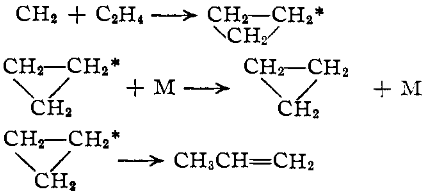

which, aside from the activation step, is identical with that of the thermal isomerization of cyclopropane. The lifetime of the "hot" cyclopropane molecules formed in these experiments is found to be *ca.* one-eightieth of that of those formed thermally. The greater reactivity of these energy rich cyclopropane molecules as compared with the thermally "hot" molecules is to be expected from the theories of both Kassel[9] and Slater.[10]

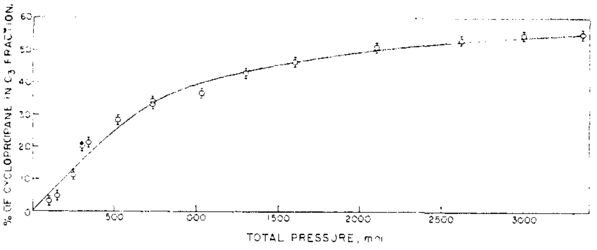

Fig. 1.

The yield of cyclopropane at high pressures tends asymptotically to a value close to 0.6. This suggests that, as in other cases investigated,[2,3,4] two competing reactions are taking place: the attack on the double bond with formation of cyclopropane in one elementary act, and the attack of the carbon–hydrogen bond. The latter leads directly to the formation of propylene.

Further experiments on the formation of three-membered rings in the gas phase and on the effects of inert gases are in progress.

It is a pleasure to thank Professor G. B. Kistiakowsky for suggesting these experiments and for many helpful discussions.

[9] L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," (The Chemical Catalog Company) Reinhold Publ. Corp., New York, N. Y., 1932.

[10] N. B. Slater, *Proc. Roy. Soc.* (*London*), **194A**, 112 (1948).

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RECEIVED JANUARY 23, 1957

INFLUENCE OF DISSOLVED AIR ON OPTICAL DENSITY MEASUREMENTS OF WATER SOLUTIONS

Sir:

In the course of studies employing measurements of optical densities, *D*, of water solutions, we have found significant variations in *D* in the region of 2000 Å. which are due to light being absorbed by variable amounts of atmospheric oxygen dissolved in the solutions. This effect is large enough to be important in the calculation of the absorbances of the other components of the solutions, but it is entirely separate from spectral changes which may occur as the result of oxidation of solute species by atmospheric oxygen. We trust that this means of reporting the effect will serve to bring it most quickly to the attention of others engaged in work of this kind.

The optical density of a 10-cm. depth of conductivity water which has been saturated with air is higher than that of the same water through which helium, nitrogen, or carbon dioxide has been bubbled by 0.09 in *D* at 2000 Å., 0.03 at 2100 Å., 0.01 at 2200 Å. and by less at longer wave lengths of ultraviolet and visible light up to at least 8000 Å. The very small oxygen content of the commercial gases employed was found to increase in the order we have cited them, but was low enough in all cases to give the same final values of *D* for the solution.

Saturation of conductivity water at 25° with oxygen at 1 atm. was found to increase *D* above the value for air saturated water by 0.47 in *D* at 2000 Å. for 10 cm. light paths, and by lesser amounts at longer wave lengths; at 2500 Å. the increase amounts to about 0.01. The effects are reversible. Typical results are presented in Fig. 1.

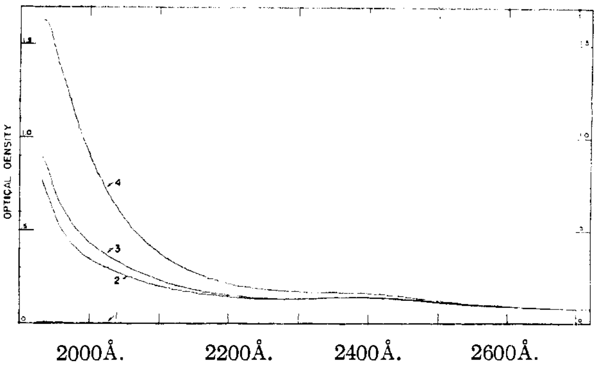

Fig. 1.—Optical densities at 25° referred to air: (1) of air and (2), (3), and (4) of a fused quartz absorption cell of 10 cm. between windows which has been filled with conductivity water freed from air and oxygen, saturated with air at 1 atm., and saturated with oxygen at 1 atm., respectively.

Similar effects have been reported for solutions of oxygen in organic solvents[1,2] such as hexane.

The absorption of light by an equivalent amount of oxygen gas at 2000 Å. and longer wave lengths is presumably negligible.[3]

The extent of the effect of dissolved oxygen on *D* depends upon the following variables: wave length of the light, composition and temperature of the solution, and the partial pressure of the oxygen gas over the solution.

In the case of alkaline solutions, the values of *D* are also affected up to even longer wave lengths by the carbon dioxide in the air, but the effect of the carbon dioxide is not reversible because of the formation of significant amounts of carbonate and bicarbonate as long as the solution remains alkaline.

We have found that objectionable gases such as oxygen may be removed from liquids most effectively with commercial helium, but the commercial grade of prepurified nitrogen is also satisfactory in many cases.

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[1] D. F. Evans (a) *J. Chem. Soc.*, 343 (1953); (b) *J. Chem. Phys.*, **23**, 1424 (1955).

[2] A. U. Munck and J. F. Scott, *Nature*, **177**, 587 (1956).

[3] G. Herzberg, *Can. J. Phys.*, **30**, 185 (1952).

The strong interaction between dissolved oxygen and water revealed by our results and the even stronger interaction between dissolved oxygen and saturated hydrocarbons such as hexane revealed by the results of others[1,2] suggest bonding between the molecular oxygen and the hydrogen of the solvent. This seems reasonable in view of the fact that the oxygen molecule is a diradical and the hydrogen atom is well known to form bonds simultaneously with two other atoms such as with the oxygen atoms in the dimer of acetic acid, with the boron atoms in B_2H_6 and with the oxygen atoms on adjacent water molecules.

In the case of oxygen dissolved in water possible structures formed when the oxygen molecule attached itself to two hydrogen atoms would be a bridge between two water molecules and alternatively a five-membered ring involving one molecule of water. In the case of oxygen dissolved in saturated hydrocarbons such as hexane, a plausible structure would be the six-membered ring in which the oxygen molecule was attached to the hydrogens on adjacent carbon atoms as well as a bridge between the hydrogen atoms on adjacent solvent molecules.

The new hydrogen bonds suggested here differ from those bridge hydrogen bonds previously recognized in that three rather than two or four electrons participate with the proton in their midst in forming the bridge between the other two atoms.

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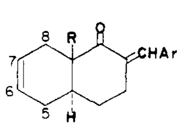
RECEIVED FEBRUARY 4, 1957

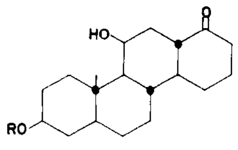
STEREOCHEMICAL CONTROL OF ANGULAR METHYLATION. A STEREOSELECTIVE TOTAL SYNTHESIS OF A 9,11-DEHYDROSTEROID

Sir:

Certain previous total syntheses of steroids, namely, estrone,[1] epiandrosterone,[2] $3\beta,11\beta$-dihydroxyandrostane-17-one,[3] and testosterone,[4] have embodied a common sequence for the elaboration of ring D involving, as key intermediates, the corresponding 18-nor-D-homo compounds (*cf.* formula III) which, after protective condensation with an aldehyde, were methylated, then oxidized to the dibasic acids and recycled to yield the five-membered ring D compounds (*cf.* formulas III → IV → V → VI). While the yields for this angular methylation-ring contraction sequence were generally good, the stereochemical course of the methylation step was always unfavorable giving a preponderance of the unnatural isomer in which the rings were *cis*-locked. This behavior is typified by the results with 2-benzylidene-1-decalone which, on methylation, afforded the *cis* and *trans* 9-methyl homologs in 68 and 23% yields, respectively.[5]



I



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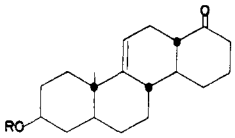

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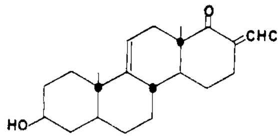

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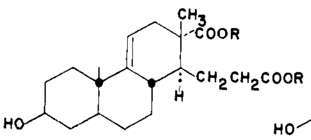

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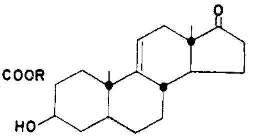

VI

For some time we have been searching for factors that influence the stereochemical course of this reaction, and wish now to disclose a method of control which leads predominantly to the desired *trans* configuration.

Models indicate that replacement of the tetrahedral carbon at certain positions, *e.g.*, C_7, of the α-decalone system by a trigonal carbon atom results in elimination of one of the axial hydrogen atoms that hinders *trans* approach to the anion by an electrophilic agent. To test the hypothesis that the stereochemical course of the methylation would thus be favorably influenced, we have examined the α-decalone system with a double bond at 6,7 (formula I), noting that the introduction of the additional trigonal carbon at C_6 does not appear to affect the hindrance on either side of the anion. 2-Furfurylidene-Δ^6-octalone-1 (I, R = H, Ar = C_4H_3O), m.p. 136–137°, C, 78.6; H, 7.02, prepared from the corresponding octalone,[6] was methylated with potassium *t*-butoxide and methyl iodide.[5] The only pure product that was isolated (in 56% yield) was indeed the desired *trans* compound I (R = CH_3, Ar = C_4H_3O), m.p. 75.5–76.5°, C, 79.2; H, 7.53. The configuration was proved by alkaline peroxide oxidation[4] followed by hydrogenation of the resulting unsaturated acid to give the known *trans*-2-carboxy-2-methylcyclohexyl-β-propionic acid, identified by comparison with authentic material.[7]

The principle was then applied to a synthesis of *dl*-3β-hydroxy-9,11-dehydroandrostane-17-one (VI). The stereoselective production of the 3β, 11β-dihydroxy-18-nor-D-homo ketone II (R = H) already has been described.[3] Treatment with succinic anhydride afforded the half-succinate which, as the methyl ester II (R = $COCH_2CH_2COOCH_3$), m.p. 168.5–169.5° C, 68.5; H, 8.59, was dehydrated with phosphorus oxychloride and pyridine to give the 9,11-dehydro compound III (R = $COCH_2CH_2COOCH_3$), m.p. 126.5–127.5°, C, 71.6; H, 8.48. Saponification followed by condensation with furfural yielded the furfurylidene ketone m.p. 190–191.5, C, 78.8; H, 8.21, and this, on

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[1] W. S. Johnson, D. K. Banerjee, W. P. Schneider, C. D. Gutsche, W. E. Shelberg and L. J. Chinn, THIS JOURNAL, **74**, 2832 (1952).

[2] W. S. Johnson, B. Bannister and R. Pappo, *ibid.*, **78**, 6331 (1956).

[3] W. S. Johnson, R. Pappo and W. F. Johns, *ibid.*, **78**, 6339 (1956).

[4] W. S. Johnson, B. Bannister, R. Pappo and J. E. Pike, *ibid.*, **78**, 6354 (1956).

[5] W. S. Johnson, *ibid.*, **65**, 1317 (1943).

[6] P. D. Bartlett and G. F. Woods, *ibid.*, **62**, 2933 (1940); *cf.* A. M. Gaddis and L. W. Butz, *ibid.*, **69**, 117 (1947).

[7] W. S. Johnson, *ibid.*, **66**, 215 (1944).