group. Thus, heating a mixture of 3.2 g. of pyridine (0.4 moles), 100 ml. of cyclohexane, 2 g. of Raney nickel, and 0.4 moles of carbon monoxide at 225° and 1.7 atm. for 14 hr. led to a 35–40% conversion to α-picoline. This observation suggests that the α-methylation of pyridines as reported in this communication may be related to the hydroformylation reaction[5] as well as to the catalytic formation of biaryls.[1] Studies which are presently underway to elaborate further the scope and mechanism of this reaction will also investigate this possibility.

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(5) C. W. Bird, Chem. Rev., 62, 283 (1962).

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Hydroformylation of Glycals

Sir:

In this communication we wish to report the application of the oxo reaction[1] in the first direct conversion of glycals[2] into anhydrodeoxyaldoses. In earlier work[3,4] it was shown that glycals react with a mixture of carbon monoxide and hydrogen to give primarily a mixture of epimeric anhydrodeoxyalditols. We have now found that careful control of the conditions of this reaction affords mixtures of epimeric anhydroaldoses as well as the corresponding epimeric anhydroalditols. Presumably, under the normal conditions for the oxo reaction,[5] the anhydroaldoses are reduced to anhydroalditols. Under the modified conditions (as described below), 3,4-di-O-acetyl-D-xylal, for example, reacts with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl to yield 4,5-di-O-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*lyxo*-hexose (I) and 4,5-di-O-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*xylo*-hexose (II), in addition to the epimeric anhydrodeoxyhexitols III and IV.
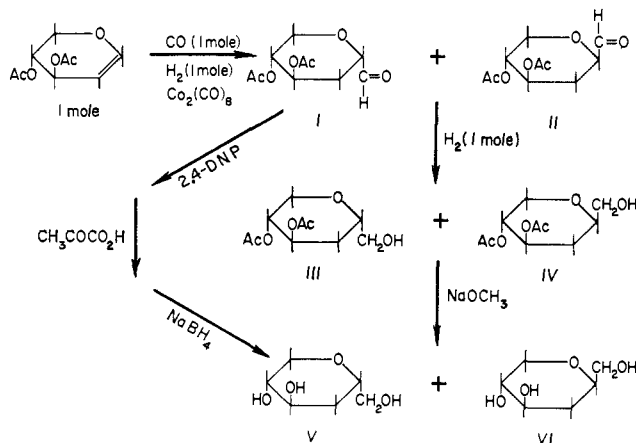
The general procedure used at the present time is as follows. A solution of 3,4-di-O-acetyl-D-xylal (12 g.), dicobalt octacarbonyl (3.4 g.), and anhydrous benzene (50 ml.) is allowed to react in a 300 ml. Aminco rocking autoclave with a mixture of 34 atm. of carbon monoxide and about 160 atm. of hydrogen at a temperature of 115°. It is important that the reaction be stopped when 2 moles of gas per mole of substrate is consumed as the aldoses are quite rapidly reduced to the alditols. Work-up of the reaction mixture as described previously[3] afforded 13 g. of sirupy product. The presence of approximately 20% of aldehydoaldoses was demonstrated by the formation of a mixture of 2,4-dinitrophenylhydrazones. A hot ethanolic saturated solution of 2,4-dinitrophenylhydrazine was added portionwise to a boiling solution of the oxo product (1.6 g) in 50 ml. of ethanol containing 4 drops of acetic acid until the color of the solution no longer changed from orange to yellow; addition of water to turbidity then resulted in the precipitation of a bright yellow solid (0.4 g.) which was removed by filtration. This solid was then triturated with warm ethanol and again removed by filtration; recrystallization from chloroform–light petroleum ether gave fine yellow needles, m.p. 225–226° dec., $[\alpha]^{22}$D −60°. This compound was identified from its n.m.r. spectrum and by conversion to authentic[3] 1,5-anhydro-4-deoxy-D-*arabino*-hexitol (V) as the 2,4-dinitrophenylhydrazone of 4,5-di-O-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*lyxo*-hexose. The acetylated anhydrodeoxyaldose (I) was regenerated by reaction of the phenylhydrazone derivative with pyruvic acid,[6] and converted by the action of sodium borohydride to a compound which was identical with an authentic sample of 1,5-anhydro-4-deoxy-D-*arabino*-hexitol.[3]

Evaporation of the filtrate obtained from the trituration of the 2,4-dinitrophenylhydrazone mixture gave a residue which was fractionated by thin layer chromatography on silica gel using chloroform as developer to afford the aforementioned 2,4-dinitrophenylhydrazone derivative of I and also the 2,4-dinitrophenylhydrazone of 4,5-di-O-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*xylo*-hexose (II), m.p. 132°, $[\alpha]^{20}$D −16°. Compound II was converted into VI following the same procedures as described above to convert I into V.

Similarly, hydroformylation of 3,4,6-tri-O-acetyl-D-glucal at 125° afforded a mixture of anhydrodeoxyheptitols (35%) and heptoses (63%). Column adsorption chromatography of this nonde-O-acetylated mixture on Florisil[7] using benzene–methanol (97:3 v./v.) as developer yielded four fractions. The fastest moving fraction, which was recrystallized from ether–light petroleum ether, m.p. 110–112°, $[\alpha]^{20}$D +96°, was proven to be 4,5,7-tri-O-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*manno*-heptose (40% yield) by conversion to authentic 2,6-anhydro-3-deoxy-D-*manno*-heptitol. The absolute stereochemistry of the latter substance was established by correlation with authentic 2,6-anhydro-3-deoxy-D-*gluco*-heptitol.[8]

Hydroformylation of 3,4-di-O-acetyl-D-arabinal yielded 33% of reducing sugars as determined by the

(1) I. Wender, H. W. Sternberg, and M. Orchin, Catalysis, 5, 73 (1957).

(2) B. Helferich, Advan. Carbohydrate Chem., 7, 209 (1952).

(3) A. Rosenthal and D. Abson, Can. J. Chem., 42, 1811 (1964).

(4) A. Rosenthal and H. J. Koch, ibid., 42, 2025 (1964).

(5) H. Adkins and G. Krsek, J. Am. Chem. Soc., 71, 3051 (1949).

(6) V. R. Mattox and E. C. Kendall, ibid., 70, 882 (1948).

(7) Product of Floridin Company, Tallahassee, Fla.

(8) J. Trotter, A. Camerman, A. Rosenthal, and H. J. Koch, Can. J. Chem., 42, 2630 (1964).

method of Somogyi[9]; the nature of this product is under investigation and will be the subject of a future communication.

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(9) M. Somogyi, J. Biol. Chem., **160**, 69 (1945).

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The Use of 2,3-Diphenylindenone Oxide as a Triplet-State Indicator

Sir:

Triplet excited states of many substances have been studied by phosphorescence,[1a,b] triplet–triplet absorption,[1c,d] and singlet-triplet absorption induced by oxygen or heavy atoms.[1e,f] However, some compounds do not lend themselves to these measurements, presumably because of rapid rearrangement or intersystem crossing of the initially formed "spectroscopic" triplet. In our studies of the photochemistry of 2,3-diphenylindenone oxide[2] (I) we have found that this compound can serve as an indicator for certain short-lived triplets when employed in simple color tests performed without the exclusion of oxygen. A description of the method as applied to a study of *trans*-stilbene follows.

Benzene solutions of colorless I undergo reversible photochemical rearrangement to the red pyrylium oxide II. The forward reaction (I → II) is photosensitized by sensitizers of triplet energy $E_T > 68$ kcal.[2] In the presence of oxygen using acetophenone ($E_T = 73.9$ kcal.)[3] or benzophenone ($E_T = 68.7$ kcal.)[3] as sensitizers, irradiation (365 mμ) produces a steady-state concentration of II controlled by photosensitized interconversion of II and I and simultaneous thermal and
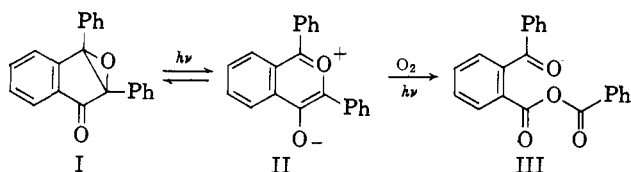
photosensitized oxidation of II to give the anhydride III.[4] The use of sensitizers of $E_T \leq 68$ kcal. in sufficient quantity to absorb nearly all of the light produces complete bleaching since reaction I → II is no longer sensitized. Lesser amounts of sensitizer produce low (weakly colored) steady-state concentrations of II by competing direct photochemical conversion of I to II. Under these latter conditions *addition of trans-stilbene* (10^{-3} to 10^{-1} M) *to the solution produced, with some sensitizers, an increase in color on irradiation*

(1) (a) A. Jablonski, Z. Physik., **94**, 38 (1935); (b) G. N. Lewis and M. Kasha, J. Am. Chem. Soc., **66**, 2100 (1944); (c) G. N. Lewis, D. Lipkin, and T. T. Magel, ibid., **63**, 3005 (1941); (d) G. Porter and M. W. Windsor, J. Chem. Phys., **21**, 2088 (1953); (e) M. Kasha, ibid., **20**, 71 (1952); (f) D. F. Evans, J. Chem. Soc., 1351 (1957).

(2) E. F. Ullman and Wm. A. Henderson, Jr., J. Am. Chem. Soc., **86**, 5050 (1964).

(3) G. S. Hammond and J. Saltiel, ibid., **84**, 4983 (1962).

(4) Wm. A. Henderson, Jr., and E. F. Ullman, unpublished observation.

relative to a simultaneously irradiated portion of the solution with no trans-stilbene added. The effect was found to be directly related to the triplet energy of the sensitizer used. Thus stilbene produced shifts in the photostationary state only when using sensitizers with $E_T \geq 44$ kcal. (Table I).
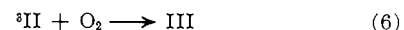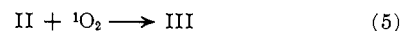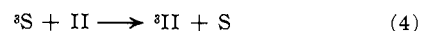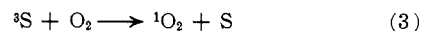
TABLE I

QUENCHING BY *trans*-STILBENE[a]

Sensitizer	E_T, kcal.	Increase in concn. of II
1,2,3,4-Dibenzanthracene	51[1f]	+
Pyrene	48[1f]	+
1,2-Benzanthracene	47[b]	+
Acridine	45[1f]	+
Phenazine	44[1b]	+
Anthracene	42[1d]	−
9,10-Dichloroanthracene	40[c]	−
Perylene	36(?)[d]	−
Naphthacene	29[c]	−

[a] Experiments carried out using sufficient sensitizer in benzene solutions of I to produce only weak color (absorptivity at λ_{max} 544 mμ of ~0.05) with 365 mμ light. Several stilbene concentrations (up to ~10^{-1} M) were used with each sensitizer to detect difficultly observable color changes with low energy sensitizers. [b] D. S. McClure, J. Chem. Phys., **17**, 905 (1949). [c] S. P. McGlynn, T. Azumi, and M. Kasha, ibid., **40**, 507 (1964). [d] G. G. Hall, Proc. Roy. Soc. (London), **A213**, 113 (1952).

The increase in the steady-state concentration of II on addition of *trans*-stilbene must arise by inhibition of a bleaching process. As *trans*-stilbene had little effect on unsensitized photochemical bleaching of II and produced no increase in the stability of II in the dark, it must be acting as an inhibitor of photosensitized oxidation of II and/or photosensitized isomerization of II to I. Since photosensitized bleaching of II was 10–100 times more efficient with oxygen present than in degassed solution, the observed shifts in the steady-state concentrations are due to inhibition of the oxidation process.

The following reactions may be involved in photosensitized oxidation of II.

$$S \xrightarrow{h\nu} {}^3S \qquad (1)$$

$$^3S \longrightarrow S \qquad (2)$$

$$^3S + O_2 \longrightarrow {}^1O_2 + S \qquad (3)$$

$$^3S + II \longrightarrow {}^3II + S \qquad (4)$$

$$II + {}^1O_2 \longrightarrow III \qquad (5)$$

$$^3II + O_2 \longrightarrow III \qquad (6)$$

Inhibition of photosensitized oxidation by *trans*-stilbene might occur either by *trapping* of singlet oxygen ($^1O_2$)[5] with *trans*-stilbene or by *quenching* of sensitizer triplet (^3S), of triplet II (^3II), or of $^1O_2$. However, of these possibilities only quenching of ^3S can explain the variation in inhibition of reaction II → III with sensitizer energy.[6]

The formation of *trans*-stilbene triplets by energy transfer from sensitizer triplets was demonstrated by the weak bleaching effect of *trans*-stilbene on solutions containing sufficient benzophenone to absorb most of the light. Since benzophenone sensitizes both reactions I → II and II → III, quenching of sensitizer

(5) We need not differentiate here between $^1O_2$ and a possible oxygen-sensitizer complex; cf. C. S. Foote and S. Wexler, J. Am. Chem. Soc., **86**, 3879, 3880 (1964).

(6) The significance of the observed fall-off in quenching efficiency at 44 kcal. (Table I) will be discussed in the full paper.