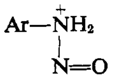
formation

$$Ru(NH_3)_6^{3+} = Ru(NH_3)_5(NH_2)^{2+} + H^+$$

During the course of our work, D. Waysbort and G. Navon[13] reported the pK_a for the above deprotonation reaction as 12.4. If their value is correct,[14] it suggests that the production of $Ru(NH_3)_5N_2^{2+}$ is extremely fast (in order to obtain yields of 100% $Ru(NH_3)_5N_2^{2+}$ even at pH 9).

Once the amide is formed, it is easy to see how NO could attack the bound NH_2^-. In a similar manner it has been suggested that N_2O_3 can attack arylamines to yield intermediate arylnitrosoamines



$$Ar-\overset{+}{N}H_2-N{=}O$$

which leads to the formation of diazonium salts.[15]

The marked reactivity of $Ru(NH_3)_6^{3+}$ in alkaline solution parallels the observation[16] that while substitution by $S_2O_3^{2-}$ or SPO_3^{3-} onto $Ru(NH_3)_6^{3+}$ is slow in acid solution, the reactions in alkaline solution proceed rapidly with the production of a sulfamate complex: $Ru(NH_3)_5NHSO_3^+$. We are carrying out further work to find additional examples of the reactivity of $Ru(NH_3)_6^{3+}$ in alkaline media.

Besides being experimentally very simple to carry out, this reaction offers a clean, rapid, and high-yield

$$Ru(NH_3)_6^{3+} + NO + OH^- \longrightarrow Ru(NH_3)_5N_2^{2+} + 2H_2O$$

method of producing $Ru(NH_3)_5N_2^{2+}$ without having to reduce the Ru(III) center with external reducing agents.

Acknowledgment. Financial support for this work was provided by an EPDA, Part E Fellowship to Steven Pell and by a Boston University Graduate School award to John N. Armor.

(13) D. Waysbort and G. Navon, *Chem. Commun.*, 1410 (1971).

(14) Previously unpublished results (submitted for publication) lead us to accept with some reservations the conclusions of Waysbort and Navon.

(15) C. Noller, "Textbook of Organic Chemistry," W. B. Saunders, Philadelphia, Pa., 1966, p 430.

(16) J. N. Armor and H. Taube, *Inorg. Chem.*, **10**, 1570 (1971).

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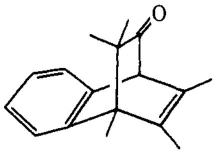
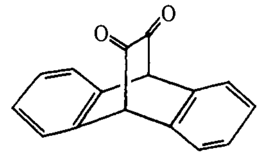
New Enone Photochemistry

Sir:

Retro Diels–Alder reactions of ethanoanthracenes and similar bridged aromatics have provided a useful synthetic route to molecules which may be otherwise inaccessible or at least difficult to obtain.[1] Elimination of the ethano bridge can be accomplished thermally or photochemically, but when the bridge contains a carbonyl group so that the eliminated molecule is a ketene, the photochemical path is much the more facile. For example, **1** readily gave dimethylketene and 1,2,3,4-tetramethylnaphthalene photochemically, whereas the thermal reaction required temperatures of 450–550°.[2] Similarly the α-diketone **2** gave anthracene and carbon monoxide photochemically, though it melts without decomposition at 200° and was recovered (80%) on being heated to 350°.[3]



1



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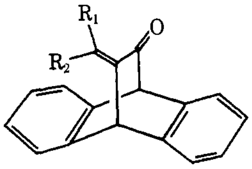
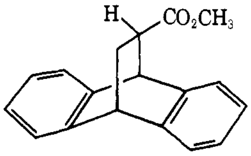


3a, $R_1 = R_2 = H$
b, $R_1 = H; R_2 = Ph$

It is not yet known, in the photolysis of **2**, whether the ethano bridge is eliminated as O=C=C=O (oxoketene or bis(carbon monoxide)) which subsequently falls apart, or whether the carbon monoxide is formed directly.[4] To probe this question further, we have synthesized and irradiated several monomethylene analogs of **2** (*i.e.*, **3a** and **3b**). We found, as had been hoped, that products derived from methyleneketenes can be obtained (depending on the substituents R_1 and R_2), but we also discovered an interesting new photoisomerization of enones.

The α-methylene ketone **3a**[5] was irradiated in methanol solution (10^{-3} *M*, Hanovia 450-W lamp, Pyrex, 1 hr), anticipating that if cleavage to anthracene and methyleneketene were to occur, the latter would be trapped as methyl acrylate. Instead the main reaction product, isolated in 93% yield, was the ester **4** (identical in all respects with an authentic sample).[6] Less than 1% of anthracene and its photodimer, both of which are easily detected, were produced.



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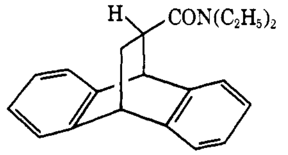

5

The formation of **4** from **3a** can be rationalized by a Norrish type I cleavage, rotation of the carbonyl group and electron delocalization, 180° C–C bond rotation and rebonding to form a ketene intermediate A.[7] Con-

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(1) For a review, see H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968); see also J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966).

(2) R. K. Murray, Jr., and H. Hart, *Tetrahedron Lett.*, 4995 (1968); A. Oku, T. Kakihana, and H. Hart, *J. Amer. Chem. Soc.*, **89**, 4554 (1967).

(3) J. Strating, B. Zwanenburg, A. Wagenaar, and A. C. Udding, *Tetrahedron Lett.*, 125 (1969).

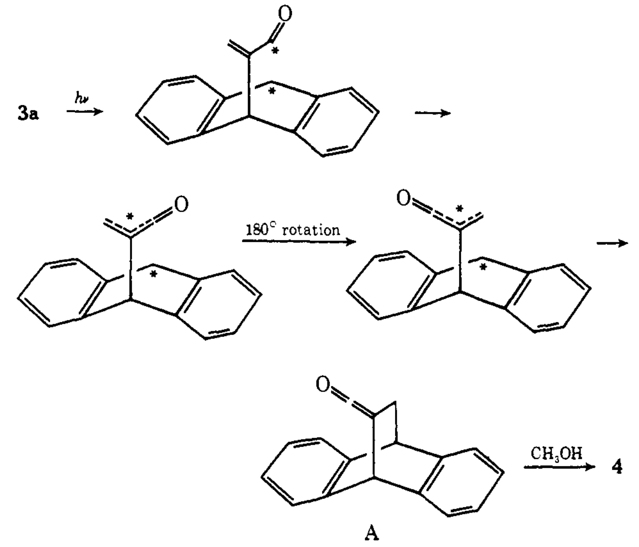
(4) The mass spectral fragmentation pattern of **2** indicated that $C_2O_2^+$ was formed, but attempts to trap the neutral molecule were unsuccessful.[3] Low-temperature irradiations of **2** have thus far failed to give unequivocal evidence for C_2O_2: H. Hart and D. L. Dean, unpublished results.

(5) E. I. Snyder and R. A. Clement, *J. Amer. Chem. Soc.*, **82**, 1424 (1960).

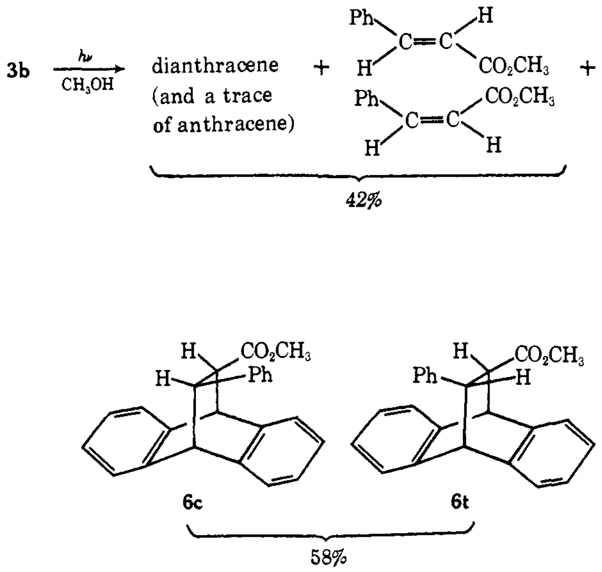
(6) R. K. Hill and G. R. Newkome, *J. Org. Chem.*, **34**, 740 (1969).

(7) An alternate path, cleavage to methyleneketene which then readds at the terminal carbon–carbon double bond faster than it reacts with methanol, seems unlikely in view of the results with **3b** (*vide infra*). The question of 180° rotation is being tested with bridgehead labeled compounds. Other mechanistic details (excited state multiplicity, whether A is a discrete reaction product or whether the nucleophilic

sistent with this scheme, irradiation of **3a** in ether solution containing 4% of diethylamine gave the amide **5**[8] in 89% yield.[9,10]



To test the generality of this reaction, the benzal ketone **3b** was synthesized[11] and irradiated in methanol. Anthracene photodimer precipitated during the photolysis, and was isolated in 42% yield.[13] The other reaction products were methyl *cis*- and *trans*-cinnamates, produced in a 1:1 ratio[14] and in comparable yield to the dianthracene, and the esters **6t** and **6c**,[15] in the ratio 68:32. Nmr analysis of the crude photolysis mixture showed that no other product was present in a significant amount. Esters **6t** and **6c** cannot be the source of the methyl cinnamates and dianthracene, since they are unaffected by irradiation through Pyrex.



Thus in the case of **3b**, the photoreaction follows two paths, rearrangement (as with **3a**) and bridge cleavage. It is possible that a single intermediate partitions along two paths (*i.e.*, to a methyleneketene and anthracene, or to a bridged ketene such as A) or that two separate routes lead to the two sets of products. This question and other mechanistic details are being studied.

There are many reported photoreactions of enones, but to the best of our knowledge all contain the carbon–carbon double bond in an open chain or in an endocyclic ring position. This is the first instance of photorearrangement in an enone where the carbon–carbon double bond is exocyclic. We are exploring the scope

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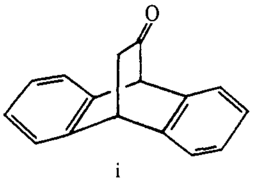
reaction occurs at an earlier stage, etc.) are being studied and the scheme dresented here is tentative. NOTE ADDED IN PROOF. The 180° rotation mechanism has now been established (work by D. N. Buchanan).

(8) The nmr spectrum of **5** obtained from **3a** was identical with that of an authentic sample prepared according to the patent of J. R. Geigy A.-G., Netherlands Appl. 6,412,205 (April 22, 1965); *Chem. Abstr.*, **63**, 14788b (1965).

(9) A slow ground-state reaction between diethylamine and **3a** was observed, by uv spectroscopy, to consume about 4% of the starting material during the time required for the photolysis.

(10) Products from the photolysis of **3a** in the absence of a nucleophile have not yet been characterized.

(11) The weakly nucleophilic base derived from hexamethyldisilizane (Dow Corning Z-6079 silane) and *n*-butyllithium was used to convert ketone i to its anion, which was then condensed with benzaldehyde to



i

give **3b** (mp 216.5–217.5°) in 52% yield: ir (KBr) 1701, 1625 cm^{-1}; uv (cyclohexane) 271 nm (ϵ 13,000), 298 (16,000), 343 (sh, 660); nmr (CDCl$_3$) τ 2.47–3.00 (m, 14, aryl and vinyl), 4.30 (s, 1, bridgehead adjacent to C=C), 4.97 (s, 1, bridgehead adjacent to C=O). The vinyl singlet was readily shifted to lower field than the aromatic protons by use of Eu(DPM)$_3$,[12] and the slopes of the vinyl and bridgehead proton shifts clearly established that the vinyl proton was cis to the carbonyl group. *The stereoisomer of* **3b** *was not isolated.*

(12) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(13) Infrared spectrum identical with spectrum 20684 in Sadtler.

(14) This is the expected photostationary state ratio under the reaction conditions; *cf.* D. R. Arnold, L. B. Gillis, and E. B. Whipple, *Chem. Commun.*, 918 (1969).

(15) Each ester, previously unknown, was synthesized independently. The known trans acid[16] was esterified with thionyl chloride and methanol to give **6t**: mp 116–116.5° (methanol); nmr (CDCl$_3$) τ 2.45–3.06 (m, 11, aryl), 3.30–3.48 (m, 2, aryl), 5.23 (d, 1, J = 2.4 Hz), 5.80 (d, 1, J = 2.4 Hz), 6.39 (d of d, 1, J = 6.0, 2.4 Hz), 6.42 (s, 3, methoxy), 7.02 (d of d, 1, J = 6.0, 2.4 Hz). Ester **6c** was prepared in two steps. Anthracene and methyl phenylpropynoate gave (4 hr reflux, *o*-dichlorobenzene solvent) in 40% yield a crystalline adduct (mp 153.5–154.5° from methanol) which was quantitatively hydrogenated (Pd/C, ethanol) to **6c** (mp 104–105° from methanol): nmr (CDCl$_3$) τ 2.28–2.48 (m, 1, aryl), 2.58–3.18 (m, 10, aryl), 3.52–3.82 (m, 2, aryl), 5.36 (d, 1, J = 1.8 Hz), 5.75 (d, 1, J = 2.4 Hz), 6.29 (d of d, 1, J = 11.8, 2.4 Hz), 6.72 (d of d, 1, J = 11.8, 1.8 Hz), 7.02 (s, 3, methoxy). The stereochemistry of each ester is clearly established from the nmr spectra; further, each ester was stereospecifically converted to the corresponding methyl cinnamate when injected into a gas chromatograph at 220–230°.

(16) E. de B. Barnett, N. F. Goodway, and E. V. Weekes, *J. Chem. Soc.*, 1102 (1935).

of these reactions to determine their synthetic utility as well as their mechanism.

Acknowledgments. We thank the National Science Foundation and the National Institutes of Health for grants whose flexibility permitted us to discover these reactions, and the Petroleum Research Fund of the American Chemical Society for funds to explore them in detail.

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*Book Reviews**

Archaeological Site Science. By F. H. Goodyear (North Staffordshire Polytechnic). American Elsevier, New York, N. Y. 1971. viii + 282 pp. $10.00.

This book is about the application of scientific technology, principally chemistry, to archaeological materials. It is written at an extremely elementary level and suffers from the fact that it gives only superficial general information, yet provides no leading references for the reader who wants to know more. It may be of some use to amateur archaeologists, but not to chemists.

The Nitrile Oxides. By Ch. Grundmann (Carnegie-Mellon University) and P. Grünanger (Universita di Pavia). Springer Verlag, New York, Heidelberg, Berlin. 1971. viii + 242 pp. $28.30.

The nitrile oxides, $R{-}C{\equiv}N{\rightarrow}O$, contain one of the more obscure functional groups in organic chemistry, although their history is one of the longest, beginning in 1800 with the preparation of mercuric fulminate (the structure of fulminic acid corresponds to formonitrile oxide). They attracted little interest until recent decades, when the growth of the concept of 1,3-dipolar cycloaddition carried them into prominence as sources of unusual heterocyclic systems.

This book covers the subject with critical thoroughness. The bulk of the text deals with preparation and reactions, but there are chapters on history, physical and physiological properties, and applications. A valuable feature is an extensive set of tables recording reported examples of cycloaddition reaction of nitrile oxides. Both authors have long experience with nitrile oxides, and they have augmented the coverage with unpublished information from their own research. The book is heavily documented, and the references extend into 1970 (how far is not stated, but the preface is dated January 1971).

Subcellular Organization and Function in Endocrine Tissues. Edited by H. Heller (University of Bristol) and K. Lederis (University of Calgary). Cambridge University Press, New York, N. Y. 1971. xxiii + 1011 pp. $37.50.

This book is No. 19 of the Memoirs of the Society for Endocrinology, and is the proceedings of a symposium held in April 1970. The full texts of the papers with many illustrations and extensive references are given along with the following discussions verbatim. It will have a strong appeal to chemists and biochemists concerned with hormone biosynthesis.

Biopharmaceutics and Pharmacokinetics. By R. E. Notari (The Ohio State University). Marcel Dekker, Inc., New York, N. Y. 1971. xi + 319 pp. $13.75.

This is a textbook for a course on the biological transport of drugs, for students and researchers in medicinal chemistry and related fields. The subject is presented at such a level that only an elementary knowledge of calculus is needed. There are references, problems, and a short index.

Synthetic Methods of Organic Chemistry. Volume 25. By W. Theilheimer. S. Karger AG, Basel. 1971. xvi + 707 pp. $71.05.

This, the final volume in the fifth series, contains the cumulative index for Volumes 21–25 (nearly 200 pages in itself!). A six-page section on "Trends" at the beginning alerts the reader to some especially significant innovations in synthetic organic chemistry in the past year (1970–1971). The body of the text, a comprehensive compendium of conversions in organic synthesis, is as usual an invaluable aid to the organic chemist. Although the bulk of the references is from 1970, there is a substantial number from 1968 and 1969. The publishers have been concerned about the continually growing size of these annual volumes and have taken steps to keep them of manageable bigness, including the use of thinner paper. A short key to supplementary references for earlier volumes occurring in Volumes 21 to 25 concludes the book.

Physical Methods of Chemistry. Parts IIA, IIB, and V. Edited by A. Weissberger and B. W. Rossiter (Eastman Kodak Co.). Wiley-Interscience, New York, N. Y. 1971. Part IIA: xiv + 723 pp. $32.50. Part IIB: xii + 425 pp. $23.50. Part V: xiv + 603 pp. $27.50.

The appearance of three more volumes in the series *Techniques of Chemistry* (successor to *Techniques of Organic Chemistry*) is a welcome event that will benefit a broad variety of chemists. Part II is titled "Electrochemical Methods" and contains nine chapters: Potentiometry: Oxidation-Reduction Potentials (S. Wawzonek); Potentiometry: pH Measurements and Ion-selective Electrodes (R. P. Buck); Conductometry (T. Shedlovsky and L. Shedlovsky); Determination of Transference Numbers (M. Spiro); Polarography (O. H. Muller); Cyclic Voltammetry, Ac Polarography, and Related Techniques (E. R. Brown and R. F. Large); Voltammetry with Stationary and Rotating Electrodes (S. Piekarski and R. N. Adams); Chronoamperometry, Chronocoulometry, and Chronopotentiometry (R. W. Murray); and Controlled-Potential Electrolysis (L. Meites). Part IIB contains six chapters: Electrochemical Synthesis (J. Chang, R. F. Large, and G. Popp); Organic Reactions in Electrical Discharges (B. D. Blaustein and Y. C. Fu); Photoconductivity in Organic Solids (R. C. Nelson); Organic Electroluminescence (D. M. Hercules); Zone Electrophoresis (S. L. Kirschner); and Electrodialysis (J. L. Eisenmann and F. B. Leitz). These two parts are separately indexed, an arrangement of much convenience to purchasers interested in only one volume.

Part V is titled "Determination of Thermodynamic and Surface Properties," and contains ten chapters: Temperature Measurement (J. M. Sturtevant); Determination of Pressure and Volume (G. W. Thomson and D. R. Douslin); Determination of Melting and Freezing Temperatures (E. L. Skau and J. C. Arthur, Jr.); Determination of Boiling and Condensation Temperatures (J. R. Anderson); Determination of Solubility (W. J. Mader and L. T. Grady); Determination of Osmotic Pressure (J. R. Overton); Calorimetry (J. M. Sturtevant); Differential Thermal Analysis (B. Wunderlich); Determination of Surface and Interfacial Tension (A. E. Alexander and J. B. Hayter); and Determination of Properties of Insoluble Monolayers at Mobile Interfaces (A. E. Alexander and G. E. Hibberd).

These volumes contain a vast amount of information of great practical value to organic, inorganic, analytical, and biological chemists, and maintain the character and quality of the series.

Preparative Inorganic Reactions. Volumes 6 and 7. Edited by W. L. Jolly (University of California). Wiley-Interscience, New York, N. Y. 1971. Volume 6: 254 pp. $17.50. Volume 7: 218 pp. $17.50.

The volumes in this series have a curious format, devoid of preface, foreword, or introduction, so that the reader has no way to tell what the intended purpose and function of the books might be;

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* Unsigned book reviews are by the Book Reviews Editor.