

established methods,<sup>13,14</sup> to octane 2-diazotate (1). Alkylation with ethyl iodide in hexamethylphosphoric triamide (HMPA)<sup>1</sup> produced active 2,  $\alpha^{30D} - 16.8^\circ$ ,<sup>12,15</sup> which was purified by distillation at 85–87° (2 Torr), followed by gas chromatography.<sup>8</sup> The distilled yield was ~50%, and the product was spectrally identical with authentic *d,l*-2.<sup>1</sup> Photochemical isomerization gave 3,  $\alpha^{30D} - 18.9^\circ$ .<sup>12,15,16</sup> A second alkylation of 1 (from *l*-urethane of 83.5% optical purity) with Meerwein's reagent gave 2,  $\alpha^{30D} - 17.1^\circ$ ,<sup>12,15,17</sup> which was isomerized to 3,  $\alpha^{30D} - 19.4^\circ$ .<sup>12,15</sup>

If the conversion of *l*-2-octylurethane, via diazotate 1 and azoxyalkane 2, to azoxyalkane 3 were completely stereospecific, then  $\alpha^{30D} - 19.15 \pm 0.25^\circ$  (neat, 1 dm) must represent optically pure (*R*)-3. Gratifyingly, (*S*)-(+)-2-chlorooctane (4),  $\alpha^{25.5D} + 24.67^\circ$ ,<sup>12</sup> 78.2% optically pure,<sup>18–20</sup> reacted with ethane diazotate in HMPA (Scheme I) to give a 22% yield of (*R*)-3,  $\alpha^{30D} - 15.09^\circ$ .<sup>12</sup> This rotation, when corrected for the optical purity of the chloride, gives  $\alpha^{30D} - 19.3^\circ$ , experimentally identical with the rotation obtained by the 1 → 2 → 3 pathway.<sup>22</sup>

We conclude that the representative azoxyalkanes 2 and 3 can be prepared stereospecifically from easily available optically active precursors. Their facile photochemical interconversion makes each available by two synthetic sequences. Further, the stereochemical data prove that diazotate alkylation occurs by SN2 attack (complete inversion<sup>20</sup>) of the diazotate on the alkylating agent.

Synthesis of specific chiral azoxyalkanes is therefore eminently practical, and the present method is applicable to syntheses of the naturally occurring compounds.<sup>23</sup> Moreover, diazotate 1 affords 2 with no loss of optical activity, which demonstrates that the diazotate is configurationally stable to the conditions of its generation. This fact, which could only be assumed until now, bears importantly on mechanistic deamination chemistry related to 1.<sup>13,24</sup>

Finally, the relatively high acidity of azoxymethane<sup>25</sup>

(14) R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

(15) Corrected for the optical purity of the urethane precursor.

(16) (a) CD data: (*R*)-2  $[\theta]_{252} + 2.12 \times 10^3$ ,  $[\theta]_{230} - 4.87 \times 10^3$ ; (*R*)-3  $[\theta]_{275} - 1.90 \times 10^3$ ,  $[\theta]_{230} + 2.69 \times 10^3$ . Both samples were measured in ethanol; ellipticities are corrected to optical purity (see below). The data for (*R*)-2 match those for (*R*)-ONN-1-cyclohexylazoxyethane.<sup>16b</sup> Note the "mirror image" CD behavior of (*R*)-2 and (*R*)-3. (b) W. J. McGahren and M. P. Kunstmann, *J. Org. Chem.*, **37**, 902 (1972).

(17) We thank Dr. Andrew Mamantov for this experiment.

(18) Based upon  $\alpha^{20D} 31.6^\circ$ : H. R. Hudson, *Synthesis*, **1**, 112 (1969), Table 5, note c; H. M. R. Hoffmann, *J. Chem. Soc.*, 1249 (1964).

(19) Chloride 4 was prepared from *l*-2-octanol,  $\alpha^{25D} - 6.89^\circ$ , 86% optically pure,<sup>21</sup> by the method of R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).

(20) 2-Octyl-X (X = NH<sub>2</sub>, OH, Hal) of the same rotational sign are of the same optical series; see M. Vogel and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2262 (1966); J. A. Mills and W. Klyne, *Progr. Stereochem.*, **194** (1954). Absolute configurations drawn in this paper derive from these relations, and from absolute assignments for 2-aminobutane: A. Kjaer and S. E. Hansen, *Acta Chem. Scand.*, **11**, 898 (1957).

(21) Based upon  $\alpha^{25D} + 8.04^\circ$ : A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **78**, 5597 (1956).

(22) Alkylation of ethane diazotate with active 4-Br or 4-I gave (–)-3 with 91 or 55%, respectively, of the maximum rotation, presumably because these 2-halo-octanes are racemized by halide anions released during the slow diazotate alkylations: G. M. Love, unpublished.

(23) R. A. Moss and T. B. K. Lee, submitted for publication.

(24) R. A. Moss and K. M. Luchter, *J. Org. Chem.*, **37**, 1155 (1972); R. A. Moss, A. W. Fritz, and E. M. Emery, *ibid.*, **36**, 3881 (1971); R. A. Moss, D. W. Reger, and E. M. Emery, *J. Amer. Chem. Soc.*, **92**, 1366 (1970).

(25) M. H. Benn and P. Kazmaier, *J. Chem. Soc., Chem. Commun.*, 887 (1972).

gave concern that 2 and 3 might not be configurationally stable to the (basic) conditions of their formation. However, when either azoxyalkane was treated overnight with refluxing 3 M NaOCH<sub>3</sub>-C<sub>2</sub>H<sub>5</sub>OD, only the  $\alpha$  or  $\alpha'$  methylene protons and not the methine protons (at the chiral centers) appeared to exchange (nmr). Active 2 racemized only to the extent of ~5% after 1 hr under these vigorous conditions.

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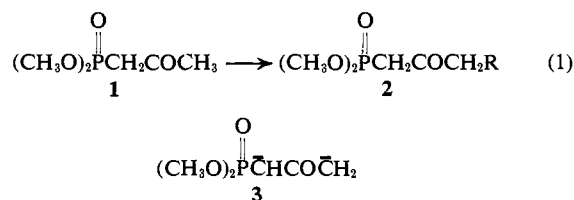
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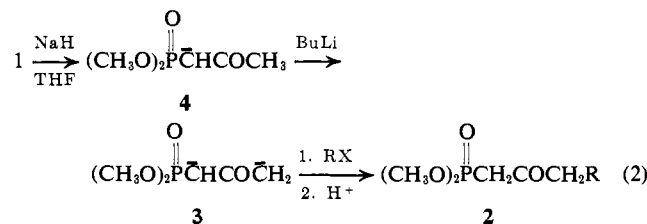
### Alkylation of the Dianion of $\beta$ -Keto Phosphonates. A Versatile Synthesis of Dimethyl (2-Oxoalkyl)phosphonates

Sir:

Recently we required a method to substitute a  $\beta$ -keto phosphonate ester at the  $\gamma$  carbon (eq 1). One method



to bring about this transformation is to alkylate the  $\gamma$  carbon of the 1,3-dianion 3. Monoanions derived from phosphonate esters which possess charge-stabilizing electron-withdrawing substituents (e.g., carbonyl) have been extremely useful in the synthesis of certain olefins from aldehydes and ketones.<sup>1</sup> However, dianions of type 3 have not previously been generated.<sup>2</sup> We now report that such dianions can be generated and undergo specific alkylation at the  $\gamma$  carbon (eq 2).



Treatment of dimethyl 2-oxopropylphosphonate<sup>3</sup> (1) with sodium hydride in THF produced the insoluble monoanion 4, and subsequent metalation of 4 with *n*-butyllithium generated the dianion 3. When a solution of 3 in THF was treated with a variety of alkylating

(1) L. Horner, H. Hoffmann, and H. G. Wippel, *Ber.*, **91**, 61 (1958); W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **93**, 1733 (1961).

(2) (a) A recent report has demonstrated that  $\beta$ -keto phosphonium salts (e.g., acetyltriphenylphosphonium chloride) undergo a sequential twofold ionization with generation of a "1,3-dianion": J. D. Taylor and J. F. Wolf, *J. Chem. Soc., Chem. Commun.*, 876 (1972). (b) For a review on dianions of  $\beta$ -dicarbonyl compounds, see T. M. Harris and C. M. Harris, "Organic Reactions," Vol. 17, Wiley, 1969, p 155; also see, L. Weiler, *J. Amer. Chem. Soc.*, **92**, 6702 (1970).

(3) F. A. Cotton and R. A. Schunn, *ibid.*, **85**, 2394 (1963).

