catalytic amount (10 mole %) of sodium acetate trihydrate, despite which they proceed to completion in less than 25 min at 25°.

As a typical example: *p*-bromophenacyl bromide (5.55 g) is dissolved in 20 ml of acetonitrile and to this a solution of 4.25 g of silver nitrate in 20 ml of acetonitrile is added. After stirring for 24 hr at room temperature the mixture is filtered, the silver bromide is washed with ethyl ether, and the combined filtrate and washings are evaporated at 30 mm (30°). The residue is taken up in ether, washed with water, and dried, and the solvent is removed. The crude nitrate ester (5.17 g) is dissolved in 100 ml of DMSO and to the stirred solution a suspension of sodium acetate trihydrate (0.27 g) in 40 ml of DMSO is added. After 25 min at 20–25° the reaction mixture is poured into 400 ml of ice water, saturated with sodium chloride, and ether extracted. The ether solution is washed with water and saturated aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. Evaporation at 30 mm (30°) yields 4.19 g (92% yield) of *p*-bromophenyl glyoxal monohydrate, mp 124–126°. Recrystallization from aqueous acetone gives 3.87 g (85% yield), mp 125–126.5°. The nmr spectrum of the recrystallized product (in DMSO) has a triplet centered at δ 5.79 (area = 1.00, J = 6.0 cps) and a doublet centered at δ 6.87 (area = 2.05, J = 6.0 cps). This accords with the structure Ar-COCH(OH)$_2$.[3] *Anal.* Calcd for $C_8H_5BrO_2\cdot H_2O$: C, 41.58; H, 3.06; Br, 34.59. Found: C, 41.65; H, 3.31; Br, 34.79.

Although the base-catalyzed elimination of nitrite ion from nitrate esters has been recognized for many years, the reaction has never achieved the status of a synthetically useful means of producing carbonyl compounds.[4] We find that even under our conditions this reaction leaves something to be desired as a method of synthesizing aromatic and aliphatic aldehydes, for, while *p*-nitrobenzyl nitrate gives an 80% yield of *p*-nitrobenzaldehyde on treatment with sodium acetate, *p*-bromobenzyl nitrate is converted into *p*-bromobenzyl acetate (59% yield), along with only a minor amount of *p*-bromobenzaldehyde (11% yield); *i.e.*, with *p*-bromobenzyl nitrate displacement of nitrate ion is the major process. In contrast, the reaction of *p*-bromobenzyl nitrate with sodium phenoxide gives an 81% yield of the aldehyde; however, sodium phenoxide transforms *n*-octyl nitrate into *n*-octyl phenyl ether (72% yield). Finally, sodium fluoride converts *n*-octyl nitrate to *n*-octaldehyde (46% yield), but a temperature of 100° for 23 hr is necessary. Clearly the preparation of aldehydes from nitrate esters lacks the elegance which characterizes the glyoxal, glyoxalic ester, and α-diketone syntheses.

[3] D. E. McGreer, R. Stewart, and M. M. Mocek, *Can. J. Chem.*, **41**, 1024 (1963); H. D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1895 (1963); O. L. Chapman and B. R. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

[4] J. U. Nef, *Ann.* 309, 175 (1899); G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, 64, 1937 (1942); J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952); N. Kornblum and H. E. De La Mare, *J. Am. Chem. Soc.*, 73, 880 (1951); M. P. Cava, D. R. Napier, and R. J. Pohl, *ibid.*, **85**, 2076 (1963); R. Breslow, D. Kivelevich, M. J. Mitchell, W. Fabian, and K. Wendel, *ibid.*, 87, 5132 (1965).

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Transfer of Asymmetry from Nitrogen to Carbon in the Stevens Rearrangement

Sir:

The classic work of Pope and Peachey[1] in the resolution of the allylbenzylmethylphenylammonium cation (I) into optical antipodes demonstrated that organic molecules could owe their optical activity to centers of asymmetry other than carbon. Since that time, a host of optically active compounds of silicon, germanium, nitrogen, phosphorus, arsenic, antimony, and sulfur have been prepared.

This investigation was undertaken to see whether asymmetry due to a tetravalent atom other than carbon could be transferred to carbon. The transfer of asymmetry, *i.e.*, the creation of one asymmetric center simultaneous with the destruction of another,[2] has been a valuable method of study of transition-state geometry.[3] For this purpose, we have investigated the Stevens rearrangement of optically active I.

Reaction of (+)-I iodide, $[\alpha]_D$ +39.6°, with potassium *t*-butoxide in dimethyl sulfoxide gave, in addition to N-methylaniline (35%) and 1-(N-methylanilino)-4-phenylbutene-1 (III, isolated as the corresponding aldehyde), 15% of 3-(N-methylanilino)-4-phenylbutene-1 (II), $[\alpha]_D$ −18.4°. The structure of II was assigned from its mass spectrum[4] (parent peak 237.1506; $C_{17}H_{19}N$ requires 237.1517), in which the base peak at 146.0971 is due to the ion $C_{10}H_{12}N^+$ (calcd, 146.0969) resulting from α cleavage of the benzyl group, and from the nmr spectrum, which showed absorption at τ 7.25 (3 H, singlet), 7.10 (2 H, doublet), 5.5 (1 H, broad), 4–5 (3 H, multiplet), and 3 (10 H, broad). Confirmation came from synthesis of the dihydro derivative (Chart I).

This reaction is believed to be the first demonstration of transfer of asymmetry from nitrogen to carbon.[5] Until the maximum rotation of II is known, it is difficult to assess the degree of stereospecificity, but based on rotations reported for similar amines, conservation of optical purity during the rearrangement to II appears to be high.

It is possible, however, by determining the absolute configurations of I and II, to deduce the transition-state geometry in this reaction. Diimide reduction of (+)-I iodide gave (*R*)-(+)-benzylmethylphenylpropylammonium iodide (IV) of established configuration.[6] The (*S*) configuration of (−)-II was proved by relating it to (*R*)-(−)-1-phenyl-2-butanol,[7] using the reactions shown in Chart I. The absolute configurations found

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[1] W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, 1127 (1899).

[2] The term "self-immolative" has been suggested to describe this special kind of asymmetric synthesis; see K. Mislow, "Introduction to Stereochemistry," W. Benjamin, Inc., New York, N. Y., 1965, p 131.

[3] See, *inter alia*, (a) R. K. Hill and R. M. Carlson, *J. Am. Chem. Soc.*, **87**, 2772 (1965); (b) R. K. Hill and A. G. Edwards, *Tetrahedron Letters*, 3239 (1964); (c) R. K. Hill and M. Rabinovitz, *J. Am. Chem. Soc.*, **86**, 965 (1964); (d) H. L. Goering and W. I. Kimoto, *ibid.*, **87**, 1748 (1965); (e) E. P. Burrows, F. J. Welch, and H. S. Mosher, *ibid.*, **82**, 880 (1960), and previous papers; (f) W. von E. Doering and R. W Young, *ibid.*, **72**, 631 (1950).

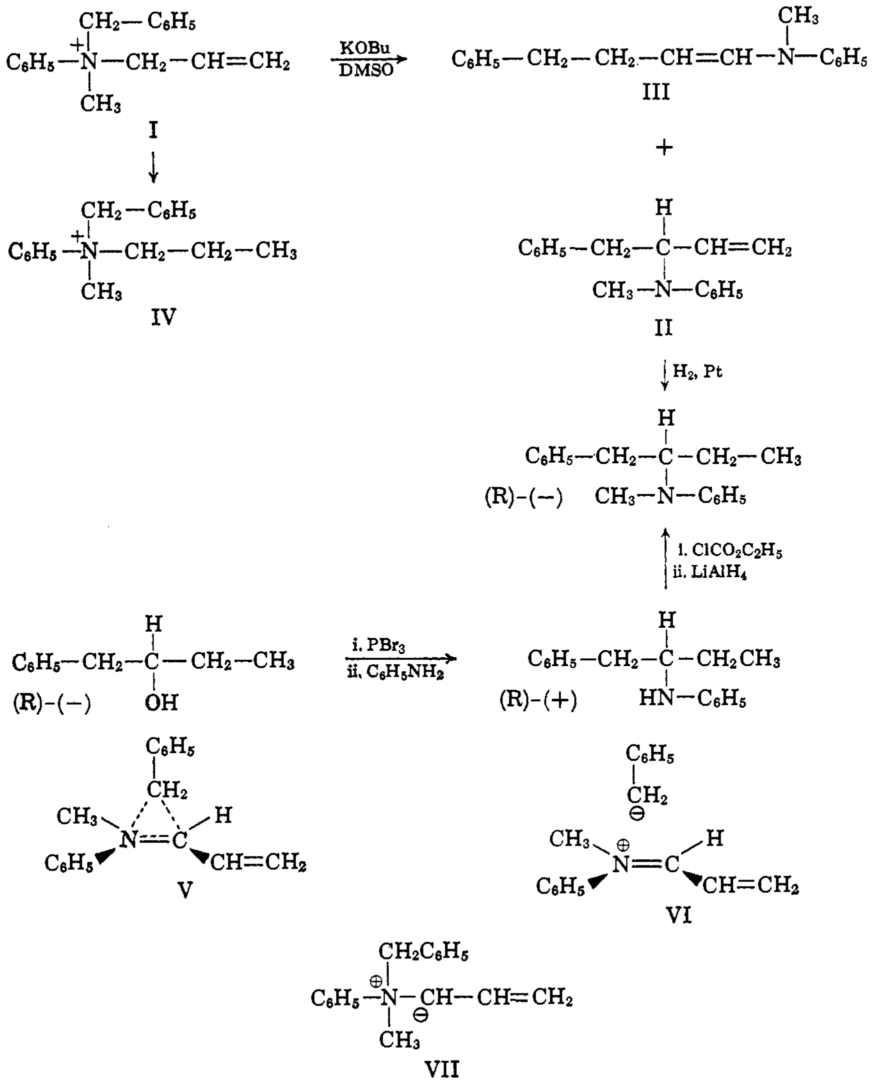
[4] We are greatly indebted to Dr. Henry Fales, National Heart Institute, for his aid in obtaining and interpreting this spectrum.

[5] For an example of transfer of *biphenyl* dissymmetry to asymmetric carbon in the Stevens rearrangement, see G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953); also K. Mislow and H. Joshua, *J. Am. Chem Soc.*, **87**, 666 (1965).

[6] L. Horner, H. Winkler, and E. Meyer, *Tetrahedron Letters*, 789 (1965).

[7] P. A. Levene and A. Walti, *J. Biol. Chem.*, **90**, 81 (1931).

Chart I



for I and II require that the stereochemistry of the transition state correspond to V, in which the unexpected *cisoid* relationship of the phenyl and vinyl groups may be due to electrostatic attraction.

These results have an important bearing on the mechanisms currently proposed for the Stevens rearrangement.[8] If, as is generally believed for most 1,2-carbanion rearrangements,[8,9] the reaction is a two-step elimination–readdition process, then the retention of optical activity demands a tight, unsymmetrical ion pair (VI), largely undissociated in dimethyl sulfoxide. Alternatively, the S_Ni mechanism proposed by Watson[10] could account for the optical activity of II by preferential displacement from one face of the carbanion carbon of ylide VII. Further experiments which may permit a choice between these two mechanisms are in progress.

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[8] For recent reviews of the Stevens rearrangement, see (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 223–238; (b) H. E. Zimmerman in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 378–382.

[9] (a) E. F. Jenny and J. Druey, *Angew. Chem.*, **74**, 152 (1962); (b) U. Schöllkopf and H. Schäfer, *Ann.*, **683**, 42 (1965).

(10) H. B. Watson, "Modern Theories of Organic Chemistry", 2nd ed, Oxford University Press, 1941, p 205. See also C. R. Hauser and S. W. Cantor, *J. Am. Chem. Soc.*, **73**, 1437 (1951), and J. H. Brewster and M. W. Kline, *ibid.*, **74**, 5179 (1952).

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