$$k_{obsd} = \frac{k_1[OH^-][k_2 + k_3K[OH^-]]}{k_{-1} + k_2 + k_3K[OH^-]} \quad (3)$$

The value of k_{-1}/k_2 could be estimated by a procedure described as follows. In the scheme, k_{-1} and k_2 represent the rate constants for the expulsion of leaving groups OH (pK_a of H_2O is 15.7) and RNH (pK_a of RNH_2 is ~27), respectively. The pK_a of $C_6H_5NH_2$ is 27,[18] and σ_I values for C_6H_5 and CH_2CH_2Br are nearly same (Appendix). The push provided by the other groups attached to the reaction center in the expulsion of the leaving groups in the k_{-1} step and k_2 step may be expected to be same, but the higher acidity of H_2O compared to that of RNH_2 could result in k_{-1} being significantly larger than k_2. However, the relatively larger leaving ability of OH group compared to RNH group from **2**, based on the difference of pK_a of their conjugate acids, could be partially off set by the larger carbon basicity of oxyanions than that of amines, for a given proton basicity. It may be worth mentioning here that an approximate value of k_{-1}/k_2 might be calculated from the Jencks' equation (eq 4),[19] which is derived for

$$\log (k_O/k_N) = -0.9pK_O + 0.7pK_N + C_t \quad (4)$$

acetate esters. In eq 4, $k_O \equiv k_{-1}$ and $k_N \equiv k_2$. If we assume that the eq 4 is valid for the present system, then the ratio k_{-1}/k_2 may be estimated to be 2.5×10^2 considering $pK_O = 15.7$, $pK_N = 27$, and $C_t = -2.40$. Although this analysis is far from exact, it indicates that $k_{-1} > k_2$.

It appears from structures **2** and **3** that k_3 may be larger than k_2 because of the relatively larger push experienced by the leaving group in the k_3 step. But $K[OH^-]$ should be far less than unity because $K = (K_a/K_w)[H_2O]$ where K_a is the ionization constant of the hydroxyl group of **2**. The value of K_a is estimated to be significantly smaller than K_w (Appendix). Thus, it may not be unreasonable to assume that $k_3K[OH^-]$ might not be very different from k_2 even at the highest concentration of $[OH^-]$ attained in the present study. These conclusions lead to a conceivable assumption that $k_{-1} > (k_2 + k_3K[OH^-])$, and application of this assumption reduces eq 3 to eq 5. Similar as-

$$k_{obsd} = (k_1/k_{-1})[k_2 + k_3K[OH^-]][OH^-] \quad (5)$$

sumption has been considered recently by Young et al.[20] to explain the observed k_{obsd}–$[OH^-]$ profile for the cleavage of dichloro-*N*-methylacetanilide. Equation 5 is similar to eq 2 with $A = k_1k_2/k_{-1}$ and $B = k_1k_3K/k_{-1}$. The observed value of k_1k_2/k_{-1} of 5.03×10^{-3} M^{-1} s^{-1} may be compared with the hydroxide ion catalyzed bimolecular rate constants, k_{OH}, for aqueous cleavages of benzamide ($k_{OH} = 1.5 \times 10^{-3}$ M^{-1} s^{-1} at 100.4 °C)[21] and phthalamic acid ($k_{OH} = 5.9 \times 10^{-5}$ M^{-1} s^{-1} at 85 °C).[14] The estimated value of k_{-1}/k_2 of 2.5×10^2 could be used to calculate k_1 from the observed value of A and the value thus obtained is ~1.2 M^{-1} s^{-1}. The value of k_1 of 1.2 M^{-1} s^{-1} is ~18 times smaller than the k_1' (21.9 M^{-1} s^{-1}) obtained for the cleavage of NBPH. Although the estimated value of k_{-1}/k_2 is not very reliable, the ratio k_1'/k_1 of ~18 is not unreasonable because hydroxide ion attack at carbonyl carbon may not be very sensitive to the pK_a of the leaving group.

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Appendix

Estimation of pK_a of Hydroxyl Group of 2. Following the approach of Fox and Jencks,[22] the approximate pK_a of the hydroxyl group of species **2** has been estimated as follows. The values of σ_I for $NHCH_2CH_2Br$ and *o*-$O_2CC_6H_4^-$ substituents are not known and the value of σ_I for O^- substituent is –0.12.[23] On the basis of values of σ_I for NH_2, $NHNH_2$, NMe_2, and CH_2CH_2Br of 0.12, 0.15, 0.06, and 0.08, respectively, it may not be unreasonable to take σ_I for $NHCH_2CH_2Br$ as 0.14 which is between the values of σ_I for NH_2 and $NHNH_2$. [The value of σ_I for Br is 0.44, and making the allowance of falloff factor of 2.0 per methylene group,[22] σ_I for CH_2CH_2Br could be estimated to be 0.11. But σ_I for Cl is 0.46 and σ_I for CH_2Cl is 0.17, which indicate that the falloff factor is ~2.7. Using this value of falloff factor, σ_I for CH_2CH_2Br was found to be 0.06. The average value (0.08) of 0.11 and 0.06 could be considered as the appropriate value of σ_I for CH_2CH_2Br.] Again, on the basis of a pK_a of 15.7 for CH_3OH[24] and σ_I of –8.2,[22] correction for O^-, $NHCH_2CH_2Br$ and C_6H_5 substituents ($-8.2 \times (-0.12 + 0.14 + 0.10) = -1.0$) gives a pK_a of 14.7 for hydroxyl group of $O^-C(C_6H_5)(NHCH_2CH_2Br)OH$. The replacement of *o*-H by *o*-CO_2^- may be assumed to increase pK_a of the hydroxyl group of $O^-C(C_6H_5)(NHCH_2CH_2Br)OH$ by ~1.3 pK, the difference between pK_2 of phthalic acid (5.51)[25] and pK_a of benzoic acid (4.19).[25] Thus, the estimated pK_a of the hydroxyl group of **2** is 16.0 (=14.7 + 1.3). Although the estimated value of 16 for pK_a of hydroxyl group of **2** is not very reliable for various reasons such as relatively unreliable value of σ_I for the electrically charged group[23] O^-, it certainly indicates that $pK_a > pK_w$.

Registry No. 1, 98945-49-4.

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Addition of Cyclopropylphosphonates to Aldehydes

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Cyclopropylphosphonates are not easily obtainable by C–P bond-forming reactions,[1] and their synthetic application has scarcely been investigated. The previous paper[2] described the reductive phosphonation of *gem*-dibromocyclopropanes with trialkyl phosphite, triethylamine, and water to afford dialkyl cyclopropylphosphonates under mild reaction conditions. We now report the reaction of

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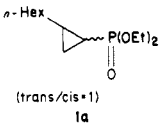
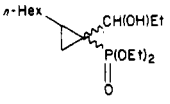
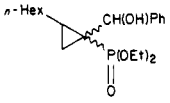
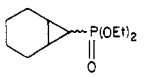
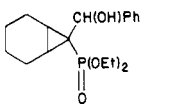
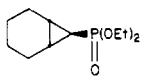
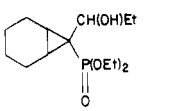
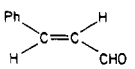
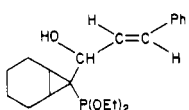
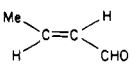
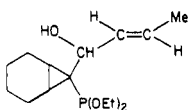
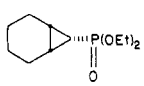
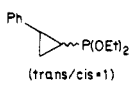
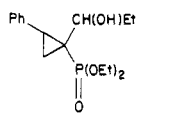
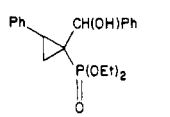
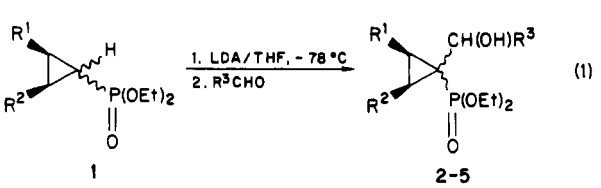
0022-3263/85/1950-5860$01.50/0

Table I. Reaction of 1 with Aldehydes

1	R^3CHO	product	yield, %
 (trans/cis = 1) **1a**	EtCHO	 **2a**	72
1a	PhCHO	 **3a**	90
 **1b**	PhCHO	 **3b**	81
 *exo*-**1b**	EtCHO	 **2b**	97
exo-**1b**		 **4b**	92
exo-**1b**		 **5b**	86
 *endo*-**1b**	EtCHO	**2b**	66
 (trans/cis = 1) **1c**	EtCHO	 **2c**	26
1c	PhCHO	 **3c**	30

cyclopropylphosphonate anions with electrophiles.

Generation of a carbanion at the α-position was achieved by treatment of the cyclopropylphosphonate with lithium diisopropylamide at −78 °C (eq 1). The carbanions derived from a mixture of diethyl *trans*- and *cis*-2-*n*-hexylcyclopropylphosphonates **1a** were trapped with chlorotrimethylsilane to produce the corresponding α-silylated cyclopropylphosphonates in 94% yield. As shown in Table I, the carbanion of **1a** reacted with propionaldehyde yielding a mixture of the *trans*- and *cis*-1-(hydroxymethyl)cyclopropylphosphonates **2a** and not the expected olefin. The addition of a mixture of *endo*- and *exo*-7-

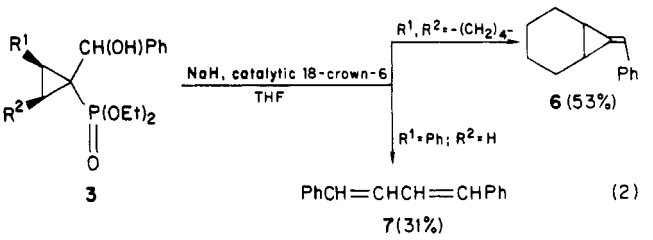


1 **2-5** (1)

(diethylphosphono)norcarane (**1b**) to benzaldehyde gave, however, only one isomer **3b** whose geometry has not yet been determined. No other adduct was detected. A similar stereoselectivity was observed in the reactions of *endo*-**1b** or *exo*-**1b** with propionaldehyde, which gave the same product **2b**. The selectivity seems to depend on the nature of the substituent on the cyclopropylphosphonate because the reaction of the phosphonate mixture **1c** (*trans*/*cis* = 1) also resulted in selective formation of only one isomer **3c**. The low yield in this reaction is due to low reactivity of **1c** because the unreacted phosphonate was recovered.

Treatment of the anion of *exo*-**1b** with α,β-unsaturated aldehydes (cinnamaldehyde or crotonaldehyde) gave only the 1,2 adduct **4b** or **5b**, respectively. The geometry of the aldehyde used was retained. Acetone, acetyl chloride, acetic anhydride, and ethyl acetate were not sufficiently electrophilic to add to the anion of *endo*-**1b**, which was isomerized to the exo isomer after workup. This indication that the anions of the trans and cis isomers equilibrate was confirmed by conversion (98%) of *endo*-**1b** into *exo*-**1b** on treatment with lithium diisopropylamide at −78 °C followed by workup at the same temperature. Thus, the isomerization may be responsible for the stereoselectivity of the addition reactions, with the aldehyde attacking the more stable anion.

The elimination of $^-OP(O)(OEt)_2$ in the Emmons–Horner olefination reaction generally requires the presence of an electron-withdrawing group at the α-position, but conversion of **3b** to 7-benzylidenenorcarane (**6**) was successfully performed by treatment with NaH and a catalytic amount of 18-crown-6[3] in THF. No elimination occurred in the absence of 18-crown-6. Under the same condition, **3c** underwent ring cleavage as well as elimination to produce 1,4-diphenyl-1,3-butadiene (**7**) (eq 2).



3 (2)

Experimental Section

General Procedure for the Preparation of Diethyl 1-(Hydroxymethyl)cyclopropylphosphonates 2–5. To a solution of *n*-BuLi (1.6 M in hexane, 2.4 mmol) in THF (15 mL) was added diisopropylamine (0.34 mL, 2.4 mmol) at −78 °C. Stirring was continued for 30 min at this temperature. The cyclopropylphosphonate **1** (2.0 mmol) in THF (5 mL) was added dropwise to the resulting solution. After the solution was kept at −78 °C for 1 h with stirring, an aldehyde (6.0 mmol) was added dropwise over 10 min. The resultant mixture was stirred at −78 °C for 2 h and then warmed up to room temperature. Saturated NH_4Cl solution (10 mL) was added to the mixture, which was extracted with ether (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was flash chromatographed to give **2–5**. The results are summarized in Table I. ^1H NMR spectra were determined at 90 MHz.

2a: IR (neat) 3620–3120, 1210, 1020, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.2 (m, 27 H), 2.7–3.4 (m, 2 H), 4.13 (quintet, 4 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.8, 16.1, 16.4, 19.9, 20.6, 22.4, 22.8, 22.9, 27.6, 27.7, 28.0, 28.6, 28.8, 29.0, 29.2, 29.5, 31.6, 61.3, 61.6, 62.0, 62.2, 74.8, 75.0; MS, m/e 320 (M^+). Anal. Calcd for $C_{16}H_{33}O_4P$: C, 59.98; H, 10.38; P, 9.67. Found: C, 60.12; H, 10.03; P, 9.85.

2b: IR (neat) 3680–3120, 1200, 1020, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.2 (m, 12 H), 1.03 (t, 3 H, J = 7.2 Hz), 1.31 (dt, 6 H, J = 6.8, 2.7 Hz), 3.1–3.7 (m, 2 H), 4.10 (quintet, 4 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 11.4, 16.0, 16.2, 17.2, 17.4, 17.5, 17.7, 18.2, 18.4, 18.5, 21.5, 21.7, 21.8, 22.7, 29.6, 29.8, 30.6, 61.1, 61.4,

61.9, 62.2, 71.0, 71.2; MS, *m/e* 290 (M^+). Anal. Calcd for $C_{14}H_{27}O_4P$: C, 57.92; H, 9.37; P, 10.67. Found: C, 58.05; H, 9.52; P, 10.58.

2c: IR (neat) 3640–3160, 1220, 1020, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.2 (m, 13 H), 2.2–3.4 (m, 3 H), 3.9–4.4 (quintet, 4 H, J = 7.2 Hz), 7.0–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 12.6, 12.8, 15.7, 16.1, 22.5, 26.8, 26.9, 28.8, 28.9, 30.5, 61.3, 61.5, 61.7, 62.0, 73.5, 73.7, 125.6, 126.5, 127.7, 135.1, 135.2; MS, *m/e* 312 (M^+). Anal. Calcd for $C_{16}H_{25}O_4P$: C, 61.53; H, 8.07; P, 9.92. Found: C, 61.37; H, 8.33; P, 10.02.

3a: IR (neat) 3600–3120, 1220, 1020, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.1, (m, 22 H), 3.3–4.7 (m, 6 H), 7.1–7.6 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 15.7, 16.0, 21.8, 22.4, 22.6, 22.8, 22.9, 27.9, 28.0, 28.9, 29.4, 29.8, 30.5, 31.6, 61.1, 61.2, 61.5, 61.8, 73.4, 73.5, 125.8, 126.6, 127.5, 143.0, 143.1; MS, *m/e* 368 (M^+). Anal. Calcd for $C_{20}H_{33}O_4P$: C, 65.20; H, 9.03; P, 8.41. Found: C, 65.11; H, 8.95; P, 8.32.

3b: IR (neat) 3680–3100, 1200, 1020, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.5 (m, 16 H), 3.1–5.3 (m, 6 H), 7.1–7.7 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.9, 16.2, 18.2, 18.3, 18.8, 19.0, 19.2, 19.4, 20.4, 20.6, 21.9, 25.1, 33.1, 61.3, 61.5, 61.6, 61.8, 69.8, 70.0, 126.3, 126.6, 127.7, 142.8; MS, *m/e* 338 (M^+). Anal. Calcd for $C_{18}H_{27}O_4P$: C, 63.89; H, 8.05; P, 9.15. Found: C, 64.09; H, 8.08; P, 9.30.

3c: IR (neat) 3540–3140, 1230, 1020, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–1.8 (m, 8 H), 2.6–3.2 (m, 1 H), 3.4–4.3 (m, 6 H), 7.0–7.6 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.7, 15.5, 15.8, 24.0, 27.1, 32.1, 61.2, 61.5, 72.3, 72.4, 125.7, 126.4, 126.6, 127.1, 127.7, 129.2, 134.9, 135.0, 142.6; MS, *m/e* 360 (M^+). Anal. Calcd for $C_{20}H_{25}O_4P$: C, 66.66; H, 6.99; P, 8.60. Found: C, 66.45; H, 6.76; P, 8.91.

4b: IR (neat) 3620–3080, 1210, 1020, 960, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–2.3 (m, 16 H), 3.8–4.6 (m, 6 H), 6.43 (dd, 1 H, J = 16.0, 4.0 Hz), 6.73 (d, 1 H, J = 16.0 Hz), 7.1–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 16.1, 16.4, 17.4, 17.5, 17.9, 18.1, 18.3, 18.7, 18.8, 21.6, 21.7, 21.9, 22.0, 23.2, 31.1, 61.7, 62.0, 62.3, 69.2, 69.3, 126.3, 127.2, 128.4, 129.1, 131.1, 131.2, 137.1; MS, *m/e* 364 (M^+). Anal. Calcd for $C_{20}H_{29}O_4P$: C, 65.92; H, 8.02; P, 8.50. Found: C, 65.88; H, 7.93; P, 8.65.

5b: IR (neat) 3620–3160, 1230, 1020, 960, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.0 (m, 19 H), 3.7–4.4 (m, 6 H), 5.5–6.0 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.0, 16.2, 17.1, 17.4, 17.7, 17.8, 18.2, 18.4, 21.6, 22.6, 30.5, 61.3, 61.6, 61.9, 69.0, 69.2, 125.0, 132.4; MS, *m/e* 302 (M^+). Anal. Calcd for $C_{15}H_{27}O_4P$: C, 59.59; H, 9.00; P, 10.25. Found: C, 59.82; H, 8.82; P, 10.37.

Isomerization of *endo*-1b. The endo phosphonate **1b** (0.116 g, 0.5 mmol) was treated with lithium diisopropylamide (0.75 mmol) in THF at −78 °C for 1 h as mentioned above and then worked up with dilute HCl (aq) at the same temperature. After the extraction with ether (3 × 10 mL), the combined organic layers were washed with saturated $NaHCO_3$ solution and dried ($MgSO_4$). Evaporation gave *exo*-**1b** (98% conversion).

Preparation of 7-Benzylidenenorcarane (6). To a suspension of NaH (0.93 mmol, washed with *n*-hexane) in THF (10 mL) was added **3b** (0.242 g, 0.715 mmol) in THF (5 mL) dropwise at room temperature. Then, a catalytic amount of 18-crown-6 was added to the reaction mixture which was stirred for 5 h at reflux. The mixture was poured into water (5 mL), which was extracted with ether (3 × 30 mL). The combined organic layers were washed with saturated $NaHSO_4$ solution and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on a silica gel column to give **6** in 53% yield.

Preparation of 1,4-Diphenyl-1,3-butadiene (7). The reaction of **3c** was carried out similarly as mentioned above to give **7** in 31% yield.

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Registry No. *cis*-**1a**, 89352-07-8; *trans*-**1a**, 89352-11-4; *endo*-**1b**, 89352-12-5; *exo*-**1b**, 89352-08-9; *cis*-**1c**, 89352-09-0; *trans*-**1c**, 89352-13-6; *cis*-**2a**, 99327-86-3; *trans*-**2a**, 99327-85-2; **2b**, 99342-36-6; **2c**, 99327-92-1; *cis*-**3a**, 99327-87-4; *trans*-**3a**, 99327-88-5; **3b**, 99327-89-6; **3c**, 99327-93-2; **4b**, 99327-90-9; **5b**, 99327-91-0; **6**, 82253-12-1; **7**, 886-65-7; LDA, 4111-54-0; EtCHO, 123-38-6; PhCHO, 100-52-7; (*E*)-3-phenyl-2-pentenal, 14371-10-9; (*E*)-2-butenal, 123-73-9.

Electron Spin Resonance Spectroscopic Study of New Persistent Nitrogen-Centered Free Radicals: *N*-(Arylthio)-4-toluenesulfonamidyls[1]

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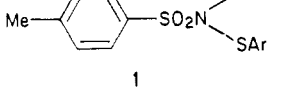
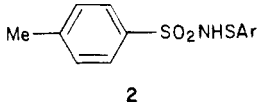
In contrast to a number of the electron spin resonance (ESR) spectroscopic studies of sulfonamidyl ($RSO_2\dot{N}R'$)[2] and *N*-alkoxysulfonamidyl radicals ($RSO_2\dot{N}OR'$),[3-5] there has appeared no ESR study of *N*-thiosulfonamidyl radicals ($RSO_2\dot{N}SR'$) in the literature.[6] We have recently studied a variety of *N*-(alkylthio)- and *N*-(arylthio)aminyl radicals ($R\dot{N}SR'$) by ESR spectroscopy.[1] These radicals are essentially fairly long-lived in solution since they are significantly stabilized by the conjugative electron delocalization from the nitrogen to the sulfur ($-\dot{N}-\ddot{S}- \leftrightarrow -\ddot{N}^- - \dot{S}^+-$), and some sterically protected *N*-thioaminyl radicals can be isolated as radical crystals[8] or hydrazine dimers.[9] To continue our interest in ESR studies on *N*-thioaminyl radicals, we dealt with *N*-thiosulfonamidyl radicals. In the radicals a donor (sulfenyl) and an acceptor (sulfonyl) group are both attached directly to the radical center, and for such a structure of radical captodative radical stabilization substituent effects might be expected.[10,11] In this paper we report the first ESR study of *N*-thiosulfonamidyl radicals.

The *N*-thiosulfonamidyl radicals treated in this work are *N*-(arylthio)-4-toluenesulfonamidyls (**3**), which have been



1



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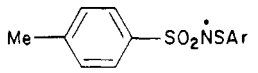

3

a, Ar = Ph **c**, Ar = 4-MeC_6H_4 **e**, Ar = 4-ClC_6H_4
b, Ar = C_6D_5 **d**, Ar = 4-$MeOC_6H_4$ **f**, Ar = 4-$NO_2C_6H_4$

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(11) Since, however, sulfonyl groups have little or no ability to delocalize the unpaired electron as mentioned below, the present case may not belong to the category of the true captodative substituent effects.

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