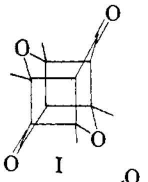
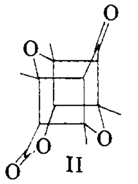
THE PHOTODIMER OF 2,6-DIMETHYL-4-PYRONE

Sir:

Recent interest in the ultraviolet irradiation of αβ-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.


I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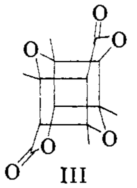
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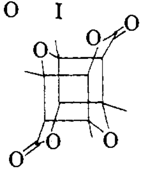
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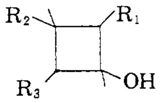

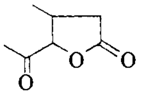
IX

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]

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[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, $C_{14}H_{20}O_2$.

[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.

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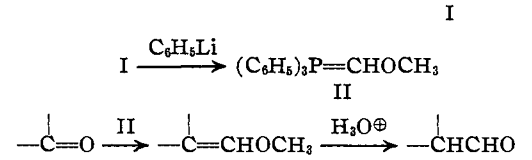
RECEIVED OCTOBER 2, 1958

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-

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[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).