Our results for the nitrous acid deamination of 2-phenyl-2-butylamine are less extensive, but they show that both 2-phenyl-2-butanol and 2-phenyl-2-butyl acetate are formed in the reaction with nitrous acid in acetic acid and that both compounds are formed with over-all retention of configuration (74% and 61%, respectively). The alcohol is of particular interest since it must be the product of an intramolecular reaction—the decomposition of a species such as VI or VIII (followed in the latter case by hydrolysis).[6] The anion exchange illustrated appears to be a general reaction of diazonium ion pairs[5]; we propose that intermediates such as VII and VIII formed in the nitrous acid deamination are similar to those such as III formed in the nitrosoamide decomposition and that there is an overlap in the mechanisms of the two reactions.[7]

Acknowledgments.—We thank Dr. Robert R. Johnson for valuable assistance and the National Science Foundation for its support of this work (G 12311).

(6) In one case, that of sterically hindered amine, the alkyl nitrite itself has been isolated (A. Brodhag and C. R. Hauser, *J. Am. Chem. Soc.*, **77**, 3024 (1955)). A similar anion exchange of VI (or VII) with nitric acid (from thed ecomposition of nitrous acid) to yield $RN_2^+NO_3^-$ could account for the nitrate esters (and from these, the carbonyl compounds) that have been isolated from a number of deaminations (*eg.*, J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4094 (1959); V. Prelog, H. J. Urech, A. A. Bothner-By and J. Würsch, *Helv. Chim. Acta.* **38**, 1095 (1955)).

(7) In this respect, one other comparison is available. The nitrous acid deamination of 1-phenylethylamine in acetic acid yielded 1-phenylethanol with 78.5% retention of configuration (R. Huisgen and C. Rüchardt, *Ann.*, **601**, 21 (1956)), whereas the nitrosoamide decomposition of the same amine in acetic acid proceeded with 81% retention of configuration.[5]

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Rates of Rotation of Asymmetric Diphenyls by Nuclear Magnetic Resonance Spectroscopy

Sir:

As a consequence of the steric requirements of *o*-substituents, the two aromatic rings of an *o*-substituted diphenyl are not coplanar. An *o*-substituent on one ring thus is located above the plane of the second, and if the second ring holds two different *o*- or *m*-groups, the substituent on the first ring is in an asymmetric environment. If that substituent contains a methylene group, its two protons thus are not necessarily magnetically equivalent even though the substituent rotates about the phenyl–substituent bond, for the conformers of the substituent about that bond (*e.g.*, Ia–c or others[1]) will not necessarily be equally populated and the environments of the two protons are different in each conformer.[2] That this can indeed be the case is clearly seen from the n.m.r. spectrum[3] of *dl*-6,6′-diethyl-2,2′-bis-(hydroxymethyl)-diphenyl (IIa, prepared by lithium aluminum hydride reduction of the corresponding diphenic ester IIb; found: C, 80.0; H, 8.2) in which the methylol proton resonance appears as an AB quartet ($\tau_A = 5.80$; $\tau_B = 5.95$; $|J_{AB}| = 12$ c.p.s.). This appears to be the first reported example of such non-equivalence which results from diphenyl asymmetry,[4]

(1) Whether energy minima in fact correspond to Ia–c in which H or X eclipses the *m*-hydrogen, to structures in which H or X and H stagger the *m*-hydrogen, to both, or to intermediate ones is not clear, but is immaterial for the non-equivalence argument.

(2) In principle, the argument holds for a *m*-substituent as well, and of course for groups other than methylene which contain two similar magnetically active units, *e.g.*, isopropyl or difluoromethylene.
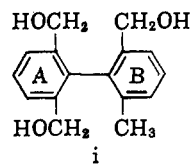
(3) N.m.r. spectra were obtained from dilute solutions in carbon tetrachloride or deuteriochloroform using Varian A-60 and DP-60 spectrometers operating at 60 Mc./sec.

(4) K. Mislow and M. A. W. Glass, *J. Am. Chem. Soc.*, **83**, 2780 (1961), and K. Mislow, E. Simon and H. B. Hopps, *Tetrahedron Letters*, 1011 (1962), have observed non-equivalent *o*-methylene protons in several bridged di-

although the corresponding phenomenon when the asymmetric environment is provided by a tetrahedral carbon holding three dissimilar groups is well known.[5,6]

IIa, Y = CH_2OH ; Z = C_2H_5
b, Y = CO_2CH_3; Z = C_2H_5
c, Y = CH_2OCOCH_3; Z = H

Non-equivalence of this type can only be observed provided rotation about the diphenyl bond is sufficiently slow, for such a rotation through 180° serves to exchange the environments of protons A and B of the AB system (compare Ia and IIIa). When such rotational exchange is rapid compared to the chemical shift difference between A and B, the same average environment is observed for both by the n.m.r. technique, producing a single line (A_2) spectrum. Indeed while the CH_2O resonance of *dl*-2,2′-bis-(acetoxymethyl)-diphenyl (IIc) is of the AB type at room temperature ($\delta_{AB} \cong 3.5$ c.p.s.; $|J_{AB}| \cong 12.6$ c.p.s.), at 127° the pattern has collapsed to a single line. Examination of the shape of the outer peaks of the AB system at intermediate temperatures,[7] where they first broaden and then disappear, reveals that at 94° the average lifetime of a molecule between rotations is 4 sec., and that the Arrhenius activation energy for rotation is approximately 13 kcal./mole. Thus the n.m.r. technique provides a means for studying the process by which an optically active diphenyl would be racemized, without requiring a resolved sample. Further, it is applicable to systems, such as the *o,o′*-disubstituted case here reported, which are difficult to study by the
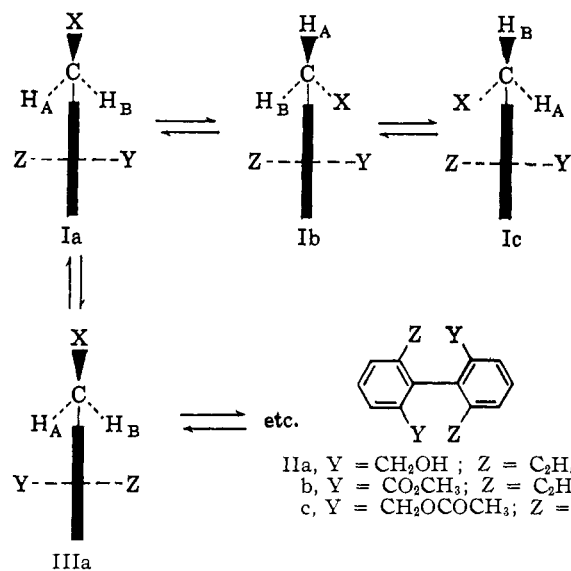
phenyls, but in these systems the methylene groups are part of a ring and thus not free to rotate. Professor Mislow has very recently informed us that he has also observed non-equivalent methylene protons in the unbridged systems II, Y = CH_2OH and Z = CH_3 ($\tau_A = 5.85$; $\tau_B = 6.02$; $|J_{AB}| = 11.6$ c.p.s.), and II, Y = CH_2OH and Z = CD_3 ($\tau_A = 5.83$; $\tau_B = 6.00$; $|J_{AB}| = 11.8$ c.p.s.). We are grateful to Prof. Mislow for communication of these results prior to publication and permission to cite them here.

(5) Early examples and a concise discussion of the principles involved are provided by P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957). An elegant test of the commonly accepted theoretical explanation is reported by G. M. Whitesides, F. Kaplan, K. Nagarajan and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1112 (1962).

(6) It should be noted that the structural requirements which permit such non-equivalence are less restrictive than those which produce molecular dissymmetry and consequently permit optical activity, just as is the case for non-equivalence due to location near "asymmetric" carbon, ref. 5. In principle, a system such as i, although unresolvable, could have non-equivalent methylene protons on the methylol groups of the A but not the B ring.

i

(7) J. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958).

polarimetric method because their half-lives are too short to permit easy optical resolution, and probably to some compounds which cannot be resolved optically because they are symmetric even in the absence of rotation.[6]

Further examples as well as other useful stereochemical information derivable from n.m.r. spectra of such diphenyls will be reported in due course.

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Solvent Effects in Organometallic Reactions. II

Sir:

Although no quantitative data from kinetic evaluations of such solvent effects have been reported previously, it is generally recognized that certain solvent types (particularly ethers) are "good" for organometallic reactions. We wish to report here quantitative findings on the variation in rates of reaction between *n*-butyllithium (BuLi) and 1-bromoöctane (RBr) as a function of the composition of the solvent system hexane–ether. The findings are revealing as to the basis of the virtue of ether as solvent in this reaction and as to structures both of butyllithium itself and of the transition state for this reaction.

Samples from hexane–ether solutions (made up with known initial concentrations of reactants and maintained at 27° in an atmosphere of nitrogen) were quenched with water and analyzed for product and reactant content by gas chromatography. Plots with the appropriately integrated equations, and other standard tests, showed that the data fit the second-order rate law (1)[1] to a fraction of reaction >90% with good reproducibility. A plot of several k_a

$$\text{rate} = k_a(\text{BuLi})_a(\text{RBr})_a \qquad (1)$$

values *vs.* the concentration of ether in the mixed solvent is shown in Fig. 1 for the range *ca.* 3–50% ether. The regular increase in k_a with added ether (the positive slope in Fig. 1) is not surprising; it would be an expected consequence of the polar solvent's effect on a reaction involving some increase in charge separation in the transition state. The unexpected feature of the slope in Fig. 1 is that it does not extrapolate back to
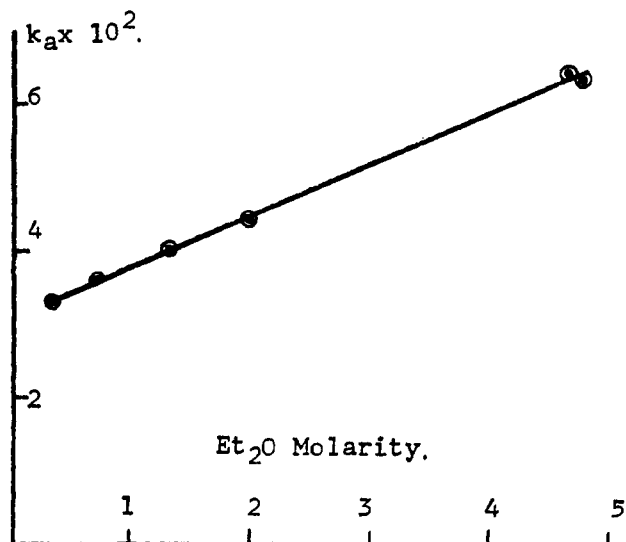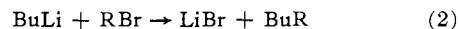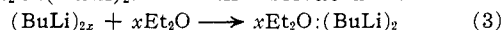

Figure 1.

an intercept even nearly approximating the low rate constant for reaction in pure hexane. The facts are that the rate of formation (2) of dodecane (BuR) is increased by a factor of over 10^8 in going from hexane to ether as solvent,[2] but that virtually all of this large acceleration is effected when only a very small amount of ether has been added to the hexane reaction solution, *i.e.*, before the first point shown in Fig. 1. In other words, there is an additional, and much larger, solvent effect by ether on this reaction in hexane.

$$\text{BuLi} + \text{RBr} \rightarrow \text{LiBr} + \text{BuR} \qquad (2)$$

Acceleration of the coupling reaction by low concentrations of ether, (Et_2O), is not a function of this concentration itself, but rather is affected by the ratio, r, of ether to butyllithium, $(\text{Et}_2\text{O})/(\text{BuLi})$. Figure 2 shows that k_a is a linear function of r up to a value of $r = 0.5$,[3] after which additional ether effects the relatively small acceleration already indicated in Fig. 1. The linearity of Fig. 2 to $r = 0.5$ and the rather sharp break thereafter strongly suggest a structural significance for this r-value. Thus, the virtue of ether as a solvent is primarily a consequence of a highly effective specific solvation phenomenon and only secondarily due to its macroscopic solvent properties, *e.g.*, dielectric constant.

We interpret the low reactivity of butyllithium in hexane to result from a large degree of association or polymerization of the organometallic reagent in the hydrocarbon solvent, and the primary solvent effect of ether to be depolymerization of the reagent. It is our hypothesis that the basic structural unit for an alkyllithium is a dimer, $(\text{BuLi})_2$, which associates in hexane to tetramers, hexamers, etc. $((\text{BuLi})_{2x})$; in ether the highly associated form dissociates (3) to the solvated dimer, $\text{Et}_2\text{O}:(\text{BuLi})_2$.[4] If the solvated dimer form

$$(\text{BuLi})_{2x} + x\text{Et}_2\text{O} \longrightarrow x\text{Et}_2\text{O}:(\text{BuLi})_2 \qquad (3)$$

(1) The subscripts a in eq. 1 indicate that the concentration terms represent apparent total or stoichiometric concentrations.

(2) In the hydrocarbon solvent, coupling is sufficiently slow that reduction becomes the major reaction; paper I in this series: J. F. Eastham and G. W. Gibson, *J. Org. Chem.*, **28**, 280 (1963).

(3) In Fig. 2, k_a values are from "initial rates," because at low ether concentrations r changes significantly as the reaction proceeds; these values were verified over a fourfold variation in butyllithium concentration (0.33–1.32 M).

(4) Our ideas on the geometry of a solvated dimer of butyllithium will be published subsequently; the concept of a four-membered (dimeric) ring involving two three-center bonds is indicated for several other organometallics; *cf.*, G. E. Coates, "Organo-Metallic Compounds," 2nd Ed., Methuen, London, 1960, pp. 57, 99, 131–133, etc. Greater association of alkyllithiums in hydrocarbon solvents has been considered extensively; *cf.*, T. L. Brown, D. W. Dickerhoof and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962), who propose structures for the tetramers and hexamers of alkyllithiums in a hydrocarbon and specifically consider their disruption by basic solvents.