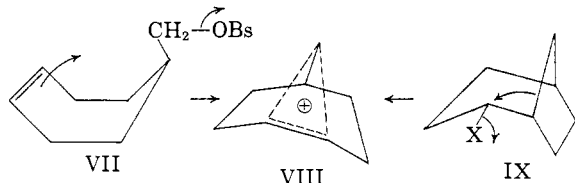
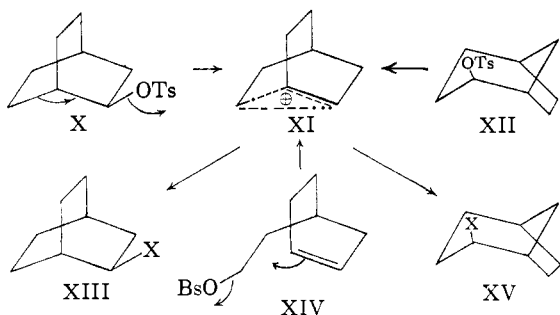


IX-OTs provides π - and σ -routes, respectively, to the non-classical cation VIII, which then gives rise to the *cis*-bicyclo[3.2.1]octyl acetate IX-OAc. In solvolysis of the related bicyclo[2.2.2]octyl and *trans*-(*axial*)-bicyclo[3.2.1]octyl toluenesulfonates X and XII, Walborsky⁹ and Goering⁸ have shown recently that both substrates give rise to the same mixture of [2.2.2]- and *axial*-[3.2.1]-products XIII and XV, none of the epimeric *cis*-[3.2.1]-



product being observed. Also, the [2.2.2]acetate XIII-OAc from optically active [2.2.2]toluenesulfonate X is formed with complete retention of configuration. Anchimerically assisted ionization of X and XII apparently represents the σ -route to the non-classical cation XI which leads only to bicyclo[2.2.2]- and *axial*-bicyclo[3.2.1]octyl products.



For the π -route to cation XI, one can visualize starting with the Δ^3 -cyclohexenylethyl system XIV, instead of VII employed by Le Ny,⁷ and we now have investigated the solvolysis of bromobenzenesulfonate¹⁰ XIV, m.p. 25–26°. The corresponding alcohol, n_D^{25} 1.4809, was obtained from hydroboration-oxidation of 4-vinylcyclohexene using excess diene; m.p. of 3,5-dinitrobenzoate,¹⁰ 63–64°. With 0.01 *M* XIV in a 0.02 *M* acetic acid solution of sodium acetate, good first order kinetics of acetolysis were observed, the rate constant at 75.1° being 7.4×10^{-6} sec.⁻¹. This value is four times the one obtained with the saturated analog¹⁰ of XIV, m.p. 37–38°. From the acetolysis of XIV at 100° and treatment of the product with lithium aluminum hydride, there was obtained an alcohol mixture which vapor phase chromatographic analysis showed was 20% cyclohexenylethanol and 80% of a 54:46 mixture of [2.2.2]-alcohol XIII-OH and *axial*-[3.2.1]-alcohol XV-OH, respectively. By preparative vapor phase chromatography, the three fractions were separated and identified further by m.p., m.p. of derivatives, and infrared spectrum:^{8,9} (i) *axial*-alcohol XV-OH, m.p. 197–198°, m.p. of bromobenzenesulfonate, 62–63°, m.p. of *p*-nitrobenzoate, 94–95°, (ii) [2.2.2]-alcohol

(9) H. M. Walborsky, M. E. Baum and A. A. Youssef, *J. Am. Chem. Soc.*, **83**, 988 (1961).

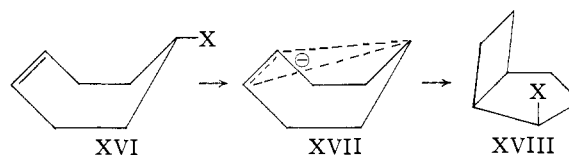
(10) Correct carbon and hydrogen analyses were obtained for all new compounds.

XIII-OH, m.p. 208–210°, m.p. of bromobenzenesulfonate, 79–80°, (iii) cyclohexenylethanol, m.p. of 3,5-dinitrobenzoate, 63–64°. Acetolysis of the mixed bromobenzenesulfonate, m.p. 44–55°, from the combined fractions (i) and (ii) led to a 53:47 mixture of alcohols XIII-OH and XV-OH.

In 0.02 *M* sodium formate in formic acid at 75.1°, the cyclohexenylethyl bromobenzenesulfonate XIV solvolyzes with a rate constant of 4.0×10^{-4} sec.⁻¹, faster than the saturated analog by roughly one power of ten. The isolated alcohol product from this formolysis is again the 54:46 mixture of [2.2.2]-alcohol XIII-OH and *axial*-alcohol XV-OH, the cyclohexenylethanol content now being almost negligible.

The present work shows that the unsaturated ester XIV tends to solvolyze predominantly by way of anchimerically assisted ionization to the non-classical cation XI. Thus, there is now unique and compelling evidence for this cation from the π -route of formation, as well as the σ , the distinction between the two carbonium ions VIII and XI being maintained whether the ions are produced by π - or σ -routes.

The pair of unsaturated systems, VII and XIV, which have been demonstrated to lead to isomeric non-classical ions and thus contrasting over-all structural and stereochemical results, represents only one example in a broader theme. The usual stereoelectronic considerations allow one to conceive other such pairs of unsaturated derivatives which would be related to isomeric bridged ions if these are formed in preference to classical ones. For example, a conceivable pair of systems includes Δ^2 -cyclopentenylethyl, related to ion II, and Δ^4 -cycloheptenyl, XVI, which is related to ion XVII and thus *cis*-2-bicyclo[3.2.0]heptyl derivatives XVIII.



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THE PHOTOCHEMICAL REARRANGEMENT OF
4,4-DIPHENYLCYCLOHEXADIENONE. PAPER I ON
A GENERAL THEORY OF PHOTOCHEMICAL
REACTIONS¹

Sir:

Organic photochemistry has not shared the mechanistic sophistication of ground state organic chemistry. A number of years ago we initiated a program to search for general principles governing organic photochemistry.

The photolysis of cyclohexa-2,5-dien-1-ones seemed of special interest not only because of the intriguingly profound molecular rearrangements occurring² but also because of an inherent enigma. While the skeletal rearrangements were suggestive

(1) Supported by the National Science Foundation.

(2) Cf. D. H. R. Barton, J. McGhie and M. Rosenberger, *J. Chem. Soc.*, 1215 (1961), for references.

of an electron deficient Pi system, contrariwise they seemed likely³ to result from an $n \rightarrow \text{Pi}^*$ excited state, the Pi system of which is electron rich.

The previously unknown 4,4-diphenylcyclohexadienone was chosen for study, thus reducing the system to its essentials.

4,4-Diphenylcyclohexadienone⁴ (I) was irradiated at 25° in aqueous dioxane with a filter cutting off sharply below 310 m μ . The dilute alkali soluble fraction gave an acid, m.p. 117°, presently being investigated. Scanning liquid-liquid partition chromatography of the remaining product indicated only three peaks. The first arose from recovered dienone. The second peak afforded a ketone (II, m.p. 140.5°, C₁₈H₁₄O). The third peak gave a phenol (III, 102°, C₁₈H₁₄O; acetate, 118°). Structures of the "photoketone" II and the "photophenol" III were established as 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one and 2,3-diphenylphenol, respectively.

The ultraviolet, infrared and n.m.r. spectra of the photoketone accorded with the umbellulone-like structure II having unconjugated phenyl groups. Ozonolysis of II in acetic acid with peracetic acid workup gave the known⁵ *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid; this, its methyl ester and anhydride were compared with independently synthesized compounds.

Of the six possible diphenylphenols, all but the 2,3- and the 3,4-isomers were known. Of these known isomers only 2,6-diphenylphenol⁶ melted near 102°, but this compound differed from our photophenol.

3,4-Diphenylphenol (m.p. 104°, acetate 131.5°) was synthesized in two unambiguous ways⁷; however, this, too, differed from the photophenol. A synthesis of 2,3-diphenylphenol gave material identical with our photophenol.⁷

It was found that 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (II) is an intermediate in the photochemical formation of 2,3-diphenylphenol (III) from 4,4-diphenylcyclohexadienone. The yield of photoketone was maximized in low conversion runs while the yields of photophenol and 117° photoacid increased with longer irradiation. Furthermore, the irradiation of photoketone itself was found to afford 2,3-diphenylphenol and photoacid.

We have felt for some time that photochemical reactions occur *via* pathways allowing continuous electronic redistribution in proceeding from excited state to product. Thus photochemical reactions

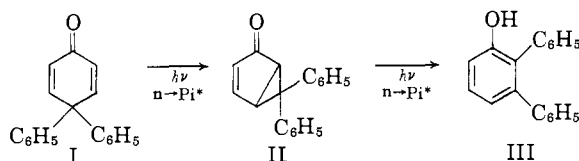
(3) *E.g.* literature reactions employing sunlight and Pyrex glass and hence light above 300 m μ .

(4) (a) The preparation of 4,4-diphenylcyclohex-2-en-1-one (m.p. 91°), from the Triton B condensation of diphenylacetaldehyde and methyl vinyl ketone, and its SeO₂ dehydrogenation to 4,4-diphenylcyclohexadienone (m.p. 123°) were modifications of the unpublished syntheses of Zimmerman and Wellman. (b) All compounds gave acceptable analyses.

(5) (a) J. Van Alphen, *Rec. Trav. Chim.*, **62**, 210 (1943); (b) W. M. Jones, *J. Am. Chem. Soc.*, **81**, 3776 (1959).

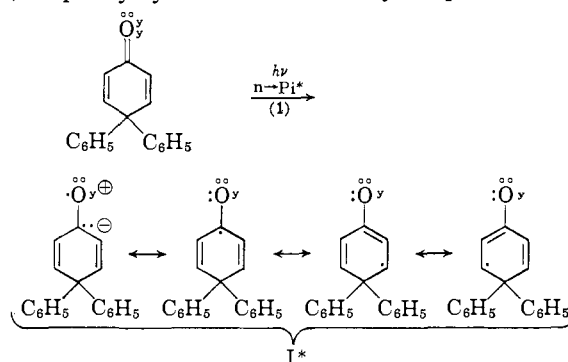
(6) A. Lüttringhaus and D. Ambros, *Chem. Ber.*, **89**, 463 (1956).

(7) 3,4-Diphenylphenol was obtained from the acid catalyzed dienonephenol rearrangement of I and from the dehydrogenation of 3,4-diphenylcyclohex-2-en-1-one. 2,3-Diphenylphenol was synthesized by the dehydrogenation of 5,6-diphenylcyclohex-2-en-1-one. Full details will be published subsequently. Prof. C. F. Koelsch has communicated privately his independent synthesis of these phenols, m.p. 101° and 102°, respectively; 2,3-diphenylphenyl acetate, m.p. 116°, in agreement with the above.



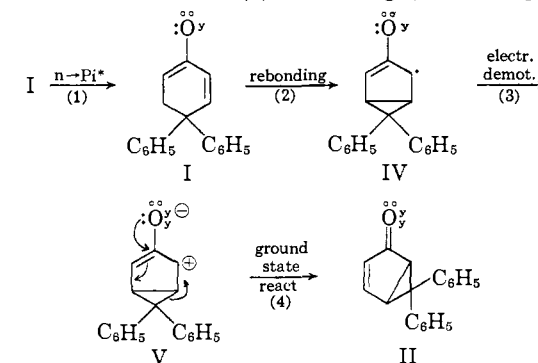
do not occur indiscriminately, despite the high energy involved. Given the structure of an excited state, the criterion of continuous electronic redistribution allows prediction of potential products.

In the present instance, the $n \rightarrow \text{Pi}^*$ excitation of 4,4-diphenylcyclohexadienone may⁸ be pictured as:⁹



Thus excited state I* has a Pi system with one more electron than the ground state, analogous to a metal ketyl, but lacks one P_y unshared electron of the ketyl. One reasonable electron redistribution process available to I* is bridging between carbons 3 and 5, yielding the bicyclic intermediate IV. Electron demotion (Pi* \rightarrow n) leads to the zwitterionic species V. Species IV and V are "coerced" to react further since each has one less bond than maximum and neither can collapse to stable product without atomic reorganization. However, V possesses the structural features of a cyclopropylcarbinyl carbonium ion and may undergo a "Roberts cyclopropylcarbinyl rearrangement" to collapse to photoketone II.¹⁰

It is noted that four steps are involved: (1) $n \rightarrow \text{Pi}^*$ excitation, (2) rebonding (here bridging),



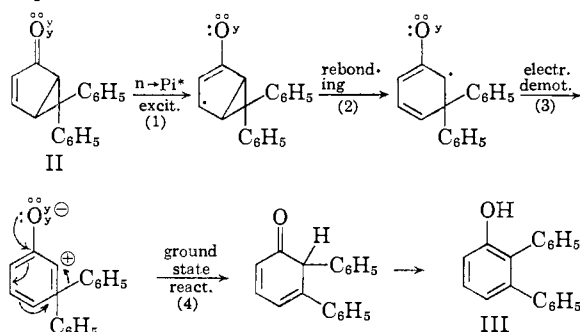
(8) *Cf.* J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958), for a discussion of $n \rightarrow \text{Pi}^*$ carbonyl excitation.

(9) Circles represent 2S unshared electrons, y's are unshared electrons in the P_y orbital in the molecular plane. Electrons in the Pi system derived from P_z orbitals are depicted either as dots or lines (for electron pairs). This is a modification of the suggestion of G. W. Wheland for simple ketones, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 283.

(10) The rearrangement is formally a 1,3-shift. The details and the question whether IV is a singlet or triplet will be discussed later.

(3) electron demotion, and (4) transformations having ground state parallel.

The II to III rearrangement again involves four steps



Significantly, this treatment reasonably accounts for the involvement of electron deficient Pi systems in $n \rightarrow \pi^*$ photochemical transformations. These mechanisms are applicable to the santonin to lumisantonin and related rearrangements, even accommodating the known¹¹ reaction stereochemistry. Furthermore, the general approach is applicable to a large number of other photochemical reactions. These points will be considered in detail in our full paper on the present subject and in related papers.

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(11) D. H. R. Barton and P. T. Gillam, *J. Chem. Soc.*, 4596 (1960); cf. ref. 2 also.

BOOK REVIEWS

Chemical Aspects of the Structure of Small Peptides. An Introduction. By DOROTHY WRINCH, M. A. Cantab, D. Sc. Oxon., D.Sc. Lond., Visiting Research Professor at Smith College, Massachusetts, USA. Enjar Munks-gaard, Ltd., 6 Nørregade, Copenhagen, Denmark. 1960. 194 pp. 18 × 25.5 cm. Price, Dan. kroner 24.—.

Dating from the earliest structural studies, there has been speculation regarding the existence of tetrahedral "orthoamide" bonds in proteins. Half a century has passed, however, and the question remains essentially unanswered. In large measure, demonstration of such bonding by chemical means is hindered by the extreme complexity of the molecule in question as well as by the existence of an "uncertainty principle": namely, that a protein cannot be readily submitted to chemical examination without some modification of its intimate structure. Detection by physical means of a small number of tetrahedral linkages in the presence of a preponderance of trigonal peptide bonds is, again, a problem of enormous proportions. In 1936, Dr. Wrinch proposed a "cyclol" theory in which amide bonds were abandoned and a totally tetrahedral structure for proteins was advanced. In more recent times, a small amount of chemical evidence has appeared which demonstrates the ability of amides to form relatively stable tetrahedral or "ortho" linkages. However, the evidence is based on circumstances which are highly specialized and geometrically favorable. Dr. Wrinch has now brought forth a Monograph in which she reviews the limited chemical data and proceeds to reapply the "cyclol" concept to small peptides. What might have been presented simply and concisely in a dozen pages has been expanded to almost two hundred by the use of a maze of symbolism and grandiloquence. The promise that "this Monograph reports results obtained in an enquiry into chemical aspects of the structure of small peptides" is not fulfilled, since no original experimental work, chemical or otherwise, is reported. On the basis of three or four reported cases of "orthoamide" linkages, Dr. Wrinch asks for "the repudiation of the amide hypothesis" for small peptides. In the face of overwhelming evidence from spectral data alone, such a request cannot merit serious consideration. Certainly, the majority of students of peptide and protein structure are aware that their best efforts, to date, have led only to primary sequences and that considerable effort will have to be expended to elucidate more intimate structural details, among which there may be found a small number of covalent linkages of the "ortho" peptide variety. This is an area in which conservatism can be displaced only by very convincing experimental data. Because of the extreme views pre-

sented, based on such meager evidence, and because of the unnecessarily lengthy text, this reviewer cannot recommend Dr. Wrinch's Monograph as a major contribution to the literature of protein chemistry.

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Gas Chromatography. Second International Symposium Held under the Auspices of the Analysis Instrumentation Division of the Instrument Society of America, June, 1959. Edited by HENRY J. NOEBELS, Beckman Instruments, Inc., Fullerton, Calif., R. F. WALL, Monsanto Chemical Co., Texas City, Tex., and NATHANIEL BRENNER, The Perkin-Elmer Corp., Norwalk, Conn. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. xvi + 463 pp. 16 × 23.5 cm. Price, \$16.00.

A graph is presented on page 375 of the volume under review on which are plotted the number of articles in the literature dealing with gas chromatography in each year from 1952 to 1959. This number has risen from a few articles in 1952 to nearly 800 in 1959; moreover the slope appears still to be rising and must be almost infinite by now. In such a situation it is almost impossible for the average chemist, who wishes to use gas chromatographic techniques as a routine tool, to keep up with the more recent developments in the field. Publication in book form of groups of papers presented at periodically scheduled symposia offers the reader an opportunity to become familiar with some of these developments in a manner which is economical of his time.

As with all collections of this nature, the quality of presentation is somewhat uneven, the topics discussed are necessarily limited, and the choice of those topics is unlikely to meet with approval, or the needs, of every reader. Nevertheless, there is much useful information in this book and it should be available to all who have any interest whatsoever in gas chromatography and its application.

The present volume contains a large selection of specific applications, several articles on detectors (including methods of expressing sensitivity) and recording systems, one on some theoretical considerations of large diameter chromatographic columns, one showing experimental relations between sample size and carrier flow rate and HETP, and, gratifyingly, two devoted to detailed consideration of the role of the solid supporting material in a column. There is