

## NOTES

### A Method for Separating Para-hydrogen from Oxygen and Carbon Monoxide

By E. BERGMANN, L. FARKAS AND L. SANDLER

Para-hydrogen has often been used as a research tool for elucidating reaction mechanisms. In order to analyze the para-ortho ratio in the hydrogen, the hydrogen has to be separated from all gases taking part in, or formed by, the reaction, so that the ortho-para ratio is not changed by this process. In most cases satisfactory separation can be achieved by the use of liquid or solid air which freeze out most of the common gases. In two important cases, however, *viz.*, when oxygen or carbon monoxide is present, liquid hydrogen had to be used for the separation process. Since liquid hydrogen is not always available and its preparation is very expensive, we have tried to substitute a chemical method of separation for the physical one. For this purpose, solutions had to be found which absorb the above gases quantitatively without causing any appreciable para-ortho conversion during the absorption process.

**Absorption of Oxygen.**—To the quantitative absorption of oxygen a method was adapted which has been devised for the purification of nitrogen by Schlenk,<sup>1</sup> and which is based on the fast and complete reaction of triphenylmethylsodium solution<sup>2</sup> with gaseous oxygen. As diethyl ether as used by Schlenk and Marcus in their investigations, has a very high vapor pressure and dissolves the grease of the stopcocks, it was replaced by dibutyl ether, having a vapor pressure of a few mm. only at 20°. The solution prepared and filtered in the usual way was evaporated in a stream of pure nitrogen and dibutyl ether added gradually during this process.

The solution actually used was saturated with triphenylmethylsodium and contained an excess of this substance in solid form so as to render possible the uptake of a large amount of oxygen. The solution was kept in a shaking vessel, attached to the high vacuum apparatus by a glass spiral and remained in use for many months without renewal. The diffusion of the gas into the solution can be accelerated by cooling the solution and is completed within less than one minute.

The following two experiments characterize the above solution:

A lock system of 5 cc. capacity was connected through a very narrow capillary tube to a washing bottle containing about 20 cc. of the solution. It was found that when 130 cubic mm. (at S. T. P.) of oxygen passed through the

(1) Schlenk, Houben-Weyl's "Methoden der organischen Chemie," 1924, Vol. 4, pp. 959, 974.

(2) Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

capillary tube no measurable amount of oxygen (less than 0.005%) could be detected by a McLeod gage on the other side of the washing bottle.

In order to test whether any appreciable ortho-para conversion takes place in presence of the triphenylmethyl sodium solution, para-hydrogen was introduced into the shaking vessel (70 cc. capacity) containing the sodium compound (30 cc.). The half-life-time of the conversion under our conditions was two and one-half hours; thus, the conversion occurring during the short period of oxygen absorption is negligible. The conversion observed is most probably due to the presence of small quantities of free (paramagnetic) triphenylmethyl.

**Absorption of Carbon Monoxide.**—For the absorption of carbon monoxide the common cuprous oxide-ammonia solution was used. In the same arrangement as used in the case of oxygen, 500 cubic mm. (S. T. P.) of carbon monoxide (at an actual pressure of 70 mm.) were made to pass the capillary tube and again no trace (less than 0.005%) of the gas could be detected on the other side of the washing bottle.

The following experimental arrangement was used in an actual experiment, carried out at low pressure ( $10^{-2}$  mm.).<sup>3</sup> The gas mixture was collected in a bulb of 700 cc. to which a smaller vessel was attached, containing 40 cc. of the absorbing solution cooled, in order to accelerate the diffusion of the gas, and separated from the larger bulb by a stopcock. The gas mixture (40 cubic mm. at S. T. P.) was collected in the large bulb, the stopcock opened and the absorption vessel shaken for a few hours. A control experiment, carried out with a mixture of 20 cubic mm. of normal hydrogen and 200 cubic mm. of carbon monoxide showed that no carbon monoxide could be detected in a micro-conductivity cell after the process of absorption, indicating that the amount of carbon monoxide was reduced to at least 0.1%.

Under the conditions used, the half-life-time of the ortho-para conversion was found to be one hundred hours, although no special care had been taken to exclude from the cuprous oxide-ammonia solution divalent (paramagnetic) copper compounds which certainly are responsible for the greater part of the conversion observed. In any case the conversion during the period of absorption again is negligible.

It is obvious that the methods described may be useful in experiments with other hydrogen modifications, too, such as ortho-deuterium or mixtures of light and heavy hydrogen and hydrogen deuteride.

(3) Farkas, Hirschberg and Sandler, *This Journal*, **61**, 3393 (1939).

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### Solvolytic Reactions of Organic Halides

By MICHAEL P. BALFE AND JOSEPH KENYON

While we cannot enter into the discussion of the kinetics of these reactions, which have been de-

scribed as unimolecular,<sup>1</sup> as bimolecular,<sup>2,3</sup> as either bimolecular or termolecular,<sup>4</sup> and as poly-molecular,<sup>5,6</sup> the diversity of conclusions suggests, as indicated by Bartlett,<sup>4</sup> that the course of these reactions is not sufficiently simple to justify the application of the kinetic method.

Our present purpose is to comment on the mode of formulation of the solvated cation which is assumed as an intermediate in these reactions by Winstein.<sup>6</sup> In the hydrolysis of halides, Winstein's formulation  $\text{H}_2\text{O}^+ - \text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$  leads to no difficulties, but is not generally applicable. The rearrangement of phenylmethylcarbonyl *p*-toluenesulfonate to *p*-tolyl- $\alpha$ -phenylethylsulfone,<sup>7</sup> a reaction which involves ionization in the same sense as the solvolytic reactions mentioned above, does not occur in solution in acetonitrile, but proceeds readily in solution in formic acid. The suggestion which seems best to explain this difference in behavior is that there is a difference between the solvating properties of the two solvents.

If solvation of the cation be assumed its formulation as  $\begin{array}{c} \text{H} \\ \diagup \\ \text{HO} \end{array} \text{C}=\text{O}^+ - \text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$  would, in our opinion, imply that phenylmethylcarbonyl formate should be a major product of the reaction, whereas it is in fact a minor product. The alternative explanation, that by two successive solvolytic reactions the sulfonate is converted first into the formate and then into the sulfone, is not consistent with the stereochemical observations recorded in the communication referred to.<sup>7</sup>

We submit, therefore, that it is undesirable to assume that in these reactions there is solvation of carbonium cations by co-valency formation between solvent and cation.

(1) Bateman, Hughes and Ingold, *THIS JOURNAL*, **60**, 3080 (1938).

(2) Olson and Halford, *ibid.*, **59**, 2644 (1937).

(3) Taylor, *J. Chem. Soc.*, 1853 (1937).

(4) Bartlett, *THIS JOURNAL*, **61**, 1630 (1939).

(5) (a) Steigmann and Hammett, *ibid.*, **59**, 2358 (1937), (b) Farinacci and Hammett, *ibid.*, **59**, 2542 (1937).

(6) Winstein, *ibid.*, **61**, 1635 (1939).

(7) Arcus, Balfe and Kenyon, *J. Chem. Soc.*, 485 (1938).

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## Organolithium Compounds of Pyridine and Quinoline

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The halogen-metal interconversion reaction observed with *m*- and *p*-bromodimethylanilines,<sup>1</sup>

(1) Gilman and Banner, *THIS JOURNAL*, **62**, 344 (1940).

mono- and dibromo- and iodocarbazoles and bromoanilines<sup>2</sup> suggested that corresponding reactions might take place with bromo- and iodopyridines and quinolines. We have found this to be the case. For example, 3-bromoquinoline and *n*-butyllithium react promptly, and carbonation of the reaction mixture gives a 52% yield of 3-quinolinecarboxylic acid. Under corresponding conditions 3-bromopyridine gives a 70% yield of nicotinic acid.

Perhaps the first evidence for the formation of Grignard reagents from 3-bromopyridine and 2-iodopyridine is to be found in a study by Harris.<sup>3</sup> Later, Overhoff and Proost<sup>4</sup> prepared 2-pyridylmagnesium bromide in quantity and obtained from it and benzaldehyde, phenyl-2-pyridylcarbinol. The formation of organolithium compounds from nitrogen heterocycles by means of other RLi compounds is of interest because it appears to be generally applicable, and because it establishes the possibility of selecting conditions to reduce the tendency of addition of an organolithium compound to the anil linkage. Under ordinary conditions, RLi compounds add promptly to the anil linkage. The reaction undoubtedly can be extended to poly-substituted nitrogen heterocycles containing functional groups in addition to bromine and iodine. For example, *o*-bromobenzoic acid and *n*-butyllithium give the lithium salt of *o*-lithiobenzoic acid, which on carbonation (followed by hydrolysis) gives a 31% yield of phthalic acid.<sup>5</sup> Details on the preparation and some reactions of the organolithium compounds of various nitrogen heterocycles will be published later.

A solution of 14.6 g. (0.07 mole) of 3-bromoquinoline in 50 cc. of dry ether was added rapidly to an ether solution of a slight excess of *n*-butyllithium. The reaction was carried out at  $-35^\circ$  for fifteen minutes, at the end of which time the transparent reddish solution was carbonated by dry-ice. On working up the reaction mixture in a customary manner, there was isolated a 52% yield of 3-quinolinecarboxylic acid. Identification was established by comparison with an authentic specimen of the acid (m. p.  $270-272^\circ$ ); in addition, the method of mixed melting points was also used with the ethyl 3-quinolinecarboxylate (m. p.,  $69.5^\circ$ ), prepared from the 3-quinolinecarboxylic acid.

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(2) Gilman, Langham and Willis, *ibid.*, **62**, 346 (1940).

(3) Harris, *Iowa State Coll. J. Sci.*, **6**, 425 (1932); [*C. A.*, **27**, 279 (1933)].

(4) Overhoff and Proost, *Rec. trav. chim.*, **57**, 179 (1938).

(5) Studies by C. E. Arntzen.