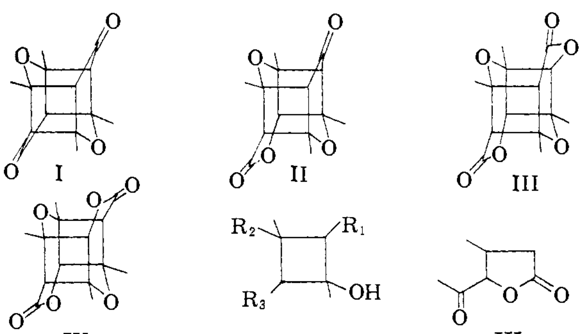
THE PHOTODIMER OF 2,6-DIMETHYL-4-PYRONE

Sir:

Recent interest in the ultraviolet irradiation of $\alpha\beta$-unsaturated carbonyl compounds[1] prompts us to report on an investigation of the dimer obtained by irradiation of 2,6-dimethyl-4-pyrone.[2]

The solid pyrone was irradiated to give the dimer,[2] m.p.[3] 281–284° dec., $\lambda_{max}^{CHCl_3}$ 5.88 μ, $\lambda_{max}^{CH_3CN}$ 233 mμ (ϵ 6,600) *anal.* Found: C, 67.54; H, 6.42), which formed a bis-2,4-dinitrophenylhydrazone, dec. *ca.* 300°, λ_{max}^{KBr} 3.05, 6.20, 6.30 μ, $\lambda_{max}^{dioxane}$ 367 mμ (ϵ 52,300) (*anal.* Found: C, 51.56; H, 4.32; N, 18.80), demonstrating the presence of two carbonyl functions; the infrared data shows that the remaining oxygen atoms are present as ether linkages. The absence of ethylenic bonds in the dimer was indicated by its infrared spectrum and by its failure to react with potassium permanganate solution, to give a color with tetranitromethane, and to absorb hydrogen over palladium-charcoal.[4] The dimer reverted to the pyrone when warmed with dilute acid. It is assigned the cage structure I on the basis of these properties and the following evidence.



VI, $R_1 = R_2 = R_3 = OH$
VII, $R_1 = R_3 = OCOC_6H_5$, $R_2 = OH$
VIII, $R_1 = CO_2H$, $R_2 = H$, $R_3 = OH$

Reaction with perbenzoic acid gave a ketolactone, dec.[3] *ca.* 280°, $\lambda_{max}^{CHCl_3}$ 5.76, 5.87 μ, high intensity end ultraviolet absorption (*anal.* Found: C, 63.82; H, 6.01), which is formulated as II.[5] Longer treatment with perbenzoic acid afforded two isomeric dilactones, III, dec.[3] 280°, $\lambda_{max}^{CHCl_3}$ 5.75 μ, end ultraviolet absorption (*anal.* Found: C, 59.96; H, 5.72), and IV, dec.[3] 340–350°, $\lambda_{max}^{CHCl_3}$ 5.75 μ, end ultraviolet absorption (*anal.* Found: C, 60.07; H, 5.86). Hydrolysis of III gave isodehydroacetic acid (V) and a product, m.p.[3] 118–120°, λ_{max}^{KBr} 2.89, 3.05 μ (*anal.* Found: C, 48.74; H, 8.18; C–CH_3, 17.5), identified as VI since it reacted with 3.9 equivalents of sodium periodate with the production of 3.8 equivalents of acid[6] and gave a dibenzoate (VII), m.p.[3] 151–153°, λ_{max}^{KBr} 2.89, 3.01, 5.81 μ (*anal.* Found: C, 67.23; H, 5.76), which failed to react with sodium periodate. Hydrolysis of IV gave an unsaturated acid which on hydrogenation yielded a saturated acid, m.p. 114–116°, λ_{max}^{KBr} 3.02, 3.20, 5.86 μ, no appreciable ultraviolet absorption (*anal.* Found: C, 52.73; H, 7.43), which reacted with 1.05 equivalents of sodium periodate and is formulated as VIII. This product readily underwent conversion to a ketolactone, $\lambda_{max}^{CHCl_3}$ 5.60, 5.83 μ (positive iodoform test), characterized as its 2,4-dinitrophenylhydrazone, m.p. 177–179°, λ_{max}^{KBr} 3.05, 5.62, 6.19, 6.29 μ, λ_{max}^{EtOH} 351 μ (ϵ 21,900) (*anal.* Found: C, 48.42; H, 4.46; N, 17.09), and assigned structure IX.

This evidence is compatible only with the formulation of the dimer as I[7]; its ultraviolet spectrum is anomalous and the band at 233 mμ presumably has its origin in transannular interactions.[8]

(1) See, for example, D. H. R. Barton and G. Quinkert, *Proc. Chem. Soc.*, 197 (1958); D. H. R. Barton and W. C. Taylor, *J. Chem. Soc.*, 2500 (1958); D. H. R. Barton, P. de Mayo and M. Shafiq, *ibid.*, 140 (1958); E. E. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky and P. Aldrich, THIS JOURNAL, *Soc.*, **80**, 501 (1958); G. Büchi and I. M. Goldman, *ibid.*, **79**, 4741 (1957); G. Büchi and N. Yang, *ibid.*, **79**, 2318 (1957); R. C. Cookson, E. Crundwell and J. Hudec, *Chemistry and Industry*, 1003 (1958); E. Zavarin, *J. Org. Chem.*, **23**, 47 (1958).

(2) E. Paternò, *Gazz. chim. ital.*, **44**, 151 (1914); M. Guia and M. Civera, *ibid.*, **81**, 875 (1951).

(3) Sealed capillary.

(4) Hydrogenation over platinum reduced the carbonyl groups to give a mixture of hydroxyethers, characterized *via* their acetates as $C_{14}H_{18}O_2(OH)_2$ (two isomers) and $C_{14}H_{19}O_2(OH)$, and an ether, $C_{14}H_{20}O_3$.

(5) The elemental analysis of this product confirms the formulation of I as a dimer rather than a trimer, in accord with the earlier molecular weight determinations.[2]

(6) *Cf.* L. Malaprade, *Bull. soc. chim. France*, [5], **1**, 833 (1934); P. W. Clutterbuck and F. Reuter, *J. Chem. Soc.*, 1467 (1935).

(7) The reduction products previously noted[4] may be rationalized in terms of hydrogenation and hydrogenolysis of the carbonyl groups.

(8) *Cf.* M. Simonetta and S. Winstein, THIS JOURNAL, **76**, 18 (1954), Footnote 19.

(9) Public Health Service Research Fellow, 1958.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
PETER YATES
MARGARET JEFRAIM JORGENSON[9]

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A NEW ALDEHYDE SYNTHESIS

Sir:

We have found that the Wittig olefin synthesis[1] can be extended to the synthesis of certain aldehydes by way of their enol ethers:

$$(C_6H_5)_3P + ClCH_2OCH_3 \longrightarrow \underset{\text{I}}{[(C_6H_5)_3PCH_2OCH_3]^+Cl^-}$$

$$\text{I} \xrightarrow{C_6H_5Li} \underset{\text{II}}{(C_6H_5)_3P{=}CHOCH_3}$$

$$-\overset{|}{C}{=}O \xrightarrow{\text{II}} -\overset{|}{C}{=}CHOCH_3 \xrightarrow{H_3O^{\oplus}} -\overset{|}{C}HCHO$$

Triphenyl-(methoxymethyl)-phosphonium chloride (I) (m.p. 191–193°; Calcd for $C_{20}H_{20}ClOP$: Cl, 10.34. Found: Cl, 10.24) from triphenylphosphine and chloromethyl methyl ether, was finely powdered, suspended in anhydrous ether, and stirred under a nitrogen atmosphere while one equivalent of ethereal phenyl lithium was gradually added. The resulting deep red solution, presumably containing methoxymethylenetriphenylphosphorane (II) in two-fold excess, reacted with 5α,-22β,25D-spirostan-3-one[2] (tigogenone), yielding 85% of 3-methoxymethylene-5α,22β,25D-spirostane (III) (m.p. 178–181°, $[\alpha]^{23}D$ −65.8°, $\bar{\nu}_{max.}$ 1683 cm.$^{-1}$. Calcd. for $C_{29}H_{46}O_3$: C, 78.68; H, 10.47. Found: C, 78.90; H, 10.37). Brief treat-

(1) For leading references, see G. Wittig, *Angew. Chemie*, **68**, 505 (1956).

(2) R. W. Marker, T. Tsukamoto and D. L. Turner, THIS JOURNAL, **62**, 2525 (1940).

ment of this enol ether with diethyl ether, previously saturated with 72% perchloric acid, resulted in nearly quantitative hydrolysis to $5\alpha,22\beta,25$D-spirostane-3-carboxaldehyde (IV), as a mixture of epimers (m.p. 160–170°, $[\alpha]^{23}\text{D}$ $-57.4°$, $\bar{\nu}_{max.}$ 2693, 1731 cm.$^{-1}$. Calcd. for $C_{28}H_{44}O_3$: C, 78.45; H, 10.34. Found: C, 78.59; H, 10.45).

This reaction sequence, when applied to the synthesis of the expected aldehydes from cyclohexanone and from acetophenone using a 100% excess of the reagent (II), resulted in incomplete reaction and lower over-all yields. Thus, from cyclohexanone, was obtained cyclohexanecarboxaldehyde 2,4-dinitrophenylhydrazone (40%), m.p. 172–173° alone or admixed with an authentic sample.[3] Acetophenone was converted in similar over-all yield to hydratropaldehyde semicarbazone, m.p. 150–151° (lit.,[4] 153–154°), which was further identified by direct conversion to the 2,4-dinitrophenylhydrazone, m.p. 134–135° (lit.,[4] 135°).

The above synthetic method for the transformation $-\overset{|}{C}{=}O \rightarrow -\overset{|}{C}HCHO$ promises to offer certain advantages over the established glycidic ester sequence[5]: (1) milder reaction conditions; (2) avoidance of certain side reactions[6]; (3) possible utility of the enol ether intermediate as a "protected" aldehyde group or (4) as a starting substance for alternative transformations.

(3) Kindly furnished by Prof. W. S. Johnson.

(4) C. F. H. Allen and J. van Allan, *Organic Syntheses*, **24**, 87 (1944).

(5) Houben-Weil, "Methoden der Organischen Chemie," Vol. VII, part 1, Georg Thieme Verlag, Stuttgart, 1954, p. 326.

(6) W. S. Johnson, J. S. Belew, L. J. Chinn and R. H. Hunt, THIS JOURNAL, **75**, 4995 (1953).

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
EASTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
PHILADELPHIA 18, PENNSYLVANIA
SAMUEL G. LEVINE

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BOOK REVIEWS

Organic Electrode Processes. By MILTON J. ALLEN, Director of the Physical Research Laboratories, Ciba Pharmaceutical Products, Inc., Summit, New Jersey. Reinhold Publishing Corporation, New York, N. Y. 1958. xiv + 174 pp. 16 × 23 cm. Price, $6.50.

The publication of Dr. Allen's monograph fills a long-felt need for an introduction to the techniques and applications of electrochemical methods to organic chemical reactions. Earlier works on the subject are out of date so that the beginner in the field has no helpful place to turn for advice. Perhaps the lack of such an aid accounts for the fact that organic chemists have been notoriously slow to use electrochemical methods, even when they were the methods of choice for the preparations at hand.

An analysis of the references cited in this monograph confirms the impression which one gains by a non-systematic approach to the literature of the field. Prior to 1890, organic chemists explored electrochemistry and came up with one generally used preparative method, the Kolbe synthesis. The period between 1890 and 1910 was the "golden age" of electro-organic chemistry with widespread and systematic exploration of the possibilities of the method. Thereafter, interest slowly waned and, after a brief revival in the 1930's, reached its lowest ebb in the 1940's. Now it is on the way up again, due to the stimulus of new and more powerful techniques.

One of the main reasons for the waning of interest in electrochemistry on the part of organic chemists, in the opinion of the present reviewer, is the fact that older procedures failed to give selectivity between various possible reaction courses, with the result that yields frequently were unsatisfactory. In his classical paper in 1898, Fritz Haber pointed out the reasons for this and the solutions in the form of controlled potentials, along with controlled acidities and temperatures. However, because of the clumsiness of Haber's apparatus for securing potential control, his methods were not widely adopted.

With the coming of modern instruments for automatic control and recording, the difficulties inherent in the Haber system disappeared and organic electrochemistry became a flexible and powerful tool for the solution to problems in synthetic organic chemistry. Allen's monograph collects and collates the information necessary to success in the application of this tool.

The inadequacies of the field as well as its strong points are revealed in the present work. Our knowledge is greatest in the field of reductions, yet even here few mechanisms have been worked through to satisfactory conclusions. This means that the systematic organization which becomes possible only with an understanding of mechanisms remains mostly for the future.

The situation with respect to oxidations is even less satisfactory. Here the two most satisfactory preparative methods are anodic halogenation and the Kolbe synthesis. The tremendous variety of possible oxidations usually has not been sorted out to ensure control in the desired direction. Anodic processes still need their Fritz Haber!

Thus Allen's monograph represents not only an excellent guide to the beginner who must master the techniques but a clear challenge to the expert in mechanisms to exploit his methods in the elucidation and organization of a field that will amply repay directed research efforts.

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE 18, MARYLAND
ALSOPH H. CORWIN

Source Book on Atomic Energy. Second Edition. By SAMUEL GLASSTONE, Consultant to the United States Atomic Energy Commission. D. Van Nostrand Co., Inc., 120 Alexander Street, Princeton, N.J. 1958. 641 pp. 15 × 23.5 cm. Price, $4.40.

This second edition of Glasstone's "Sourcebook of Atomic Energy" enlarges and brings up to date the excellent first edition, which since its appearance in 1950 has sold 50,000 copies. It would require a shelf of texts to exhaust the subject matter of the topics treated in the book. These range from the foundations of atomic theory to health physics, with sections on natural radioactivity, properties and measurement of radiations, isotopes, the fundamental particles, nuclear forces and nuclear structure, fission, nuclear reactions, the new elements, cosmic rays and strange particles, and other subjects. The author has succeeded in giving an introduction to each of these which makes an integrated whole bound together with the threads of basic principles.

The book is not a popularization of "atomic energy" for the lay reader but rather a scientifically sound introduction to the areas covered. It is written with Glasstone's usual ability for lucid presentation of complex matters. The reader new to these fields will get a maximum yield of information and understanding per I.Q.-hour invested.

In reading this book one senses warmly the philosophical, dramatic and human aspects of the discoveries through