Asymmetric Synthesis with (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Benzoylformate[1]

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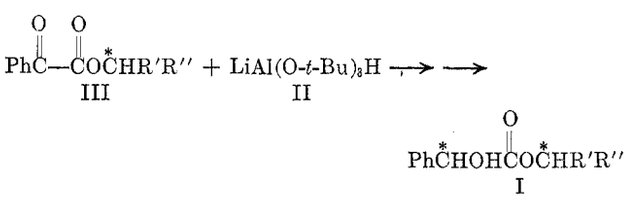
We have found that the reaction of methylmagnesium iodide in ether with (*S*)-(−)-*n*-butyl-*tert*-butylcarbinyl benzoylformate preferentially attacks the *re* face of the α-keto group to give a 7.5% excess of the (*S*)-atrolactate diastereomer. Based on the premise that *tert*-butyl acts as a larger group than *n*-butyl this result is in accord with Prelog's generalization concerning the course of this reaction. In tetrahydrofuran, however, the stereoselectivity was essentially zero. On the other hand, reduction of this same substrate by lithium tri-*tert*-butoxyaluminohydride in either tetrahydrofuran or ether resulted in preferential attack on the *si* face of the α-keto group to give the (*R*)-mandelate diastereomer in excess (13 and 8%, respectively). This reversal in stereoselectivities between the Grignard addition and lithium tri-*tert*-butoxyaluminohydride reductions emphasizes the caution necessary in extrapolating stereoselectivities from one seemingly closely related reaction to another, especially when the stereoselectivities are low and the nature of steric differences are not clearly evident. Stereochemical analysis of the reaction mixtures was greatly facilitated by the use of the nmr enantiomer reagent, α-methoxy-α-trifluoromethylphenylacetic acid, alone and in conjunction with europium nmr shift reagents.

Previous nuclear magnetic resonance (nmr) studies on a series of chiral esters (I) of mandelic acid[3] which were prepared by lithium tri-*tert*-butoxyaluminohydride (II) reduction[4] of the chiral benzoylformate esters (III) led to one or more of the following con-

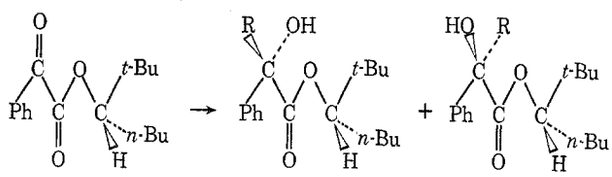


clusions: (a) that the stereochemical course of this reaction[5] did not follow Prelog's generalization[6] assuming that the *tert*-butyl group exerts greater steric nonbonded interactions than the *n*-butyl group (an assumption which had been found to satisfactorily rationalize our results in earlier asymmetric reduction studies[5]), (b) that our nmr configurational correlation model[3,7] did not hold in this case, (c) that the configurational assignment for (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol is wrong. It thus became necessary to determine unequivocally which of these alternative conclusions was unreliable.

The stereochemistry of the acid moiety of the mandelate ester (IV, R = H) was established by lithium aluminum hydride reduction to the corresponding phenylethylene glycol of known configuration[8,9] and that of the atrolactate ester (IV, R = CH_3) by hydrolysis to atrolactic acid of known configuration. The (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol was recovered unchanged. The stereoselectivities observed are given in Table I.

TABLE I

STEREOSELECTIVITIES IN THE LiAl(O-*t*-Bu)$_3$H AND MeMgI ADDITIONS TO (*S*)-(−)-*n*-BUTYL-*tert*-BUTYL BENZOYLFORMATE



(*S*)-III[a] (*S,S*)-IV (*R,S*)-IV

R	Reagent	Solvent	Stereoselectivity	Yield, %
H	LiAl(O-*t*-Bu)$_3$H	Et_2O	8% excess *R,S*	92
H	LiAl(O-*t*-Bu)$_3$H	THF	13% excess *R,S*	99
CH_3	MeMgI	Et_2O	7.5% excess *S,S*	94
CH_3	MeMgBr	THF	*R,S* ≅ *S,S*	95

[a] Formula drawn according to Prelog model in ref 6b. An earlier model[6] which predicts the same stereochemistry has the small rather than large group eclipsing the C–O–C bond.

It is apparent that the stereoselectivities for the LiAl(O-*t*-Bu)$_3$H reduction and MeMgI addition in either solvent are reversed. Thus alternative (a) above is the root of the discrepancy but only for the reduction reaction since the methylmagnesium iodide reaction did follow the Prelog generalization based on the stated assumption. From these results it is seen that the stereoselectivities are not high. In fact in THF the reaction with methylmagnesium bromide[10] showed zero stereoselectivity within experimental limits.

It is reasonable to conclude that the steric interactions of *n*-butyl and *tert*-butyl might be effectively different in different reactions. The *tert*-butyl group could show greater steric hindrance to reactions which are centered near the attachment of the *tert*-butyl group, as for instance in the asymmetric reduction of alkyl or aryl *tert*-butyl ketones, while the *n*-butyl group might more effectively block one face of a carbonyl group which was further away as in the benzoylformate

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(2) On leave from Department of Chemistry, Tohoku University, Sendai, Japan.

(3) J. A. Dale, Ph.D. Thesis, Stanford University, 1970.

(4) (a) H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, **80**, 5372 (1958); (b) H. C. Brown and H. R. Deck, *ibid.*, **87**, 5620 (1965); (c) H. Haubenstock and E. L. Eliel, *ibid.*, **84**, 2363 (1962); (d) E. C. Ashby, J. P. Sevenair and F. R. Dobbs, *J. Org. Chem.*, **36**, 197 (1970).

(5) W. M. Foley, F. J. Welch, E. M. La Combe and H. S. Mosher, *J. Amer. Chem. Soc.*, **81**, 2779 (1959).

(6) (a) V. Prelog and H. L. Mier, *Helv. Chim. Acta*, **36**, 320 (1953); (b) V. Prelog, *Bull. Soc. Chim. Fr.*, 987 (1956); (c) see review in J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, pp 50–83.

(7) James A. Dale and H. S. Mosher, *J. Amer. Chem. Soc.*, in press. This empirical correlation model predicted from the nmr spectrum alone that the *S,S* diastereomer with the upfield *tert*-butyl signal was produced in 10% excess over the *R,S* diastereomer.[3]

(8) J. A. Berson and M. A. Greenbaum, *J. Amer. Chem. Soc.*, **81**, 6456 (1959).

(9) J. A. Dale and H. S. Mosher, *J. Org. Chem.*, **35**, 4002 (1970).

(10) Methylmagnesium iodide is not soluble as such in THF, giving a precipitate of MgI_2; we therefore used methylmagnesium bromide in the THF reaction. Similarly, the lithium tri-*tert*-butoxyaluminohydride reagent is not soluble in ether although it rapidly went into solution as the reaction progressed.

esters such as III. It is more difficult to rationalize the reversal of stereoselectivities observed when the same substrate is being acted on by two different reagents. Intimate details of the transition states of these reactions are not known and thus reasons for the observed reversal of stereoselectivities in these two cases cannot be carried much beyond these speculations. Differences in stereoselectivities of 7–13% at 35° represent $\Delta\Delta G^{\ddagger}$ values of only 75 to 150 cal/mol; our understanding of transition states is seldom good enough to account for such small differences even in closely comparable competitive reactions of the asymmetric synthesis type. Thus we feel that such results, taken together, are indicative of subtle interactions between solvent, reagent, and conformational factors, a greater knowledge of which are requisite to a more detailed understanding of transition states.

Another example of reversal of stereoselectivities has been reported[8] in the lithium aluminum hydride reduction of phenyldihydrothebainyl benzoylformate *vs.* the addition of methylmagnesium iodide to the same substrate. The reduction product upon hydrolysis gave (*S*)-(+)-phenylethylene glycol while the Grignard product on hydrolysis gave (*R*)-(−)-atrolactic acid; these two products have opposite configurational relationships. This was rationalized by assuming that in this substrate the ester carbonyl group was reduced faster than the α-keto group. Stereochemical control of the further reduction of the α-keto group once an intermediate hemiacetal was formed would be quite different from the initial reduction of the α-keto group.[11] The present example cannot be explained on this basis since even in the presence of substantial excess of lithium tri-*tert*-butoxyaluminohydride only mandelate ester was formed; no phenylethylene glycol could be detected.

An interesting analytical point is the use of Sievers europium reagent[12] Eu(fod)$_3$ to spread out and separate the signals of the diastereomeric atrolactates of *n*-butyl-*tert*-butylcarbinol. Whereas the uncomplexed atrolactate ester had coincident signals for the α-methyl groups of the *S,R* and *S,S* diastereomers, in the presence of 0.6 molar amount of Eu(fod)$_3$ these signals occurred almost completely separated at δ 6.33 (*S,S* diastereomer) and 6.43 (*R,S* diastereomer) ppm, respectively, so that they could be readily integrated and the percentage diastereomer composition ascertained. The use of lanthanide chemical shift reagents constitutes a valuable adjunct technique in stereochemical studies such as these.

Experimental Section[13]

(*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Benzoylformate (III).—A solution of oxalyl chloride (4.4 g, 34.8 mmol) in carbon tetrachloride (6.7 ml) was added to the stirred, ice-cooled suspension of sodium benzoylformate (3.5 g, 20 mmol, thoroughly dried in a vacuum desiccator over P_2O_5) in carbon tetrachloride (10 ml) and pyridine (0.4 ml) according to a modification of the method of Stork and Clark.[14] After stirring for 12 hr, the reaction mixture was evaporated under reduced pressure below 40°, diluted with carbon tetrachloride (10 ml), and evaporated (1–2 mm) again to remove excess oxalyl chloride. The residue was diluted with carbon tetrachloride (10 ml); to the stirred suspension was added a solution of (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol[5] [0.72 g, $[\alpha]^{22.5}D$ −39.2° (*c* 23.3, cyclopentane)] in pyridine (2.5 ml) and carbon tetrachloride (2.5 ml) during a 5-min period while it was cooled with ice. After stirring for 12 hr at room temperature, the reaction mixture was poured onto ice and extracted with ether. The ether extract was successively treated with cold dilute HCl, dilute NaOH, and H_2O and dried (Na_2SO_4). The ether was removed under reduced pressure to give an oil, which was purified (silica gel column, benzene solvent). Obtained was 1.2 g (87%) of ester: $[\alpha]^{22.8}D$ −30.3° (CCl_4, *c* 9.08); ir 1730 (ester C=O), 1694 cm^{-1} (α-keto), nmr δ 0.96 [s, $C(CH_3)_3$].

Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.98; H, 8.71.

Reaction of (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Benzoylformate with Methylmagnesium Iodide.—An aliquot of ethereal Grignard reagent (3.01 ml, 3.6 mmol), prepared from sublimed magnesium and methyl iodide and standardized by neutralization titration just before use, was added to (*S*)-(−)-*n*-butyl-*tert*-butylcarbinyl benzoylformate [III, 0.5 g, 1.8 mmol, $[\alpha]^{22.8}D$ −30.3° (CCl_4)] in ether (2.0 ml) at 0° under N_2. After 14 hr, the reaction mixture was hydrolyzed (saturated NH_4Cl solution) and extracted with ether. The extracts were washed (dilute HCl, dilute NaOH, H_2O), dried (Na_2SO_4), and concentrated under reduced pressure to give 0.50 g of *n*-butyl-*tert*-butylcarbinyl atrolactate as a pale yellow oil, isolated yield 94%, $[\alpha]^{20.0}D$ −23.4° (*c* 8.25, CCl_4). The spectra were taken on a sample of the ester which was purified (silica gel column, benzene solvent): ir 1725 cm^{-1}; nmr δ 0.60 (s, *t*-Bu, *S,S* diastereomer), 0.87 (s, *t*-Bu, *S,R* diastereomer), 1.72 ppm (s, α-CH_3), and complex multiplet for *n*-butyl group.

The higher field signal (δ 0.60, arising from the *tert*-butyl group of the *S,S* diastereomer) is stronger than that of the lower field signal (δ 0.87, arising from the *tert*-butyl group of the *S,R* diastereomer). However, overlapping signals from the *n*-butyl group made an accurate direct analysis of the diastereomeric composition of these esters by integration of these signals either at 60 or 100 MHz impossible. The addition of the chemical shift reagent[12] Eu(fod)$_3$ caused a shift of nmr resonances so that the previously unresolved α-methyl signals (δ 1.73 ppm) were removed to an uncomplicated region of the spectrum: δ 6.33 (*S,S* diastereomer), 6.43 ppm (*R,S* diastereomer). Although the signals were not completely resolved, the upfield resonance was clearly more intense and represented 7 ± 2% excess of the *S,S* diastereomer.

Hydrolysis of (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Atrolactates.—The above mixture of atrolactates (0.40 g, without further purification), methanol (4.5 ml), water (0.9 ml), and potassium hydroxide (0.27 g) was gently refluxed for 5 hr under nitrogen atmosphere.[6] The reaction mixture was poured onto ice and extracted three times with ether. The extracts were washed (dilute HCl, H_2O), dried (Na_2SO_4), and concentrated to give 0.18 g (91%) of *n*-butyl-*tert*-butylcarbonol, $[\alpha]^{23.4}D$ −38.0° (*c* 8.80, cyclopentane). The aqueous basic solution was acidified (cold dilute HCl) and extracted three times with ether. These extracts were washed (H_2O), dried (Na_2SO_4), and concentrated to give 0.20 g (88%) atrolactic acid, $[\alpha]^{27.5}D$ +2.8° (*c* 10.23, C_2H_5OH). Taking the value of $[\alpha]^{13.8}D$ 37.7° (C_2H_5OH)[15] as enantiomerically pure atrolactic acid, this corresponds to 7.5% excess of the (*S*)-(+) isomer in accord with Prelog's rule where *tert*-butyl is acting as a larger group than *n*-butyl.

Reaction of *n*-Butyl-*t*-butylcarbinyl Benzoylformate with Methylmagnesium Bromide in THF.—To a cold stirred solution of (−)-*n*-butyl-*tert*-butylcarbinyl benzoylformate (III, 0.28 g, 1 mmol) in THF (1 ml) was added 4.3 ml (2 mmol) of methylmagnesium bromide reagent[10] under N_2. The reaction mixture was decomposed (saturated NH_4Cl) and processed as in the previous preparation in ether solvent to give 0.28 g (95%) of atrolactate ester (IV, R = CH_3) as a colorless oil. The nmr of this ester (41 mg in CCl_4) mixed with Eu(fod)$_3$ (Eu-Resolve II, 86 mg,

(11) This explanation has been questioned based upon subsequent experiments: J. A. Dale and H. S. Mosher, *J. Org. Chem.*, **35**, 4002 (1970).

(12) For leading reference on the use of lanthanide chemical shift reagents, see R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971); fod stands for the anion from 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione. This extension of the use of lanthanide shift reagents for the determination of enantiomeric composition as well as configuration by nmr is being studied further.

(13) Ir spectra were taken on a Perkin-Elmer Model 137B grating instrument; nmr spectra were taken either on a Varian T-60 or Varian HR-100 instrument as appropriate. Chemical shifts are reported in δ, parts per million, downfield from internal tetramethylsilane in carbon tetrachloride solvent. Optical rotations were taken on a Perkin-Elmer Model 141 electronic polarimeter in 1-dcm tubes with a reproducibility of ±0.002°.

(14) G. Stork and T. Clark, Jr., *J. Amer. Chem. Soc.*, **83**, 3114 (1961).

(15) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **97**, 1016 (1910).

molar ratio 1:0.6)[12] showed that the signal for the α-methyl group of the atrolactate moiety (δ 1.73 ppm unresolved) was shifted downfield and separated into two signals (δ 6.03 and 6.13 ppm) which within experimental limits (*ca.* ±2%) had the same integrated area, indicating essentially zero stereoselectivity for this reaction in THF solvent.

Reduction of (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Benzoylformate with Lithium Tri-*tert*-butoxyaluminohydride in THF.—A solution of (*S*)-(−)-*n*-butyl-*tert*-butylcarbinyl benzoylformate [III, 0.68 g, $[\alpha]^{22.8}D$ −30.3° (CCl_4)] in THF (2.5 ml, distilled from $LiAlH_4$) was added to a solution of $LiAlH(O\text{-}t\text{-}Bu)_3$[4] (1.36 g in 25 ml THF) over a 5-min period with ice cooling. After 2-hr stirring, 1 ml of water was added. Ether extracts of the acidified (dilute HCl) reaction mixture were washed (dilute NaOH, H_2O), dried (Na_2SO_4), and concentrated to give 0.63 g (92%) of *n*-butyl-*tert*-butylcarbinyl mandelate: mp 54–58°; $[\alpha]^{24}D$ −35.8° (*c* 10.18, $CHCl_3$); ir 1727 cm^{-1}; nmr δ 0.55 (s, *t*-Bu, *S,S* diastereomer), 0.87 (s, *t*-Bu, *S,R* diastereomer).

Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.33; H, 9.41. Found: C, 73.44; H, 9.18.

In the nmr spectra of the mandelates the two *tert*-butyl signals are more clearly separated from the *n*-butyl resonances than in the atrolactates. The lower field signal by integration was 13% greater than the higher field signal, *i.e.*, 13% excess of *S,R* diastereomer. This nmr analysis was confirmed by the following experiment.

Reduction of (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Mandelate with Lithium Aluminum Hydride.—A solution of the above mandelates without further purification (0.57 g, in 3.0 ml of ether) was added dropwise with stirring to a solution of $LiAlH_4$ (0.76 g in 9.5 ml of ether) at 0°. After 1-hr reflux, excess $LiAlH_4$ was decomposed with water (3 ml) and the hydrolysis mixture was treated with dilute HCl and extracted with ether. The combined ether extracts were washed (dilute Na_2CO_3, H_2O), dried (Na_2SO_4), and concentrated under vacuum at 0° to give 0.49 g of colorless oil which was purified (silica gel column, CH_2Cl_2 followed by CH_3OH) to give a first fraction containing 0.26 g (88%) of (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol [$[\alpha]^{20.4}D$ −39.0° (*c* 10.81, cyclopentane] and a second fraction containing 0.20 g (71%) of (−)-phenylethylene glycol which was further purified by sublimation: mp 68–71°; $[\alpha]^{21.5}D$ −7.7° (*c* 9.38, $CHCl_3$). Based on the reported maximum rotation of $[\alpha]^{25.5}D$ −63.7° (*c* 5.45, $CDCl_3$)[5,9] for (*R*)-(−)-phenylethylene glycol, this represents 12% excess of the (*S*)-*n*-butyl-*tert*-butylcarbinyl (*R*)-mandelate.

Reduction of (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Benzoylformate with $LiAl(O\text{-}tert\text{-}Bu)_3H$ in Ether.—An ether solution (2 ml) of (−)-*n*-butyl-*tert*-butylcarbinyl benzoylformate (III, 0.28 g) was added to an ice-cold suspension of lithium tri-*tert*-butoxyaluminohydride[4] (0.55 g) in ether (30 ml). After 10 min the reagent was dissolved and after 2 hr the reaction mixture was worked up as indicated in the previous reaction in THF to give 0.28 g (99%) of mandelate ester as colorless crystals. Integration of the nmr spectrum indicated an 8% excess of the *S,R* diastereomer (*tert*-butyl signal δ 0.7, *S,R* diastereomer). This compares to the 13% excess of the same stereoisomer observed during the reduction in THF.

Optical Rotation of *n*-Butyl-*tert*-butylcarbinol in Cyclopentane.—The original sample[5] of (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol obtained by resolution [$[\alpha]^{27.0}D$ −32.46° (neat, *l* 1); $[\alpha]^{27.0}D$ −39.4° (neat)] was found to give rotations in cyclopentane which were nearly the same as that of the neat liquid and not strongly concentration dependent: $[\alpha]^{21.5}D$ −39.2° (*c* 49.14), $[\alpha]^{22.5}D$ −39.2° (*c* 23.3), $[\alpha]^{21.5}D$ −40.0° (*c* 10.16), $[\alpha]^{23.5}D$ −39.9° (*c* 8.92), $[\alpha]^{24}D$ −40.4° (*c* 4.46).

The (*R*)-(+)-α-methoxy-α-trifluoromethylphenyl esters [*R*-(+)-MTPA esters] prepared in the usual way[9] from racemic *n*-butyl-*tert*-butylcarbinol gave *tert*-butyl signals at δ 0.83 corresponding to the *S,R* diastereomer and at 0.92 corresponding to the *S,S* diastereomer. The nmr spectrum of the *R*-(+)-MTPA ester prepared from the above sample of (−)-*n*-butyl-*tert*-butylcarbinol [$[\alpha]^{27.0}D$ −32.46° (neat, *l* 1)] gave only one *tert*-butyl signal at δ 0.83 with no detectable signal from the diastereomer. The prior resolution[5] was therefore complete. The overlapping OCH_3 proton signals in the nmr spectrum of the diastereomeric mixture (*R,R*, δ 3.50; *R,S*, δ 3.55) were widely separated and their positions reversed upon the addition of 0.2 molar equivalents of $Eu(fod)_3$[12] (*R,R*, δ 5.57; *R,S*, δ 5.40).

Registry No.—(*S*)-III, 35147-13-8; (*S,S*)-IV (R = CH_3), 35147-12-7; (*R,S*)-IV (R = CH_3), 35147-14-9; (*S,S*)-III (R = H), 35147-15-0; (*R,S*)-IV (R = H), 35147-16-1; (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol, 35147-17-2; (*R*)-(−)-phenylethylene glycol, 16355-00-3.

Photoreduction of Aromatic Esters with Some Electron-Withdrawing Substituents

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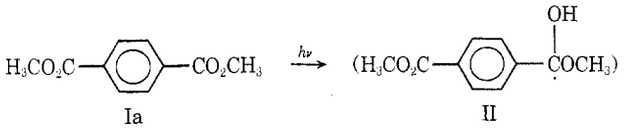
The photoreduction of aromatic esters, having an electron-withdrawing substituent such as an ester or cyano group, by aromatic hydrocarbons is described. The photoreduction of para- or meta-substituted aromatic esters led to the formation of the two possible types of pinacols and carbinols depending on the aromatic hydrocarbons employed. In the case of ortho-substituted aromatic esters, various benzo-γ-lactone derivatives were produced. It is demonstrated that steric effects play an important role in the hydrogen transfer step and that an excited charge-transfer complex between the aromatic ester and the aromatic hydrocarbon may be the photoreactive species.

Although many studies have been done on the photoreduction of aromatic ketones by a variety of hydrogen donors, such as alcohols,[1] ethers,[1a] hydrocarbons,[1a,2] and amines,[3] the photoreduction of aromatic esters has not yet been reported.

Recently, we reported[4] that dimethyl terephthalate (Ia) was readily photoreduced by various aromatic



Ia II

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(3) S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); **91**, 3690 (1969); R. S. Davidson, *Chem. Commun.*, 575 (1966); R. S. Davidson and P. F. Lambeth, *ibid.*, 1098 (1969); C. Pac, H. Sakurai, and T. Tosa, *ibid.*, 1311 (1970); S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967); *J. Phys. Chem.*, **72**, 3782 (1968); R. S. Davidson, P. F. Lambeth, F. A. Younis, and R. Wilson, *J. Chem. Soc. C*, 2204 (1969); R. A. Caldwell, *Tetrahedron Lett.*, 2121 (1969); S. G. Cohen and J. B. Guttenplan, *ibid.*, 5353 (1968); 2125, 2129 (1969); G. A. Davis, P. A. Carapelluci, K. Szoc, and J. D. Gresser, *J. Amer. Chem. Soc.*, **91**, 2264 (1969); G. A. Davis and S. G. Cohen, *Chem. Commun.*, 622 (1970); S. G. Cohen and B. Green, *J. Amer. Chem. Soc.*, **91**, 6824 (1969); A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *ibid.*, **91**, 1857 (1969).

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