussed in detail, only two pages are devoted to the tendering effect of certain anthraquinone dyes on cellulose; only Dörr's paper is discussed in this field, although there are at least ten valuable contributions to this problem.

Although the free electron method of H. Kuhn and N. S. Bayliss has been more successful than other methods in the calculation of absorption bands of dyes in the visible spectrum, the MO treatment certainly merits more than 1.5 pages.

Organic chemists will miss structural formulas of many dyes; very often a certain dye's behavior in some photochemical respect is discussed in detail which might be more illustrative if its constitution were given. A more thorough discussion, including formulas, would also be desirable for photodegradation products of dyes.

In several places one has the impression that the author is not well acquainted with physical organic chemistry (p. 10, $-\text{NH}_3^+$ is not a $-M$ -substituent in Ingold's nomenclature; on page 112 one feels that Hammett's σ_p relationship could be something specific for the rate of fading; on pp. 72–73 the author seems to think that the decrease of acidity of phenols and the increase of basicity of anilines are different effects).

On the other hand, it should be emphasized that the central part of the book—photoconductivity of dyes—is excellent and authoritative. Those parts of the book in which the author discusses the importance of photoconductivity for complex processes, *e.g.*, for biological processes such as the assimilation of CO_2 in plants catalyzed by the chlorophylls, are very remarkable.

This discussion will stimulate further work in this field, especially because the author differentiates clearly between experimental facts, definite conclusions drawn from these facts, and hypotheses which need further work in the laboratory. The discussion on the photoelectric theory of the photodynamic effect (pp. 338–351) is a good example of this.

In conclusion, this book can be highly recommended for all who are interested in photoelectric and photodynamic effects of dyed molecules. Beginners as well as experts will find the book stimulating. The book is, in spite of the remarks in this review, also useful for chemists who are interested in dyes in the technological sense (dyeing of fibers, plastics *etc.*) or in the organic chemistry of the processes involved in the reactions between dyes and light. For these, however, it does not emphasize the main problems, but provides suggestions of a different point of view. In this sense it is also welcome for this group of chemists.

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Handbuch der Präparativen Anorganischen Chemie. Band II. Edited by GEORG BRAUER, Professor für anorganische Chemie an der Universität Freiburg im Breisgau. Ferdinand Enke Verlag, 7000 Stuttgart W, Hasenbergsteige 3, Germany. 1962. xii + 1611 pp. 16.5 × 24.5 cm. Price, geheftet, DM 102; ganzleinen, DM 108.

Brauer's "Handbuch" is not a text-book. It is a reference work with contributions from a distinguished and highly capable group of inorganic chemists who have accepted responsibility for selecting those synthetic procedures with which each is thoroughly familiar through teaching and research. Reproducibility of experimental procedures is therefore guaranteed. That such a compilation should come from Germany is itself an indication that teaching and research in inorganic chemistry in the German speaking countries still strongly accent preparative and experimental chemistry, as contrasted with the physico-chemical approach which characterizes the English speaking world.

In its organization the second edition follows the pattern set by the first edition which appeared in 1954. Both are divided into three "large" chapters dealing with (I) Preparative Methods, (II) Elements and Compounds, and (III) Special Classes of Substances. The original one-volume edition (1439 pages) has been expanded into two volumes totaling 1611 pages (including a complete formula index and a subject matter index in Volume II). Volume I (pages 1–877) appeared in 1960 and was reviewed (*J. Am. Chem. Soc.*, **83**, 505 (1961)) by Anderson. Volume I included the general chapter on Preparative Methods and the first 18 sections of Chapter II covering the preparation of the elements and compounds of hydrogen and the seven regular groups in the Periodic Table. Volume II (pages 878–1611) with the date line 1962 includes: (a) eleven additional sections devoted to the preparative chemistry of the transition elements, thus completing Chapter II and (b) all of Chapter III on Special Classes of Substances.

The preparative chemistry of the transition elements and their compounds is the work of Glemser and Sauer (Cu, Ag, Au), Wagenknecht and Juza (Zn, Cd, Hg), Wetzel (Sc, Y, the rare earths), Ehrlich (Ti, Zr, Hf, Th), Brauer (V, Nb, Ta), Hein and Herzog (Cr, Mo, W, V), Lux (Mn), Glemser (Re), Lux (Fe), Glemser (Co, Ni), and Grube (Pt metals).

Particularly interesting are the sections which make up Chapter III, although it is not clear why the five specific topics should have been selected, except that the authors of each are well-known for their researches in the respective fields. The section by Wagner on Adsorption and Catalytically Active Substances is especially to be commended for its coverage of a wide variety of materials which find use as catalysts (active metals, compound