4, $H_{2,3,6,7}$), 8.15–8.80 (m, 6, $H_{1,4,5,8,9,14}$).

Method B. Bromination of 4 (507 mg, 1.8 mmol) with NBS (385 mg, 2.16 mmol) was conducted in the presence of dibenzoyl peroxide (20 mg) in refluxing CCl_4 (100 mL) under N_2 for 45 min. Succinimide was filtered off and the solvent evaporated to yield crude **5** as a yellowish oil; the NMR spectrum of **5** exhibited a characteristic bromomethine peak at σ 5.66. A suspension of **5** (758 mg) and equal weights of Ag_2CO_3 in aqueous dioxane (50:50) was heated at reflux for 1 h.[19] Conventional workup afforded **6** (408 mg, 60%), the physical properties of which were identical with those of **6** obtained by method A.

Dehydrobromination[4b] of **5** by stirring with DBN (0.6 mL) in THF (60 mL) at 0 °C overnight also furnished **7** (25% yield).

Dehydration of **6** with *p*-tosic acid in refluxing benzene for 1 h gave **7** (98%): mp 167–169 °C (lit.[3] mp 168–169 °C); NMR ($CDCl_3$) δ 2.28–2.67 (m, 2, H_{11}), 3.00 (d, 2, $J_{10,11}$ = 8 Hz, H_{10}), 5.92–6.25 (m, 1, H_{12}), 6.62 (d, 1, $J_{12,13}$ = 10 Hz, H_{13}), 7.41–7.73 (m, 4, $H_{2,3,6,7}$), 8.17 (s, 1, H_{14}), 8.25 (s, 1, H_9), 8.40–8.80 (m, 4, $H_{1,4,5,8}$).

Method C. A solution of **4** (500 mg, 1.9 mmol) in benzene (150 mL) was heated with DDQ (410 mg) at reflux for 10 min. NMR analysis of the crude product isolated by conventional workup showed the presence of **4** (83%), **7** (8%), and **1** (8%). The presence of **7** was confirmed by Prêvost reaction to provide the corresponding *trans*-dibenzoate ester identical with that from authentic **7**.

Prêvost Reaction of 7. A solution of silver benzoate (8.7 g, 38 mmol) and I_2 (4.8 g, 19 mmol) in dry benzene (200 mL) was refluxed for 30 min. A solution of **7** (5.3 g, 19 mmol) in benzene (150 mL) was added, and the resulting solution was stirred at reflux for 24 h under N_2. Workup in the usual manner[4b,5b] afforded the crude product which was purified by chromatography on Florisil. Elution with benzene gave *trans*-10,11-bis(benzoyloxy)-10,11,12,13-tetrahydro-1 (**9**) as a white solid (7.98 g, 80%): mp 180–181 °C; NMR ($CDCl_3$) δ 2.26–2.66 (m, 2, H_{12}), 3.07–3.46 (m, 2, H_{13}), 5.50–5.86 (m, 1, H_{11}), 6.73 (d, 1, $J_{10,11}$ = 5.5 Hz, H_{10}), 7.0–8.65 (m, 20, aromatic).

***trans*-10,11-Bis(benzoyloxy)-10,11-dihydrodibenz[*a*,*c*]anthracene (2b). NBS Method.** To a solution of **9** (3.02 g, 5.78 mmol) from the previous reaction in CCl_4 (50 mL) was added NBS (1.09 g, 6.1 mmol) and benzoyl peroxide (10 mg), and the resulting suspension was heated at reflux under N_2 for 35 min. The insoluble succinimide was filtered off and the solvent evaporated. The residue was dissolved in THF (20 mL), the solution was cooled to 0 °C, and DBN (15 mmol) was added. The resulting solution was stirred at 0 °C overnight and worked up conventionally. Chromatography on Florisil eluted with benzene furnished **2b** (1.02 g, 34%) as a colorless solid: mp 183–184 °C; NMR ($CDCl_3$) δ 5.99 (dd, 1, H_{11}), 6.21 (dd, 1, H_{12}), 6.80 (d, 1, H_{10}), 6.98 (d, 1, H_{13}), 7.15–8.80 (m, 20, aromatic), $J_{10,11}$ = 6 Hz, $J_{11,12}$ = 4 Hz, $J_{12,13}$ = 10 Hz.

DDQ Method. A solution of the dibenzoate ester (2.0 g, 3.8 mmol) and DDQ (1.09 g, 4.8 mmol) in dioxane (150 mL) was refluxed under N_2 for 96 h. Chromatography on a column of neutral alumina eluted with benzene gave **2b** (1.37 g, 69%).

(±)-*trans*-10,11-Dihydroxy-10,11-dihydrodibenz[*a*,*c*]anthracene (2a). To a solution of **2b** (1.1 g, 2.1 mmol) in THF (35 mL) was added a solution of $NaOCH_3$ (232 mg, 4.3 mmol) in methanol (20 mL) and the resulting solution stirred at 60 °C for 20 min. Conventional workup gave **2a** (567 mg, 86%) as a white solid: mp 210–212 °C dec; NMR (Me_2SO-d_6) δ 4.36 (ddd, 1, H_{11}), 4.80 (d, 1, H_{10}), 6.03 (dd, 1, H_{12}), 6.70 (dd, 1, H_{13}), 7.55–7.88 (m, 4, $H_{2,3,6,7}$), 7.42–7.86 (m, 6), $H_{1,4,5,8,9,14}$, $J_{10,11}$ = 9.5 Hz, $J_{11,12}$ = 2 Hz, $J_{12,13}$ = 10 Hz, $J_{11,13}$ = 2 Hz.

(±)-*trans*-10,11-Dihydroxy-*anti*-12,13-epoxy-10,11,12,13-tetrahydrodibenz[*a*,*c*]anthracene (3). A solution of **2a** (88 mg, 0.28 mmol) and *m*-chloroperbenzoic acid (487 mg) in 40 mL of dry THF was stirred at room temperature under N_2 for 1.5 h. The solution was chilled and partitioned between ethyl acetate–ether (1:1) and cold 10% aqueous NaOH solution as rapidly as possible. The organic layer was washed with cold water, dried, and evaporated, avoiding heating.[20] Trituration of the residue with ether provided **3** (52 mg, 56%) as a white solid: mp 167–169 °C dec; NMR Me_2SO-d_6, D_2O δ 3.77 (apparent d, 1, H_{12}), 3.93 (apparent d, 1, H_{11}), 4.34 (d, 1, H_{13}), 4.79 (d, 1, H_{10}), 7.5–7.9 (m, 4, $H_{2,3,6,7}$), 8.57–9.07 (m, 6, $H_{1,4,5,8,9,14}$), $J_{10,11}$ = 9 Hz, $J_{11,12} \simeq$ 1 Hz, $J_{12,13}$ = 4.5 Hz.

Acknowledgment. This investigation was supported by Grant No. CA 11968 and CA 14599 and Research Contract No. CP 033385 from the National Cancer Institute, DHEW. We also wish to thank Ms. Cynthia Leyba for her valuable technical assistance.

Registry No. 1, 215-58-7; (±)-2a, 72100-19-7; (±)-2b, 72100-20-0; (±)-3, 72150-71-1; 4, 25486-89-9; 5, 72100-21-1; 6, 39081-07-7; 7, 39081-08-8; 8, 39081-06-6; (±)-9, 72100-22-2; triphenylene, 217-59-4; silver benzoate, 532-31-0.

---

[19] Flesher, J. W.; Soedigdo, S.; Kelley, D. R. *J. Med. Chem.* **1967**, *10*, 932.

[20] Like other diol epoxides, 3 is thermally and acid sensitive and tends to decompose on attempted chromatography.

Reduction of α,β-Diarylacrylonitriles by Sodium Borohydride

Stuart S. Kulp* and Craig B. Caldwell[1]

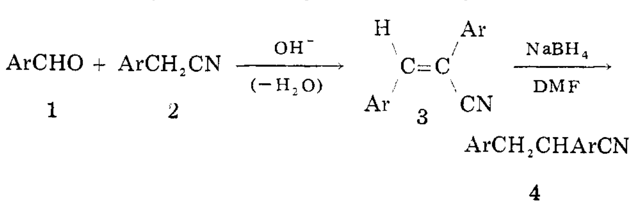
Department of Chemistry, Moravian College, Bethlehem, Pennsylvania 18018

Received July 13, 1979

The ready accessibility of α,β-diarylacrylonitriles and their highly selective rapid reduction by $NaBH_4$ provides an excellent synthesis of α,β-diarylpropionitriles. The conversion of 23 combinations of aromatic aldehydes and arylacetonitriles by the two-step sequence to the corresponding substituted propanenitriles is reported. We recommend this sequence as the method of choice for the syntheses of these compounds since both condensation and reduction processes occur in very high yield (80–90%). Furthermore, anhydrous conditions are not necessary, reaction times are short, and workups are simple. We have also examined the kinetics of the reduction reaction in this series for 11 cases.

Corey and others[2] have recently reported the use of magnesium in methanol and $NaBH_3CN$[3] on a millimole scale, for related reductions. The rates of $NaBH_4$ reduction of α-phenylcinnamates by competition runs were reported.[4] Refluxing THF,[5] employed for three α-cyanostilbene reductions, was unnecessary for our compounds. We employed DMF as the solvent and obtained fast reactions at ambient or lower temperatures.

Direct measurement of the progress of conversion of **3** to **4** was readily monitored by infrared analysis.[6] Removal of aliquots at various time intervals showed a decrease in absorbance at 2215 cm^{-1} (conjugated CN) as a corre-



---

[1] Taken in part from the Senior Honors Thesis of C.B.C., Moravian College, 1973.

[2] J. A. Profitt, D. S. Watt, and E. J. Corey, *J. Org. Chem.*, **40**, 127 (1975).

[3] R. O. Hutchins, D. Rotstein, N. Natale, and J. Fanelli, *J. Org. Chem.*, **41**, 3328 (1976).

[4] J. H. Schauble, G. J. Walter, and J. G. Morin, *J. Org. Chem.*, **39**, 755 (1974).

[5] J. Knabe, P. Herbort, and N. Ruppenthal, *Arch. Pharm.* (*Weinheim, Ger.*), **299**, 534 (1966).

[6] S. S. Kulp, R. W. Schmoyer, D. E. Freeze, and J. Buzas, *J. Org. Chem.*, **40**, 453 (1975).

Table I. Reduction of 3 to 4

compd no.	mp, °C	substituents		temp, °C	$t_{1/2}$, min	product	mp, °C [bp, °C (mm)]
		β	α				
3a	108.5-109	*p*-chlorophenyl	*p*-chlorophenyl	0	too fast	4a	89-90
3b	110-110.5	phenyl	*p*-chlorophenyl	0	0.2	4b	84-85
3c	101-101.5	*p*-chlorophenyl	phenyl	0	2.8	4c	110-111.5
3d	85-86.5	phenyl	phenyl	0	27	4d	51-51.5
3e	110-111	*p*-fluorophenyl	phenyl	25	1.25	4e	85.5-87.5
3f	127.5-128.5	*p*-anisyl	*p*-chlorophenyl	25	1.00	4f	111-112.5
3d		phenyl	phenyl	25	1.46	4d	
3g	57.5-59	*p*-tolyl	phenyl	25	3.32	4g	[137 (1)]
3h	93.5-94.5	*p*-anisyl	phenyl	25	13.5	4h	85.5-87
3i	92.5-93.5	phenyl	*p*-anisyl	25	105	4i	68-69
3j	137-138	*p*-(dimethylamino)phenyl	phenyl	25	518	4j	76-77.5
3k	107-107.5	*p*-anisyl	*p*-anisyl	25	615	4k	115-116.5
3l	108.5-109	*p*-chlorophenyl	*p*-anisyl			4l	69.5-71
3m	189-190	*p*-(dimethylamino)phenyl	*p*-chlorophenyl			4m	112-114
3n	149.5-150	*p*-(dimethylamino)phenyl	*p*-anisyl			4n	102-104
3o	110-110.5	α-naphthyl	phenyl			4o	82-83
3p	174-175	α-naphthyl	*p*-chlorophenyl			4p	63-64
3q	104.5-105	α-naphthyl	*p*-anisyl			4q	94.5-96.5
3r	42.5-43	α-furyl	phenyl			4r	[176-177 (21)]
3s	80-80.5	α-furyl	*p*-chlorophenyl			4s	[196-197 (21)]
3t	61-62	α-furyl	*p*-anisyl			4t	[207-208 (21)]
3u	90-90.7	α-thienyl	phenyl			4u	[206-207 (21)]
3v	135-136	α-thienyl	*p*-chlorophenyl			4v	84.5-86
3w	76.5-77	α-thienyl	*p*-anisyl			4w	[191-192 (2)]

sponding increase at 2245 cm^{-1} (saturated CN) occurred. While the intensity of the conjugated nitrile absorbances is approximately twice as great as that of the nonconjugated analogues, this had no effect on the rate equation derived. Least-squares regression gave k and $t_{1/2}$ with typical correlation coefficients of 0.998.

The data for these reductions are recorded in Table I. The relative rates correlate very well with the data of Schauble.[4] The parent compound (**3d**) reacts ≃18 times faster at 25 than at 0 °C. Electron-withdrawing substituents (**3a**, **3b**, **3c**, **3e**, and **3f**) increase the rate. A substituent on the α-phenyl is more effective than one on the β-phenyl. For example, the relative rates of compounds **3d**:**3h**:**3i**:**3k** at 25 °C are 1:9:70:420.

A Hammett plot by computer for compounds **3d**, **3e**, **3g**, **3h**, and **3j** gave ρ = 3.86 with a correlation coefficient of 0.984. It is clear that there is substantial negative charge development on the nitrogen of the nitrile, and the β-carbon of the α,β-acrylonitrile is more susceptible to hydride attack as its positive charge is increased by the appropriate substituents. Our ρ value is much higher than that for the corresponding acrylates[4] but not as high as some other ρ values (5.3 and 6.0).[7]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 237B instrument. Melting points were determined on a Mel Temp apparatus. All compounds gave NMR and IR spectra consistent with those expected for the formula. These spectra will be included in the Sadtler series at a later date. All new compounds gave analyses (by G. I. Robertson Laboratories, Florham Park, N.J.) within ±0.30% of theory.

α,β-Disubstituted Acrylonitriles (3). These compounds were prepared by a literature method[8] from the arylacetonitriles and aromatic aldehydes with 40% aqueous NaOH. Table I lists the melting points for the compounds utilized. The yields were consistently in the 80–90% range. These compounds were purified by recrystallization from ethanol.

α,β-Diarylpropanenitriles (4). General Synthetic Procedure. A solution of 4 g (0.1 mol) of NaBH$_4$ dissolved in 100 mL of DMF was added to a solution of the appropriate α,β-diarylacrylonitrile (0.05 mol in 50 mL of DMF or THF). The mixture was stirred overnight at ambient temperature, poured over ice, neutralized with 6 M HCl, and filtered or extracted with ether. The products were purified by recrystallization or distillation, and their melting points are recorded in Table I. Many solids were sufficiently pure as isolated and did not require further purification. The yields were consistently in the 90% range. Recrystallizations were done from ethanol.

Table II

time, min	absorbance *A*	absorbance *B*	ln (1 + *B*/*A*)
15.0	0.208	0.031	0.1389
20.0	0.198	0.038	0.1756
30.0	0.221	0.051	0.2076
40.0	0.210	0.069	0.2841
50.0	0.179	0.073	0.3420
60.0	0.145	0.078	0.4304
80.0	0.115	0.085	0.5534
90.0	0.105	0.092	0.6292
100.0	0.081	0.081	0.6931

Kinetics. (a) Four grams of NaBH$_4$ (0.1 mol) was dissolved by vigorous shaking in 100 mL of DMF, and the solution was filtered. A solution of 0.05 mol of the appropriate conjugated nitrile in 50 mL of DMF was prepared and filtered. The two solutions were added to a 500-mL round-bottom flask equipped with a magnetic stirrer. At appropriate time intervals, based on the speed of the reaction, 10-mL aliquots were removed by pipet and quenched in 50 mL of ice water. The solution was neutralized with 2 M HCl, and the solid precipitate was extracted with 6 mL of either CCl$_4$ or CHCl$_3$. The organic layer was washed twice with water to remove DMF. A portion of the organic layer was transferred to a 75-mm test tube containing anhydrous MgSO$_4$. After the solution was shaken and left to settle, a syringe was used to inject some of the solution into a sealed sodium chloride cell with a 0.2-mm path length. A matched solvent filled cell was the reference. Typical data are listed in Table II.

(b) For very rapid reactions at 0 °C, the two solutions were prepared as above. To 10 mL of the NaBH$_4$ solution in a 150-mm test tube containing a thermometer was added 5 mL of the nitrile solution, and a stopwatch was started. At selected time intervals, the reaction mixture was quenched in 50 mL of cold water. Workup was the same as that in procedure a but required 9–10 mL of extraction solvent.

Infrared Data and Calculations. The absolute concentrations of reactant and product were not necessary. However, the

---

[7] C. D. Johnson, "The Hammett Equation", Cambridge University Press, New York, 1973, pp 97 and 181.

[8] S. Wawzonek and E. M. Smolin, "Organic Synthesis", Collect. Vol. III, Wiley, New York, 1953, p 715.

ratio of their infrared absorbances was employed. For the pseudo-first-order reaction, the equation $B_t/A_t = 1/e^{kt} - 1 = e^{kt} - 1$ reduces to $\ln (1 - B/A) = kt$. A and B are absorbances read directly from the IR charts. The data for α-(*p*-methoxyphenyl)cinnamonitrile (**3i**) are typical (Table II).

Acknowledgment. The assistance of Dr. Morris Bader in processing the infrared data is gratefully acknowledged.

Registry No. 1 (Ar = *p*-chlorophenyl), 104-88-1; 1 (Ar = phenyl), 100-52-7; 1 (Ar = *p*-fluorophenyl), 459-57-4; 1 (Ar = *p*-anisyl), 123-11-5; 1 (Ar = *p*-tolyl), 104-87-0; 1 (Ar = *p*-(dimethylamino)phenyl), 100-10-7; **1** (Ar = α-naphthyl), 66-77-3; 1 (Ar = α-furyl), 98-01-1; 1 (Ar = α-thienyl), 98-03-3; **2** (Ar = *p*-chlorophenyl), 140-53-4; **2** (Ar = phenyl), 140-29-4; 2 (Ar = *p*-anisyl), 104-47-2; **3a**, 3695-94-1; **3b**, 3695-93-0; **3c**, 3695-92-9; **3d**, 2510-95-4; **3e**, 324-61-8; **3f**, 72030-11-6; **3g**, 6443-76-1; **3h**, 5432-07-5; **3i**, 5840-59-5; **3j**, 1222-61-3; **3k**, 6443-74-9; **3l**, 72030-12-7; **3m**, 2958-46-5; **3n**, 6582-06-5; **3o**, 65260-38-0; **3p**, 72030-13-8; **3q**, 72030-14-9; **3r**, 1207-91-6; **3s**, 72030-15-0; **3t**, 10280-99-6; **3u**, 72030-16-1; **3v**, 72030-17-2; **3w**, 72030-18-3; **4a**, 36770-81-7; **4b**, 5681-31-2; **4c**, 32970-79-9; **4d**, 3333-14-0; **4e**, 72035-44-0; **4f**, 5422-48-0; **4g**, 32970-77-7; **4h**, 32970-78-8; **4i**, 5840-58-4; **4j**, 72035-45-1; **4k**, 72035-46-2; **4l**, 72035-47-3; **4m**, 72035-48-4; **4n**, 72035-49-5; **4o**, 72035-50-8; **4p**, 72035-51-9; **4q**, 72035-52-0; **4r**, 1207-90-5; **4s**, 782-21-8; **4t**, 785-05-7; **4u**, 72035-53-1; **4v**, 72035-54-2; **4w**, 72035-55-3.

α-Bromoalkylides in Trisubstituted Olefin Synthesis. Regiospecific Entry to 4-Bromo-1,4-dienes

Roger H. Smithers

Department of Chemistry, University of Malaya, Kuala Lumpur 22-11, West Malaysia

Received July 3, 1979

Interest continues to be shown in synthetic routes to stereo- and regiodefined trisubstituted olefins,[1] mainly because of the occurrence in nature of many compounds of this class having significant biological activity. Recent reports of novel synthetic methods for 1,4-dienes, including some of this class,[2] prompt us to disclose our own results in this area.

We have previously shown[3] that triphenylphosphonium dibromomethylide (**1**) can be successfully alkylated with methyl and ethyl bromides to give the salts **2a** and **2b** (eq 1). Treatment of these salts with *n*-BuLi in THF at low

$$\underset{\mathbf{1}}{\mathrm{Ph_3\overset{+}{P}{-}\overset{-}{C}Br_2}} + \mathrm{RBr} \rightarrow \mathrm{Ph_3\overset{+}{P}{-}CBr_2R\ Br^-} \qquad (1)$$

$$\begin{array}{l}\mathbf{2a},\ \mathrm{R = Me}\\ \mathbf{2b},\ \mathrm{R = Et}\\ \mathbf{2c},\ \mathrm{R = CH_2CH{=}CH_2}\end{array}$$

$$\mathbf{2} + n\text{-BuLi} \xrightarrow[-40\ ^\circ\mathrm{C}]{\mathrm{THF}} \underset{\mathbf{3}}{\mathrm{Ph_3\overset{+}{P}{-}\overset{-}{C}BrR}} + n\text{-BuBr} \qquad (2)$$

$$\mathbf{3} + \mathrm{R'CHO} \rightarrow \underset{\mathbf{4},\ \mathrm{R'} = \text{alkyl, aryl}}{\mathrm{R'CH{=}CBrR}} \qquad (3)$$

temperature (eq 2) gives rise to α-bromoalkylides **3**, products of halogen–metal exchange. As indicated in eq 3, these intermediates react with aldehydes in Wittig fashion, furnishing the corresponding trisubstituted bromo olefins **4**, often with high stereoselectivity.

Table I. Products from the Reaction of Triphenylphosphonium 1-Bromo-3-butenylide with Aldehydes

aldehyde	bromo olefin	$Z:E$[a] ratio	% yield[b]
$C_6H_{13}CHO$	$C_6H_{13}CH{=}CBr$-$CH_2CH{=}CH_2$ (**6**)	36:64	78
PhCHO	$PhCH{=}CBrCH_2CH{=}CH_2$ (**7**)	20:80	68

[a] Diastereomers easily separable by GC on 5% SE30. The *E* isomer was identified as the major component in each case from the NMR appearance of the olefinic proton on the trisubstituted double bond. In (*E*)-**6**, the proton appears at lower field than in the *Z* isomer, as would be anticipated from its position *cis* to the vicinal Br. In addition, the same proton also displays the *smaller* allylic coupling. *Transoid* allylic couplings in related bromo olefins are smaller than *cisoid* couplings (see ref 3). [b] Obtained after chromatography on silical gel; purity (GC) exceeded 95% in both cases.

It occurred to us that, depending upon the availability of salt **2c**, the method might be extended to regiospecific synthesis of unsymmetrical functionalized 1,4-dienes. As it turned out, when **1** was alkylated with allyl bromide, the desired precursor **2c**, (1,1-dibromo-3-butenyl)triphenylphosphonium bromide, could be isolated as a white solid, mp 187–189 °C, in 60–68% yield.

It should be mentioned that attempts to extend these alkylations to the *dichloromethylide*[4] system, i.e., $PH_3P^+{-}^-CCl_2$, were unsuccessful, and the only alkylated products obtained in this case were the salts which arise via direct alkylation of the phosphine, viz., **5**. This result sheds further light on the mechanism of tetrahalomethane–triphenylphosphine reactions, which have merited some previous investigation.[5a,b] For the corresponding difluoromethylide,[5b] it has been demonstrated that stable ylide solutions are provided by a mobile equilibrium of the type shown in eq 4. In the present case, the existence of

$$\mathrm{Ph_3P + BrCX_3 \rightarrow Ph_3\overset{+}{P}{-}CX_3\ Br^-}$$

$$\begin{array}{ccccc} \mathrm{Ph_3\overset{+}{P}{-}CX_3\ Br^-} + & \mathrm{Ph_3P} & \rightleftharpoons & \mathrm{Ph_3\overset{+}{P}{-}\overset{-}{C}X_3} & + \mathrm{Ph_3PXBr} \qquad (4)\\ & \downarrow \mathrm{RBr} & & \downarrow \mathrm{RBr} & \\ & \underset{\mathbf{5}}{\mathrm{Br^-\ Ph_3\overset{+}{P}{-}R}} & & \mathrm{Ph_3\overset{+}{P}{-}CX_3R\ Br^-} & \end{array}$$

a similar equilibrium whose position depends critically upon the nature of the halogen accommodates the results. While for X = Cl, as for F, the equilibrium must lie predominantly to the left, for X = Br, the absence of products corresponding to **5** requires it to lie far to the right.

When **2c** was treated with BuLi followed by 1 equiv of heptanal and the resulting pale yellow solution worked up in the usual way (see Experimental Section), a 78% yield of 4-bromoundeca-1,4-diene was obtained. The details of this reaction, as well as that occurring with benzaldehyde, are summarized in Table I.

Compounds **6** and **7** appear to be the first reported examples of this class, possibly because a regiospecific entry to this group has not hitherto been possible. The stereoselectivities in these reactions are somewhat lower than that observed with the corresponding α-bromoethylide—they are also quite strikingly reversed. As Table I shows, while both **6** and **7** are preferentially formed with

---

[1] See for example: (a) D. E. Van Horn and E. Negishi, *J. Am. Chem. Soc.*, **100**, 2252 (1978); (b) E. Negishi, N. Okukado, A. O. King, D. E. Van Horn, and B. I. Spiegel, *ibid.*, **100**, 2254 (1978).

[2] (a) R. O. Hutchins and N. R. Natale, *J. Org. Chem.*, **43**, 2299 (1978); (b) C. Cahiez, A. Alexakis, and J. F. Normant, *Synthesis*, 528 (1978); (c) G. L. Van Mourik and H. J. J. Pabon, *Tetrahedron Lett.*, 2705 (1978).

[3] R. H. Smithers, *J. Org. Chem.*, **43**, 2833 (1978).

[4] From the reaction of bromotrichloromethane and triphenylphosphine, see B. A. Clement and R. L. Soulen, *J. Org. Chem.*, **41**, 556 (1976).

[5] (a) For a review of the tetrachloromethane–tertiary phosphine system, see: R. Appel, *Angew. Chem., Int. Ed. Engl.*, 14, 801 (1975); (b) D. G. Naae, H. S. Kesling and D. J. Burton, *Tetrahedron Lett.*, 3789 (1975).

0022-3263/80/1945-0173$01.00/0