position would not be accommodated easily, and that is actually what is observed.

The Role of Water of Hydration of the Annular Nitrogen Group.—In the work reported here and previously, it is apparent that the ring nitrogen acts as though it were a large substituent on an aromatic ring. This effect is attributed to the presence of water of hydration which modifies the steric configuration of the hapten and affects its combination with antibodies.

That pyridine is hydrated in aqueous solution is apparent from the fact that it is miscible with water, whereas benzene is only slightly soluble. Moreover, the heat of hydration of pyridine has been measured by Briegleb[15] and has been found to be 12 kcal. per mole.

Carsten and Eisen[16] reported the heat of reaction of a hapten (ϵ-DNP-lysine) with its specific antibody to be about 1 kcal. Since the heat of hydration of pyridine is much greater than this value, further evidence points to the fact that combination of the pyridine and quinoline carboxylates with antibody, in the systems studied here, takes place with the water of hydration still attached to the nitrogen atom. Otherwise, the combination would be very weak if energy were required to break the water away first.

For the same reasons, biological reactions in general involving similar annular nitrogen compounds may specifically require the hydrated form for combination to take place.

[15] G. Briegleb, *Z. Elektrochem.*, **53**, 350 (1949).

[16] M. Carsten and H. Eisen, THIS JOURNAL, **77**, 1273 (1955).

BUFFALO 3, NEW YORK

COMMUNICATIONS TO THE EDITOR

ORGANIC FREE RADICALS IN THE SOLID STATE[1,2]

Sir:

Solid solutions of triphenylmethyl in fluorene, phenanthrene, and triphenylamine, respectively, of unknown composition have been prepared. The solid solutions were the characteristic corn color of the solutions in liquid benzene, in all three cases. They were prepared by dissolving chosen amounts of hexaphenylethane and the other component in benzene and evaporating the benzene at room temperature in a pure nitrogen atmosphere in a dry box.

It is to be assumed that all the hexaphenylethane that dissolved in the second component was dissociated into free radicals since a planar structure would be required in order that the crystal lattice of the planar fluorene or phenanthrene could accommodate it. Triphenylamine is also sufficiently planar that the hexaphenylethane could hardly dissolve in it as such. Thus the susceptibility gave a measure of the concentration in the solid solution.

Susceptibilities were measured with a Gouy balance at room temperature and the amount of free radical in the sample tube calculated by the method of Roy and Marvel.[3] The mole fractions of triphenylmethyl in solid solution in fluorene, triphenylamine, and phenanthrene were found to be approximately 0.24, 0.22, and 0.17, respectively, assuming complete dissociation in the solid solution. If all the hexaphenylethane were in solid solution, the dissociation in each case would be 17, 14, and 10%, respectively.

In all cases the resultant diamagnetic susceptibility was somewhat less than half that calculated if there were no dissociation to free radicals. If all samples obeyed the Curie–Weiss law, the same amount of free radical would correspond to a considerable paramagnetism at helium temperatures.

The susceptibility was therefore studied by an inductance method down to 1.6°K.; the method was sufficiently sensitive to detect one per cent. of the hexaphenylethane present if it were in the form of free radical active as a perfect paramagnetic substance (due to spin only). No paramagnetism was detected.

However, it was found that under similar conditions hexabiphenylethane, which is completely dissociated into free radicals in the solid at room temperature also gave no paramagnetism. Hexabiphenylethane roughly follows the Curie–Weiss law down to liquid nitrogen temperatures.[4] We found that the susceptibility measured by the inductance method was also essentially zero at 20°K. The "paramagnetism" measured in the Gouy balance in this laboratory at room temperature corresponded to complete dissociation. The solid solutions are being investigated spectroscopically and the transition below 70°K. responsible for loss of paramagnetism of tribiphenylmethyl is being investigated.

We wish to thank Dr. C. Haas for the opportunity to use his Gouy balance.

[1] Publication No. 97 of the Cryogenic Laboratory of the College of Chemistry and Physics, The Pennsylvania State University, University Park, State College, Pennsylvania.

[2] Supported by Contract No. NSF-G1611 with the National Science Foundation.

[3] M. L. Roy and C. S. Marvel, *J. Am. Chem. Soc.*, **69**, 2622 (1937).

[4] E. Müller, I. Müller and W. Bunge, *Ann.*, **520**, 235 (1935).

[5] On leave from the University of Osaka, Japan.

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RECEIVED JANUARY 25, 1957

THE BIOSYNTHETIC PRECURSOR OF THE EXTRA CARBON ATOM IN THE SIDE-CHAIN OF STEROIDS[1]

Sir:

The concept of the biosynthesis of steroids from acetate through squalene accounts for the source of all the carbon atoms of C_{27} and C_{30} compounds

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