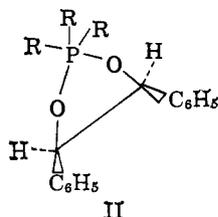are *trans* while in the starting epoxide they are eclipsed. Conversely, the fact that *trans*-stilbene oxide is not isomerized to *cis*-stilbene oxide probably reflects the fact that the phenyl groups are eclipsed in the corresponding intermediate II.

II

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Hexamethylphosphoramide. An Aprotic Solvent for Active Metals

Sir:

Active metals of group I and II dissolve in liquid ammonia to yield blue solutions. Extensive investigations of the conductance,[1] e.s.r.,[2] n.m.r.,[3] and ultraviolet absorption spectroscopy,[4] respectively, of these solutions establish that they contain solvated electrons. Similar solutions have been prepared with other simple primary amines, diamines, and ethers, the latter being of low concentration.[5] So far no tertiary amine or aprotic organic compound has been found to dissolve metals in the manner and concentrations obtained with liquid ammonia.

We have now found that sodium, potassium, and lithium dissolve in hexamethylphosphoramide to give blue solutions, up to 1 *M* and stable for several hours.[6,7] The solvent peaks in the n.m.r. spectra of these solutions are broadened with respect to those in the pure amide. On admission of oxygen to these solutions the blue color disappears and the solvent peaks (n.m.r.) become sharp again. The e.s.r. absorption consists of a single sharp line at $g = 2.00210$ (width 0.4 gauss),[8] close to the value for the free electron, $g = 2.0022$.

After several hours storage at room temperature these solutions turned red and were no longer paramagnetic. The blue solutions reacted violently with water, alkyl halides, and olefins and took fire in air. On the basis of all this information and by analogy to the results for simple amines there is no doubt that the blue color comes from solvated electrons.[9]

Attempts to obtain similar solutions to those described above with tris(dimethylamino)phosphine so far have failed.

Hexamethylphosphoramide is an excellent solvent for organometallic compounds.[10] We have found that both Grignard reagents and organolithium compounds form solid complexes with it. These complexes could be handled briefly in air but decomposed on standing.[11]

Since hexamethylphosphoramide, HMPA, is a good solvent for active metals it might be expected to be a good medium for reduction reactions. Actually, both Grignard reagents and organolithium compounds may be prepared in it in good yields: (1) Simple aliphatic halides, methyl iodide, bromoethane, and 1-bromopropane were all converted with magnesium in HMPA at 80° to the corresponding Grignard reagents. (2) These latter reactions have been accomplished in 90% benzene–10% HMPA at 30°. (3) The corresponding organolithium compounds were made by adding the halides to lithium wire in HMPA at room temperature. Under all these circumstances blue color was not generated. (4) Addition of organic halides to solutions of sodium, potassium, and lithium in HMPA yielded only Wurtz coupling products. (5) Benzophenone treated with sublimed magnesium and traces of MgBr₂ in HMPA at room temperature gave both blue (monomeric) and red (dimeric) forms, respectively, of the ketyl radical ion.[12] The latter was recognized by the identity of its e.s.r. spectrum with that of benzophenone radical ion obtained by Hirota and Weissman.[13] Approximately 10% of the benzophenone was converted to dibenzpinacol when these solutions were allowed to stand 24 hr. at room temperature.

The fact that solvated electrons have been detected in so many different basic solvents (ammonia,[1-4] aliphatic amines,[1-4] HMPA, certain polyethers,[5] water,[14]

(1) (a) C. H. Kraus, *J. Am. Chem. Soc.*, 30, 1323 (1908); 43, 749 (1921); (b) W. C. Fernelius and G. W. Watt, *Chem. Rev.*, 20, 195 (1937); (c) S. Naidlich in "Solutions Métal-Ammoniac, Propriétés Physicochimiques," G. Lepoutre and M. J. Sienko, Ed., W. A. Benjamin, New York, N. Y., 1964, pp. 113–137; E. Arnold and H. Patterson, ref. 1c, pp. 160–167.

(2) C. H. Hutchison and R. C. Pastor, *J. Chem. Phys.*, 21, 1959 (1953); R. Catterall and M. C. R. Symons, ref. 1c, pp. 277–285.

(3) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, 26, 1517 (1957); S. R. Gunn and L. G. Green, *ibid.*, 36, 363 (1962); K. S. Pitzer, ref. 1c, pp. 194–198; T. R. Hughs, ref. 1c, pp. 211–215.

(4) M. Gold and W. L. Jolly, *Inorg. Chem.*, 1, 818 (1962); R. C. Douthit and J. L. Dye, *J. Am. Chem. Soc.*, 82, 4472 (1960); W. L. Jolly *et al.*, ref. 1c, pp. 174–186.

(5) J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959); F. A. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, 31, 809 (1959); F. S. Dainton, D. M. Wiles, and H. N. Wright, *J. Chem. Soc.*, 4283 (1960).

(6) First observed by John P. Matanovich, N.S.F. Undergraduate Research Participant, Summer 1962.

(7) The hexamethylphosphoramide was kindly donated by Tennessee Eastman Corporation, Kingston, Tenn. The material was distilled and carefully degassed before use.

(8) All e.s.r. spectra were determined with the Varian V4502 electron resonance spectrometer, at 3400 gauss and a frequency of 9.5 kMc., 100 kc. modulation. We are indebted to Dr. J. G. Calvert for letting us use this instrument.

(9) The possibility that phosphoryl radical ions (Me₂N)₃PO⁻ or any other radicals exist in these solutions to any measurable extent is excluded by the absence of fine structure in the e.s.r. spectra. It is doubtful whether fast electron exchange between phosphoryl radicals and solvent molecules could be responsible for our results.

(10) V. R. Sandell and H. H. Friedman, *J. Am. Chem. Soc.*, 85, 2328 (1963).

(11) The products of decomposition of these complexes appear to be phosphorylated derivatives of the organometallic compounds.

(12) W. Bachman, *J. Am. Chem. Soc.*, 55, 1179 (1933).

(13) N. Hirota and S. T. Weissman, *ibid.*, 86, 2537, 2538 (1964).

(14) J. W. Boag and E. J. Hart, *Nature*, 197, 45 (1963); E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, 84, 4090 (1962); L. M. Dorfman and I. A. Taub, *ibid.*, 86, 4218 (1964).

and alcohols[15]) raises the question that solvated electrons may be involved in reduction reactions by metals in basic solvents. It is recognized that such reactions may be driven to completion because basic atoms in the solvent molecules complex with metal ions. Now it is likely that ionization of metals is facilitated in all these media by electron solvation, the mean lifetimes of the solvated electrons changing among the different solvents, and that the reducing species is the solvated electron.

The utility of HMPA as a medium for Birch[16] reductions is under investigation.

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(15) I. A. Taub, D. H. Harter, M. C. Sauer, and L. M. Dorfman, *J. Chem. Phys.*, **41**, 979 (1964).
(16) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); H. S. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 151–279.

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A New Class of Activated Esters. The 1-Acyloxy-2(1H)-pyridones[1]

Sir:

Electrophilic attack of acyl halides on 2-ethoxypyridine 1-oxide (I) has been found to proceed exothermally with the evolution of ethyl chloride to produce 1-acyloxy-2(1H)-pyridones (III) in excellent yields. The reaction undoubtedly involves a mechanistic pathway of the type illustrated in structure II.[2] For example, slow addition of I to acetyl chloride at room temperature resulted in an immediate evolution of gas and produced in 86% yield 1-acetoxy-2(1H)-pyridone (III, R = CH_3), m.p. 93–94°,[3] ν^{Nujol} 1800 and 1655 cm.$^{-1}$
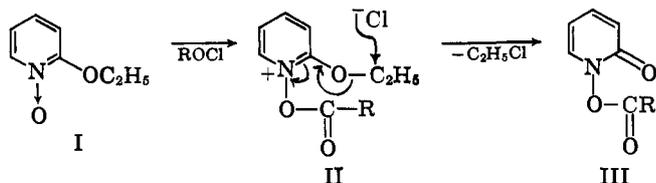
(ester and amide carbonyls, respectively).[4] Similarly, benzoyl chloride afforded 1-benzoyloxy-2(1H)-pyridone (III, R = C_6H_5), m.p. 140°,[3] ν^{Nujol} 1780 and 1670 cm.$^{-1}$, in 93% yield.[6]

It is now well documented[7] that increased reactivity in nucleophilic reactions involving carbonyl groups is paralleled by a marked shift of the infrared absorption of the carbonyl bands toward shorter wave lengths. The infrared data relating to the ester carbonyls of III

(1) Unsaturated Heterocyclic Systems, part XIV. For part XIII, see L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, in press.
(2) This mechanism is formally analogous to that by which 2-ethoxypyridine is converted by alkyl halides into 1-alkyl-2(1H)-pyridones; see L. A. Paquette and N. A. Nelson, *J. Org. Chem.*, **27**, 1085 (1962).
(3) Satisfactory analyses were obtained for all new compounds.
(4) Preparation of III (R = CH_3) by an unequivocal route was achieved by acetylating 1-hydroxy-2(1H)-pyridone[5] with acetic anhydride.
(5) G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, 1864 (1948).
(6) A wide variety of other acyl halides has also been employed with equal success.
(7) H. A. Staab, *Angew. Chem. Intern. Ed. Engl.*, **1**, 351 (1961).

most strikingly indicate that these substances must be activated esters. This has been found to be the case. Thus, dissolution of the acetyl derivative in a minimum quantity of purified water at room temperature resulted in the quantitative deposition of colorless crystals of 1-hydroxy-2(1H)-pyridone. With *n*-butyl alcohol and *n*-butylamine extremely facile transfer of acetyl from III (R = CH_3) was also observed.

The high reactivity of the 1-acyloxy-2(1H)-pyridones can also be applied to the construction of peptide units. For example, reaction of phthaloyl-L-phenylalanyl chloride (IV)[8] with I afforded a quantitative yield of the
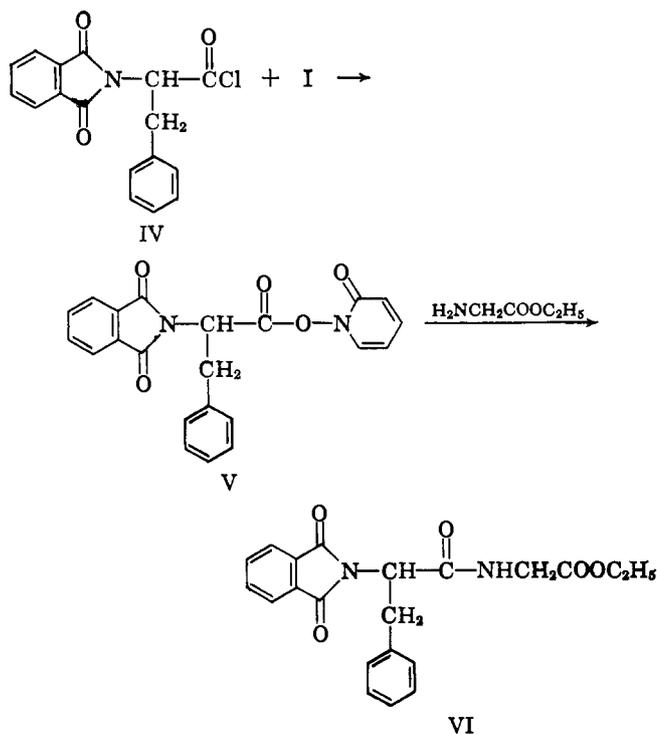
activated ester V which, in turn, was readily condensed with glycine ethyl ester to give a 79.7% yield (from IV) of optically pure phthaloyl-L-phenylalanylglycine ethyl ester (VI), $[\alpha]^{29}D$ −145° (in EtOH). Consequently, carboxyl activation of amino acids *via* 1-hydroxy-2(1H)-pyridone esters appears suitable for the synthesis of peptides and could find application in those cases where liberation of the elements of hydrogen chloride is not desirable. Furthermore, esters of type III are particularly attractive because of their very high reactivity, their high crystallinity, and especially because of the high water solubility of the N-hydroxy-2(1H)-pyridone by-product.[9]

(8) J. C. Sheehan, D. W. Chapman, and R. W. Roth, *J. Am. Chem. Soc.*, **74**, 3822 (1952), report $[\alpha]^{29.55}D$ −146° for VI.
(9) It should be noted that the 1-acyloxy-2(1H)-pyridones represent the latest class of activated esters based upon hydroxylamine which have been recently studied: (a) esters of N-hydroxyphthalimide: G. H. L. Nefkens and G. I. Tesser, *ibid.*, **83**, 1263 (1961); G. H. L. Nefkens, G. I. Tesser, and R. J. F. Nivard, *Rec. trav. chim.*, **81**, 683 (1962); (b) esters of N-hydroxysuccinimide: G. W. Anderson, J. E. Zimmerman, and F. M. Callahan, *J. Am. Chem. Soc.*, **85**, 3039 (1963); **86**, 1839 (1964); (c) esters of oximes: G. Losse, A. Baeth, and K. Schatz, *Ann.*, **677**, 185 (1964).
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