4:1) and afforded isopropyl *p*-methoxybenzoate (16.7 mg, 4.3%) and isopropyl *p*-methoxyphenylglyoxylate (134 mg, 30.1%).

α-Keto esters and esters thus obtained were characterized by ^{1}H NMR, IR, MS, and elemental analysis. Satisfactory data were obtained in all cases. Unless otherwise stated, the yield of keto ester and ester was estimated by GC analysis of reaction mixtures with an internal standard (based on halide charged). The spectral and analytical data of isolated keto esters are shown below.

Methyl phenylglyoxylate: IR (neat) 1735 (CO_2Me), 1687 (PhCO) cm^{-1}; NMR δ 3.97 (s, 3 H, Me), 7.4–8.2 (m, 5 H, Ph).

Ethyl phenylglyoxylate: IR (neat) 1737 (CO_2Et), 1685 (PhCO) cm^{-1}; NMR δ 1.41 (t, J = 7 Hz, 3 H, CH_3), 4.45 (q, J = 7 Hz, 2 H, CH_2), 7.4–8.2 (m, 5 H, Ph).

***n*-Butyl phenylglyoxylate**: IR (neat) 1733 (CO_2Bu), 1690 (PhCO) cm^{-1}; NMR δ 0.97 (t, J = 7 Hz, 3 H, CH_3), 1.15–2.0 (m, 4 H, CH_2CH_2), 4.41 (t, J = 7 Hz, 2 H, CH_2O), 7.4–8.2 (m, 5 H, Ph); MS, m/e (relative intensity) 206 (M^+, 0.2), 105 ($PhCO^+$, 100), 77 (Ph^+, 38).

Isobutyl phenylglyoxylate: IR (neat) 1733 (CO_2-*i*-Bu), 1688 (PhCO) cm^{-1}; NMR δ 1.00 (d, J = 7 Hz, 6 H, CH_3), 2.10 (m, 1 H, CH), 4.19 (d, J = 7 Hz, 2 H, CH_2), 7.4–8.15 (m, 5 H, Ph); MS, m/e (relative intensity) 206 (M^+, 0.2), 105 ($PhCO^+$, 100), 77 (Ph^+, 34).

***sec*-Butyl phenylglyoxylate**: IR (neat) 1741 (CO_2-*sec*-Bu), 1683 (PhCO) cm^{-1}; NMR δ 0.98 (t, J = 7 Hz, 3 H, CH_3CH_2), 1.38 (d, J = 6 Hz, 3 H, CH_3CH), 1.73 (m, 2 H, CH_2), 5.18 (m, 1 H, CH), 7.4–8.15 (m, 5 H, Ph); MS, m/e (relative intensity) 206 (M^+, 0.1), 105 ($PhCO^+$, 100), 77 (Ph^+, 45).

Neopentyl phenylglyoxylate: bp 86 °C (0.15 mmHg) (Kugelrohr); IR (neat) 1731 (CO_2R), 1685 (PhCO) cm^{-1}; NMR δ 1.00 (s, 9 H, *t*-Bu), 4.10 (s, 2 H, CH_2), 7.4–8.15 (m, 5 H, Ph); MS, m/e (relative intensity) 220 (M^+, 0.1), 105 ($PhCO^+$, 100), 77 (Ph^+, 30). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.83; H, 7.34.

Cyclohexyl phenylglyoxylate: IR (neat) 1729 (CO_2R), 1686 (PhCO) cm^{-1}; NMR δ 1.0–2.3 (m, 10 H, $(CH_2)_5$), 4.9–5.3 (m, 1 H, CH), 7.3–8.2 (m, 5 H, Ph); MS, m/e (relative intensity) 105 ($PhCO^+$, 72), 83 ($C_6H_{11}^+$, 59), 77 (Ph^+, 34), 55 (100).

α-Phenethyl phenylglyoxylate: IR (neat) 1727 (CO_2R), 1682 (PhCO) cm^{-1}; NMR δ 1.70 (d, J = 7 Hz, 3 H, Me), 6.20 (q, J = 7 Hz, CH), 7.25–8.05 (m, 10 H, Ph); MS, m/e (relative intensity) 105 ($PhCO^+$, 100), 77 (Ph^+, 34).

Pinacolyl phenylglyoxylate: IR (neat) 1730 (CO_2R), 1690 (PhCO) cm^{-1}; NMR δ 0.97 (s, 9 H, *t*-Bu), 1.33 (d, J = 7 Hz, 3 H, Me), 5.03 (q, J = 7 Hz, 1 H, CH), 7.4–8.1 (m, 5 H, Ph).

Isopropyl phenylglyoxylate: IR (neat) 1724 (CO_2R), 1682 (PhCO) cm^{-1}; NMR δ 1.40 (d, J = 6 Hz, 6 H, Me), 5.33 (m, 1 H, CH), 7.3–8.1 (m, 5 H, Ph); MS, m/e (relative intensity) 192 (M^+, 0.3), 105 ($PhCO^+$, 100), 77 (Ph^+, 78).

Isopropyl [*p*-(isopropoxycarbonyl)phenyl]glyoxylate: bp 122 °C (0.1 mmHg) (Kugelrohr); IR (neat) 1728, 1721 (CO_2R), 1698 (ArCO) cm^{-1}; NMR δ 1.39 (d, J = 6 Hz, 6 H, Me), 1.42 (d, J = 6 Hz, 6 H, Me), 5.30 (m, 1 H, CH), 5.35 (m, 1 H, CH), 8.12 (d, J = 8 Hz, 2 H, Ar), 8.16 (d, J = 8 Hz, 2 H, Ar). Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.99; H, 6.62.

Isopropyl (*p*-chlorophenyl)glyoxylate: bp 74 °C (0.08 mmHg) (Kugelrohr); IR (neat) 1731 (CO_2R), 1688 (ArCO) cm^{-1}; NMR δ 1.40 (d, J = 6 Hz, 6 H, Me), 5.33 (m, 1 H, CH), 7.51 (d, J = 9 Hz, 2 H, Ar), 7.99 (d, J = 9 Hz, 2 H, Ar). Anal. Calcd for $C_{11}H_{11}ClO_3$: C, 58.29; H, 4.89. Found: C, 58.12; H, 4.85.

Isopropyl *p*-tolylglyoxylate: bp 136 °C (15 mmHg) (Kugelrohr); IR (neat) 1730 (CO_2R), 1680 (ArCO) cm^{-1}; NMR δ 1.40 (d, J = 6 Hz, 6 H, Me_2C), 2.43 (s, 3 H, MeC_6H_4), 5.33 (m, 1 H, CH), 7.33 (d, J = 8 Hz, 2 H, Ar), 7.92 (d, J = 8 Hz, 2 H, Ar). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.69; H, 6.85.

Isopropyl *p*-anisylglyoxylate: bp 130 °C (0.1 mmHg) (Kugelrohr); IR (neat) 1727 (CO_2R), 1675 (ArCO) cm^{-1}; NMR δ 1.40 (d, J = 6 Hz, 6 H, Me_2C), 3.89 (s, 3 H, MeO), 5.32 (m, 1 H, CH), 6.98 (d, J = 9 Hz, 2 H, Ar), 8.00 (d, J = 9 Hz, 2 H, Ar). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.67; H, 6.34.

Isopropyl (*p*-cyanophenyl)glyoxylate: bp 106 °C (0.19 mmHg) (Kugelrohr); IR (neat) 2228 (CN), 1723 (CO_2R), 1692 (ArCO) cm^{-1}; NMR δ 1.42 (d, J = 6 Hz, 6 H, Me), 5.35 (m, 1 H, CH), 7.86 (d, J = 8.5 Hz, 2 H, Ar), 8.19 (d, J = 8.5 Hz, 2 H, Ar). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10. Found: C, 65.99; H, 5.09.

Isopropyl 2-thienylglyoxylate: bp 122 °C (12 mmHg) (Kugelrohr); IR (neat) 1725 (CO_2R), 1657 (ArCO) cm^{-1}; NMR δ 1.39 (d, J = 6 Hz, 6 H, Me), 5.29 (m, 1 H, CH), 7.21 (dd, J = 4.8 and 4.0 Hz, 1 H, C_4H_3S), 7.83 (dd, J = 4.8 and 1.2 Hz, 1 H, C_4H_3S), 8.13 (dd, J = 4.0 and 1.2 Hz, 1 H, C_4H_3S). Anal. Calcd for $C_9H_{10}O_3S$: C, 54.53; H, 5.08. Found: C, 54.45; H, 5.10.

Isopropyl 5-thiazolylglyoxylate: bp 114 °C (10 mmHg) (Kugelrohr); IR (neat) 1720 (CO_2R), 1677 (ArCO) cm^{-1}; NMR δ 1.43 (d, J = 6 Hz, 6 H, Me), 5.30 (m, 1 H, CH), 8.91 (s, 1 H, C_3H_2NS), 9.13 (s, 1 H, C_3H_2NS). Anal. Calcd for $C_8H_9NO_3S$: C, 48.23; H, 4.55. Found: C, 48.00; H, 4.58.

Isopropyl β-styrylglyoxylate: bp 125 °C (0.05 mmHg) (Kugelrohr); IR (neat) 1724 (CO_2R), 1695 (RCO), 1665 (C=C) cm^{-1}; NMR δ 1.38 (d, J = 6 Hz, 6 H, Me), 5.23 (m, 1 H, CHO), 7.2–7.75 (m, 5 H, Ph), 7.32 (d, J = 16 Hz, 1 H, C=CH), 7.87 (d, J = 16 Hz, 1 H, C=CH). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.38; H, 6.51.

Registry No. THF, 109-99-9; DMF, 68-12-2; HMPA, 680-31-9; dppp, 6737-42-4; $PdCl_2(PPh_3)_2$, 13965-03-2; *p*-$MeOC_6H_4CO_2Pr$-*i*, 6938-38-1; *p*-$MeOC_6H_4COCO_2Pr$-*i*, 101128-44-3; $PhCOCO_2Me$, 15206-55-0; $PhCOCO_2Et$, 1603-79-8; $PhCOCO_2Bu$, 5524-55-0; $PhCOCO_2Bu$-*i*, 31197-67-8; $PhCOCO_2Bu$-*sec*, 95653-53-5; $PhCOCO_2CH_2Bu$-*t*, 101128-42-1; $PhCOCO_2C_6H_{11}$, 61598-01-4; $PhCOCO_2CHMePh$, 93011-90-6; $PhCOCO_2Pr$-*i*, 31197-66-7; *p*-(*i*-Pr)$O_2CC_6H_4COCO_2Pr$-*i*, 111160-42-0; *p*-$ClC_6H_4COCO_2Pr$-*i*, 30565-44-7; *p*-$MeC_6H_4COCO_2Pr$-*i*, 101128-43-2; *p*-$NCC_6H_4COCO_2Pr$-*i*, 111160-43-1; $PhCH{=}CHCOCO_2Pr$-*i*, 111160-44-2; *p*-$MeOC_6H_4I$, 696-62-8; PhI, 591-50-4; *p*-(*i*-Pr)$O_2CC_6H_4I$, 111160-45-3; *p*-ClC_6H_4I, 637-87-6; *p*-MeC_1H_4I, 624-31-7; *p*-NCC_1H_4I, 3058-39-7; $PhCH{=}CHI$, 101349-79-5; *i*-PrOH, 67-63-0; MeOH, 67-56-1; EtOH, 64-17-5; BuOH, 71-36-3; *i*-BuOH, 78-83-1; *sec*-BuOH, 78-92-2; *t*-$BuCH_2OH$, 75-84-3; $C_6H_{11}OH$, 108-93-0; PhMeCHOH, 98-85-1; CO, 630-08-0; NEt_3, 121-44-8; *t*-BuOH, 75-65-0; $PhCH_2OH$, 100-51-6; PhOH, 108-95-2; *t*-BuMeCHOH, 464-07-3; PPh_3, 603-35-0; NEt_2Ph, 91-66-7; NMe_3, 75-50-3; $NMe(CH_2)_4$, 120-94-5; NPr_3, 102-69-2; NBu_3, 102-82-9; $NMe(i\text{-}Pr)_2$, 10342-97-9; $NEt(i\text{-}Pr)_2$, 7087-68-5; $NMe(C_6H_{11})_2$, 7560-83-0; $NMe_2(C_6H_{11})$, 98-94-2; CH_2Cl_2, 75-09-2; CH_3CN, 75-05-8; PhBr, 108-86-1; $PhCH_2Cl$, 100-44-7; $P(p\text{-}MeOC_6H_4)_3$, 855-38-9; $P(p\text{-}MeC_6H_4)_3$, 1038-95-5; $PPh(p\text{-}MeC_6H_4)_2$, 19934-95-3; $PPh_2(p\text{-}MeC_6H_4)$, 1031-93-2; $P(p\text{-}PhC_6H_4)_3$, 13885-05-7; $P(p\text{-}FC_6H_4)_3$, 18437-78-0; PCy_2Ph, 6476-37-5; PCy_3, 2622-14-2; $P(Pr\text{-}i)_3$, 6476-36-4; $PCyPh_2$, 6372-42-5; $PEtPh_2$, 607-01-2; $PPh_2(o\text{-}Tol)$, 5931-53-3; $P(OPh)_3$, 101-02-0; $PPh(o\text{-}Tol)_2$, 18803-09-3; PMe_2Ph, 672-66-2; $P(o\text{-}Tol)_3$, 6163-58-2; $P(C_6F_5)_3$, 1259-35-4; PBu_3, 998-40-3; PMe_3, 594-09-2; $P(OMe)_3$, 121-45-9; $P(OCH_2)_3CEt$, 111160-46-4; $PPh_2(OEt)$, 719-80-2; $PhCO_2Pr$-*i*, 939-48-0; *p*-(*i*-Pr)$O_2CC_6H_4CO_2Pr$-*i*, 6422-84-0; *p*-$ClC_6H_4CO_2Pr$-*i*, 22913-11-7; *p*-$MeC_6H_4CO_2Pr$-*i*, 19277-55-5; $PhCH_2CO_2Pr$-*i*, 4861-85-2; *p*-$NCC_6H_4CO_2Pr$-*i*, 29240-33-3; $PhCH{=}CHCO_2Pr$-*i*, 7780-06-5; pinacolyl phenylglyoxylate, 40121-97-9; isopropyl 2-thienylglyoxylate, 31697-81-1; isopropyl 5-thiazolylglyoxylate, 101128-45-4; 2-iodothiophene, 3437-95-4; 5-bromothiazole, 3034-55-7; pinacolyl alcohol, 464-07-3; hexane, 110-54-3; benzene, 71-43-2; isopropyl 2-thienecarboxylate, 111160-47-5; isopropyl 5-thiazolecarboxylate, 111160-48-6.

The Correct Structure of the Base $C_{12}H_{17}NO$, a Product of Cyclization of Tris(γ-chlorocrotyl)amine

M. Hudlický*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24060

F. K. Ross

Research Reactor, University of Missouri, Columbia, Missouri 65211

Received May 11, 1987

In 1948, one of us (M.H.) published a paper on the structure of an artifact resulting from the action of concentrated sulfuric acid on tris(γ-chlorocrotyl)amine (eq 1).[1]

0022-3263/87/1952-5740$01.50/0

Table I. Compounds Derived from 2 Incorrectly Formulated[1] on Basis of Structure 1 for $C_{12}H_{17}NO$

compd.[a]	reagent	formula[b]	mp, °C (deriv)
XI	Wolff-Kishner[c] redn	$C_{12}H_{19}N$[d]	210–211 (picrate)
XV	Meerwein–Ponndorf redn	$C_{12}H_{19}NO$	102–103, 194–195 (picrate)
XIX	$KMnO_4$		280–285°
unmarked	Clemmensen redn	$C_{12}H_{19}NO$[e]	221–222 (picrate), 182 (oxime)
XIV	O_3	$C_9H_{15}NO_5$	220–240 dec, 280 dec (oxime)
XVI	$4NaHg_x$	$C_{12}H_{21}NO$[f]	225–227 (picrate)
unmarked	$2NaHg_x$ after Clemmensen redn		188–190 (oxime)
X	$2NaHg_x$	$C_{12}H_{19}NO$[g]	52–53, 241–242 (picrate), 196–197 (oxime)
VIII	O_3 on X	$C_{12}H_{19}NO_5$	230–235 dec (titration equiv 128)
XXI	Wolff-Kishner[c] on X	*h*	237 (picrate)
XVII	Br_2	$C_{12}H_{19}Br_2NO$	202–203
XVIII	H_2/PtO_2		122, 234–235 (picrate)
XX	H_2O_2	$C_{12}H_{19}NO_2$	102–103, 235–247 (picrate)

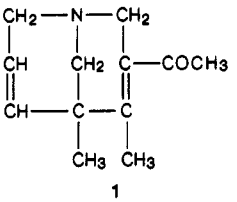
[a] Compound number in ref 1. [b] Correct elemental analysis. [c] Kizhner, according to the Russian transliteration. [d] Bp 119–121 °C (21 mm). [e] Bp 133–135 °C (5 mm). [f] Bp 162–163 °C (5 mm). [g] Bp 140–142 °C (5 mm). [h] Bp 95–96 °C (3 mm).

Under such conditions, vinylic halides are converted to ketones (Wichterle reaction)[2] (eq 2). With two γ-chlorocrotyl residues in one molecule, subsequent aldol condensation takes place.[3,4]

$$(CH_3CCl{=}CHCH_2)_3N \xrightarrow{H_2SO_4} C_{12}H_{17}NO \quad (1)$$

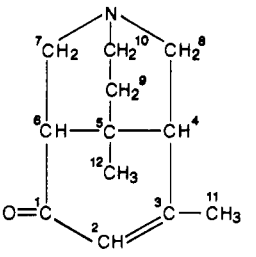
$$CH_3CCl{=}CHCH_2R \xrightarrow{H_2SO_4} CH_3COCH_2CH_2R \quad (2)$$

In the case of three γ-chlorocrotyl groups in one molecule, aldol condensation was expected to give a rather complicated bicyclic compound. On the basis of the genesis and use of Bredt's rule for sorting out some possibilities, two structures were considered for the product of the reaction with sulfuric acid. However, the results of ozonolysis could not be reconciled with either of them, and an amended structure 1 was proposed. This structure, which was consistent with the results of the ozonolysis, assumed a rearrangement of one methyl group in the medium of concentrated sulfuric acid.



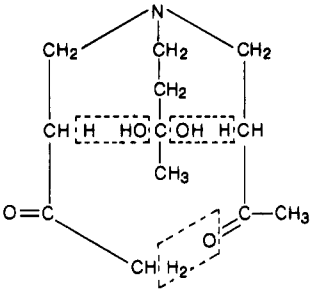
1

In an attempt to verify the structure, spectral analysis of the compound was carried out. IR spectra were in agreement with the proposed structure of an α,β-unsaturated ketone (1710 cm^{-1} for C=O, 1670 cm^{-1} for conjugated C=C). However, ^1H NMR showed the presence of only two methyl groups and of only one vinylic hydrogen. Even more conclusive was the ^{13}C NMR INEPT spectra which showed the presence of three quaternary, three tertiary, four secondary, and two primary carbons. These results were in complete disagreement with the expectations based on structure 1 and led to the revised structure 2, which is in perfect agreement with the NMR data. Final proof of the corrected structure was provided by X-ray diffraction (Tables II–IV and Figures 1 and 2 in supplementary material).



2

Once the structure of the compound was established, it was not difficult to rationalize the formation of the compound. In the aldol condensation of the assumed intermediate triketone 3, one of the carbonyl groups became linked not to one but to two carbons, each adjacent to one carbonyl group. Subsequent intramolecular condensation of the two acetyl groups produced compound 2.



3

Because the structure of the compound originally proposed was proven incorrect, the structures of all the derivatives listed in the original paper have to be corrected. These compounds are listed in Table I. Most of the results of the derivatization are easily accounted for by using the corrected formula, but structures have not been established by spectral data. However, some products of the ozonolysis as suggested in the original paper do not fit the correct structure 1, and additional data are needed.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer 710B spectrophotometer. ^1H NMR spectra were recorded on a Bruker WP 270 instrument and ^{13}C NMR spectra on a Bruker NR 80 spectrophotometer using $CDCl_3$ as the solvent and TMS as the internal standard. Numbers in brackets preceding the ^1H NMR shifts (δ) are the numbers of carbons in formula 2 to which the protons are bound.

The compound $C_{12}H_{17}NO$ was prepared by the method described in the original paper.[1] From 6.75 g of tris(γ-chlorocrotyl)amine treated with 9 mL of 93% sulfuric acid for 69 h at room temperature, 1.25 g (27.4%) of the compound was obtained: bp 102–104 °C (0.2 mm); mp 63–64 °C (after recrystallization from pentane).

Compound 2, 7-aza-2,9-dimethyltricyclo[3.3.1.$2^{7,9}$]undec-2-en-4-one: ^1H NMR δ [2] 5.55 (m, 1 H), [7, 8, 10] 2.72–3.22 (m,

(1) Hudlický, M. *Collect. Czech. Chem. Commun.* **1948**, *13*, 206.
(2) Wichterle, O. *Collect. Czech. Chem. Commun.* **1947**, *12*, 93.
(3) Wichterle, O.; Hudlický, M., *Collect. Czech. Chem. Commun.* **1947**, *12*, 101, 129.
(4) Wichterle, O.; Procházka, J.; Hofman, J. *Collect. Czech. Chem. Commun.* **1948**, *13*, 300.

6 H), [6] 2.08 (m, 1 H), [11] 1.91 (d, J = 1.3 Hz, 3 H), [4] 1.88 (dt, J = 10, 2.3 Hz, 1 H), [9] 1.43–1.52 (m, 2 H), [12] 1.00 (s, 3 H); IR (neat) 3000, 2940, 1710, 1670, 1480, 1415, 1360, 1290, 1080, 1060, 1025 cm^{-1}.

Acknowledgment. We wish to express thanks to Drs. H. M. Bell and H. C. Dorn for valuable discussions of rather complex NMR spectra and to Messrs. G. Iannaccone and W. R. Bebout for recording the spectra. We also recognize partial support from the Department of Energy through a Reactor Sharing Grant at the Univesity of Missouri Research Reactor.

Registry No. 1, 111349-98-5; 2, 111349-99-6; VIII (original), 111350-06-2; X (original), 111350-05-1; X (revised), 111350-15-3; XI (original), 111350-00-6; XI (revised), 111350-12-0; XIV (original), 111350-03-9; XV (original), 111350-01-7; XV (revised), 111350-13-1; XVI (original), 111350-04-0; XVI (revised), 111350-14-2; XVII (original), 111350-07-3; XVIII (original), 111350-08-4; XIX (original), 111350-10-8; XX (original), 111350-09-5; XX (revised), 111350-17-5; XXI (original), 111378-85-9; XXI (revised), 111350-16-4; 1,2,3,6-tetrahydro-3-methyl-3-(1,2-dimethyl-3-oxo-1-butenyl)pyridine, 111350-02-8; 1,2,3,6-tetrahydro-3-methyl-3-(1,2-dimethyl-3-oxobutyl)pyridine, 111350-11-9.

Supplementary Material Available: Tables II–V and Figures 1 and 2, showing details of X-ray crystallography, for $C_{12}H_{17}NO$ (6 pages). Ordering information is given on any current masthead page.

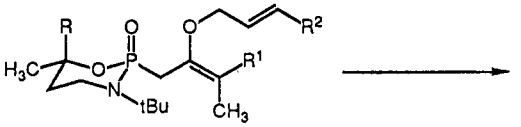
Communications

Carbanion-Accelerated Claisen Rearrangements. 4. Asymmetric Induction via 1,3,2-Oxazaphosphorinanes[1a]

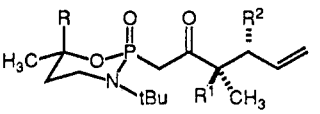
Summary: The anions dervied from allyl vinyl ethers **1** and **2** undergo rapid and highly selective Claisen rearrangements. The degree of asymmetric induction has been found to be uniformly high (ca. 90:10) for various substituent patterns but depends markedly on the presence of lithium cations. The absolute sense of asymmetric induction has been established using chiral, nonracemic 1,3,2-oxazaphosphorinane **2**. Two proposals for the transition structures of the phosphorus-stabilized anions are discussed.

Sir: Previous reports from these laboratories have established the accelerating effect of carbanionic functions in the Claisen rearrangement. Both sulfur-[2] and phosphorus-based[3] anion stabilizing groups have been shown to bring about enhancements in rate (>300-fold[4]) and internal stereoselectivity.[2c] One of the unique aspects of this carbanion-accelerated Claisen rearrangement (CACR) is the potential for asymmetric induction via chiral, anion-stabilizing groups. In particular, the phosphorus-based groups offer the advantage that their chirality may be auxiliary-derived by using readily available, recoverable diamines and amino alcohols, thus obviating the need for asymmetric synthesis at the heteroatom.[5,6] In this study we report that cyclic phosphoramidates **1** and **2** (Scheme I) rearrange anionically under mild conditions in good yields with significant levels of diastereoface selectivity. We also report herein the absolute stereochemical course of the rearrangements.

Scheme I



R = CH_3: **1**
R = H: **2**



R = CH_3: **3**
R = H: **4**

The amino alcohols **6**[7] and (*S*)-**8**[7] used in this study to create the chiral auxiliaries were easily prepared in large quantities as shown in Scheme II. (*S*)-Ethyl 3-hydroxybutanoate was obtained by yeast reduction[8] in excellent enantiomeric purity.[9a] The crystalline *tert*-butylamide (*S*)-**7**,[7,9b] prepared by the method of Weinreb,[10] was reduced with BH_3·THF to the requisite, chiral amino alcohol

(1) (a) Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, 1987; ORGN 228. (b) NSF Presidential Young Investigator 1985–1990. A. P. Sloan Fellow 1985–1987.

(2) (a) Denmark, S. E.; Harmata, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 4972. (b) Denmark, S. E.; Harmata, M. A. *Tetrahedron Lett.* **1984**, *25*, 1543. (c) Denmark, S. E.; Harmata, M. A. *J. Org. Chem.* **1983**, *48*, 3369. (d) Harmata, M. A. Ph.D. Thesis, University of Illinois, Urbana, 1985. (e) Denmark, S. E.; Harmata, M. A.; White, K. S. *J. Org. Chem.* **1987**, *52*, 4031.

(3) Denmark, S. E.; Marlin, J. E.; Dorow, R. L. "Abstracts of Papers", 191st National Meeting of the American Chemical Society, New York, April 1986; American Chemical Society: Washington, DC, 1986; ORGN 273.

(4) Leung, T. K., M. S. Thesis, University of Illinois, Urbana, 1985.

(5) For recent examples of this concept, see: (a) Hanessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5754. (b) Hua, D. H.; Chan-Yu-King, R.; McKie, J. A.; Myer, L. *Ibid.* **1987**, *109*, 5026.

(6) Auxiliary-based asymmetric induction in the Claisen rearrangement has been demonstrated. (a) Kurth, M. J.; Decker, O. H. W.; Hope, H.; Yanuck, M. D. *J. Am. Chem. Soc.* **1985**, *107*, 443. (b) Kurth, M. J.; Decker, O. H. W. *J. Org. Chem.* **1986**, *51*, 1377. (c) Kallmerten, J.; Gould, T. J. *Ibid.* **1986**, *51* 1152.

(7) All new compounds have been fully characterized by ^1H, ^{13}C, and ^{31}P NMR, IR, mass spectrometry and combustion analysis (±0.4%). Nondistillable phosphorus compounds have been identified by high-resolution MS.

(8) (a) Seebach, D.; Sutter, M. A.; Weber, R. H.; Zuger, M. F. *Org. Synth.* **1984**, *63*, 1. (b) Ehrler, J.; Giovannini, F.; Lamatsch, B.; Seebach, D. *Chimia* **1986**, *40*, 172.

(9) (a) The enantiomeric excess of the 3-hydroxybutanoate was determined by using both optical rotation and Mosher analytical methods. Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543. (b) Enantiomeric excess established by the method of Pirkle. Pirkle, W. H.; Mahler, G.; Hyun, M. H. *J. Liquid Chromatogr.* **1986**, *9*, 443.

(10) Basha, A.; Lipton, M.; Weinreb, S. M. *Tetrahedron Lett.* **1977**, 4171.

0022-3263/87/1952-5742$01.50/0