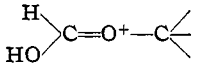
scribed as unimolecular,[1] as bimolecular,[2,3] as either bimolecular or termolecular,[4] and as polymolecular,[5,6] the diversity of conclusions suggests, as indicated by Bartlett,[4] that the course of these reactions is not sufficiently simple to justify the application of the kinetic method.

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.[6] In the hydrolysis of halides, Winstein's formulation $\mathrm{H_2O^+{-}C}{\lessdot}$ leads to no difficulties, but is not generally applicable. The rearrangement of phenylmethylcarbinyl *p*-toluenesulfinate to *p*-tolyl-α-phenylethylsulfone,[7] 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  $\mathrm{(H)(HO)C{=}O^+{-}C}{\lessdot}$ would, in our opinion, imply that phenylmethylcarbinyl 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 sulfinate is converted first into the formate and then into the sulfone, is not consistent with the stereochemical observations recorded in the communication referred to.[7]

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,[1] mono- and dibromo- and iodocarbazoles and bromoanilines[2] 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.[3] Later, Overhoff and Proost[4] 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.[5] 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° 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°); in addition, the method of mixed melting points was also used with the ethyl 3-quinolinecarboxylate (m. p., 69.5°), prepared from the 3-quinolinecarboxylic acid.

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