## A Palladium-Catalyzed Conjugated Diene Synthesis

rinses were saturated with sodium chloride and extracted with cyclohexane  $(2 \times 25 \text{ ml})$ . The combined cyclohexane rinses and extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated at reduced pressure. GLC analysis (10 ft  $\times$ 0.25 in. FFAP column, 100°) of the residue indicated a single hydrocarbon product, which was purified by GLC (above conditions) to give 15 as a clear oil:  $\delta_{TMS}(CDCl_3)$  1.16 (s, 3 H, CH<sub>3</sub>) and 0.8-2.3 (br m, 13 H); v (CCl<sub>4</sub>) 3020, 2990, 2875, 2850, 1455, 1340, 1160, 1140, 1105, 1055, 990, 965, and 945 cm<sup>-1</sup>; MS m/e (rel intensity) 148 (100), 133 (60), 107 (36), 106 (71), 105 (50), 93 (52), 92 (52), 91 (73), and 79 (80).

Anal. Calcd for C11H16: C, 89.12; H, 10.88. Found: C, 88.96; H, 10.99.

Acknowledgment. This work was supported by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the University of Delaware Research Foundation, and the Delaware Institute of Medical Education and Research.

Registry No.-1, 10497-56-0; 2, 28673-75-8; 4a, 54003-44-0; 4b, 54003-45-1; 5, 54003-46-2; 6, 54003-47-3; 7, 54019-69-1; 7 3,5-dinitrobenzamide derivative, 54003-48-4; 8, 54003-49-5; 9, 53075-01-7; 11, 53075-02-8; 12, 53075-00-6; 13, 53075-04-0; 14, 53075-03-9; 15, 54003-50-8.

#### **References and Notes**

- (1) For a preliminary account of a portion of this work, see R. K. Murray, Jr., and K. A. Babiak, Tetrahedron Lett., 319 (1974).
- (2) For a summary of adamantane chemistry, see E. M. Engler and P. v. R. Schleyer, MTP Int. Rev. Sci.: Org. Chem., Ser. One, 239 (1973); R. C. Bingham and P. v. R. Schleyer, "Chemistry of Adamantanes", Springer-Verlag New York, New York, N.Y., 1971; R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, 64, 277 (1964).
- (3) J. E. Baldwin and W. D. Foglesong, J. Am. Chem. Soc., 90, 4303 (a) J. E. Baldwin and W. D. Foglesong, J. Am. Chem. Soc., 90, 4303 (1968).
   (4) H. W. Whitlock, Jr., and M. W. Siefken, J. Am. Chem. Soc., 90, 4929
- (1968).
- (5) R. K. Murray, Jr., and T. K. Morgan, Jr., *Tetrahedron Lett.*, 3299 (1973).
   (6) R. K. Murray, Jr., and K. A. Babiak, *Tetrahedron Lett.*, 311 (1974).
- (7) R. K. Murray, Jr., and K. A. Babiak, J. Org. Chem., 38, 2556 (1973) (8) R. K. Murray, Jr., and T. K. Morgan, Jr., J. Org. Chem., submitted for
- publication.

- (9) For a review, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
- (10) C. A. Cupas, W. Schumann, and W. E. Heyd, J. Am. Chem. Soc., 92, 3237 (1970). By this method 2 can be prepared in two steps from tropy-lium tetrafluoroborate in an overall yield of ca. 35%.
- (11) By contrast, direct (absence of a sensitizer) irradiation of 2 does not afford 1.
- (12) S. G. Levine, J. Am. Chem. Soc., 80, 6150 (1958); G. Wittig, W. Böll,
- (12) S. dt. Levine, J. J. M. Cham. Oran. Oran. Col., 100, 1350 (1350), dt. Wildy, W. Boll, and K.-H. Krück, Chem. Ber., 95, 2514 (1962).
   (13) A. Ferwanah, W. Pressler, and C. Reichardt, Tetrahedron Lett., 3979 (1973); C. Reichardt, private communication.
- (14) A similar sequence of reactions has been employed to prepare 2-adamantanecarboxylic acid from adamantanone: A. H Wynberg, and J. Strating, *Synth. Commun.*, **2**, 79 (1972). H. Alberts, H.
- (15) R. F. Borch, M. D. Bernstein, and H. D. Durst, J. Am. Chem. Soc., 93, 2897 (1971).
- (16) R. Greenwald, M. Chaykovsky, and E. J. Corey, J. Org. Chem., 28, 1128 (1963)
- (17) An analogous reaction with adamantanone has been reported: J. Ku-than, J. Paleček, and L. Musil, Collect. Czech. Chem. Commun., 38, 3491 (1973).
- (18) (a) R. C. Fort, Jr., and P. v. R. Schleyer, J. Org. Chem., 30, 789 (1965);
   (b) F. W. van Deursen and P. K. Korver, Tetrahedron Lett., 3923 (1967);
   (c) F. W. van Deursen and A. C. Udding, Recl. Trav. Chim. Pays-Bas, 87, 1243 (1968); (d) F. W. van Deursen and J. Bakker, Tetrahedron, 27, 4593 (1971).
- (19) Initial report: A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, Chem. Commun., 657 (1966)
- For examples with acyclic  $\beta$ ,  $\gamma$ -unsaturated ketones see E. Baggiolini, K. (20)Schaffner, and O. Jeger, Chem. Commun., 1103 (1969); W. G. Daube M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, J. Am. Chem. Soc., 92, 1786 (1970). For examples with cyclic  $\beta$ , $\gamma$ -unsaturated ketones see J. Ipaktschi, *Tetrahedron Lett.*, 2153 (1969); H. Hart, R. K. Murray, Jr., and G. D. Appleyard, ibid., 4785 (1969); J. Ipaktschi, ibid., 3179 (1970); R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, J. Am. Chem. Soc., 93, 3957 (1971).
- The <sup>1</sup>H NMR spectrum of enone **13** (see Experimental Section) permits assignment of the upfield and downfield olefinic "triplets" in the <sup>1</sup>H NMR spectrum of **2**<sup>10</sup> to the hydrogens at C-4 and C-5, respectively. (21)
- (22) P. S. Engel and M. A. Schexnayder have previously reported [*J. Am. Chem. Soc.*, 94, 9252 (1972)] an "unprecedented triplet 1,3-acyl shift" in the photochemistry of a  $\beta,\gamma$ -unsaturated ketone. It is not clear if a similar isomerization is occurring in the present study or if the formation of 13 from 12 with triplet sensitization simply results from some "leakage" to the excited singlet of 12 under the photolysis conditions em-R. L. Augustine, Ed., "Reduction Techniques and Applications in Organic
- (23)Synthesis'', Marcel Dekker, New York, N.Y., 1968, pp 171-185, and references cited therein
- (24) For the successful Wolff-Kishner reduction of ketone 1, see ref 7,

# A Palladium-Catalyzed Conjugated Diene Synthesis from Vinylic Halides and Olefinic Compounds

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Received October 22, 1974

Conjugated dienes are obtained when vinylic bromides or iodides are treated with olefinic compounds in the presence of a trialkylamine and a catalytic amount of  $Pd[P(C_6H_5)_3]_2(OAc)_2$  at 100-150°. In some instances, with the less substituted reactants, the initially formed dienes undergo subsequent Diels-Alder reactions. The new conjugated diene synthesis shows appreciable stereospecificity when (Z)- or (E)-vinylic halides are treated.

The palladium-catalyzed reaction of vinylic halides with olefinic compounds in the presence of a trialkylamine to form conjugated dienes has been noted previously,<sup>1,2</sup> but the scope of the reaction has not been investigated. We report herein an investigation of the reaction with a variety of vinylic halides and olefinic compounds.

#### **Results and Discussion**

Eight vinylic halides with different structural features were treated with various olefinic compounds to demonstrate several applications of the reaction. The results are summarized in Table I.

The reaction is believed to occur in three steps.<sup>2</sup> The "catalyst" is first reduced by the olefinic compound to a

palladium(0) phosphine complex, which then reacts with the vinylic halide by oxidative addition. The vinylic palladium complex formed next adds to the olefin and the adduct eliminates an hydridopalladium group, forming the conjugated diene. The hydrido complex then loses hydrogen halide to the tertiary amine present, re-forming the palladium(0) phosphine complex, and the cycle is complete.

The reaction may be complicated by the conjugated diene product undergoing subsequent reactions such as double-bond isomerization or Diels-Alder reactions with starting material. The reaction of the 1-halo-1-hexenes with ethylene, for example, produces mainly the rearranged diene, 2,4-octadiene, rather than the expected 1,3-octa-

			0	l lefin Viny	apie 1 lation Reactions		
Vinylic halide (mmol)	Olefinic reactant (mmol)	Et3N,	p	Reaction	Products (% yield)	Bp or mp o	
(registry no.)	(registry no.)	mmol	Catalyst	time, hr	(registry no.)	(reported), C	NMR spectrum, $ au$
Vinyl iodide (20) (593-66-8)	Methyl acrylate (50) (96-33-3)	25	A	$32^{b}$	Dimethyl <i>cis</i> -cyclohexene-3,4- dicarboxylate (54354-48-2)	bp 100–110 (1.3 mm)	(CCl <sub>4</sub> ) s (broad) 4.37 (2 H), s 6.36 (6 H), m 6.45-8.30 (6 H)
					Dimethyl cyclohexene-2,3-di- carboxylate $(52)^{c,d}$ (41902- 36-7)		$(CC1_4)$ m 3.07 (1 H), s 6.34 (3 H), s 6.39 (3 H), m 6.64 (1 H), m 7.60-8.70 (6 H)
2-Bromopropene (40) (557-93-7)	Methyl acrylate (100)	50	¥	$36^b$	Dimethyl $cis$ -1-methylcyclo- hexene-3,4-dicarboxylate (62.5) (54354-49-3)	bp $98-100^{\circ}$ (1.3 mm) <sup>e</sup>	$\begin{array}{c} (\text{CC1}_{4}) & \text{m 4.66} (1 \text{ H}), \text{ s 6.37} \\ (\text{6 H}), \text{m 6.48-8.15} (6 \text{ H}), \\ \text{s (hroad) 8 32 (2 \text{ H})} \end{array}$
2-Bromopropene (20)	Styrene (25) (100- 42-5)	25	В	96 <sup>°</sup>	Dimethyl 1-methyl-3-phenyl- cyclohexene-4,5-dicarboxy- late	Solid, <sup>f</sup> mp 111–112 bp 138–150 (0.15 mm)	$(C_6D_6) \approx 2.88 (5 H), m$ ( $C_6D_6$ ) $\approx 2.88 (5 H), m$ (broad) $4.51-4.82 (1 H), m$ 5.85-7.22 (3 H), s 6.57 (3 H), s 6.77 (3 H), s
	Dimethyl maleate (25) (624-48-6)				Two isomers: solid (24.2) (54354-50-6), liquid (28.0) (54382-88-6)	Liquid" bp 138–150 (0.15 mm)	m (broad) 7.56–8.00 (2 H), s (broad) 8.42 (3 H) $(C_{6}D_{6})$ s 2.83 (5 H), m (broad) 4.71 (1 H), m 5.55–7.22 (3 H), s 6.62 (3 H), s 6.77 (3 H), m 7.67–7.93 (2 H), s
1-Bromo-2-methyl-pro- pene (20) (3017-69-4)	Methyl acrylate (25)	25	A	40L	Methyl 5-methyl-2,4-hexadi- enoate (75) <sup>2</sup>		
Methyl $(E)$ -3-bromo-2- methylpropenoate (200) (40053-01-8)	Methyl acrylate (250)	250	A	$6^{b,h}$	Dimethyl $(E, E)$ -5-methyl-2,4- hexadienedioate $(60)^{i}$ (39995- 94-3)	bp 89 (0.65 mm), mp 54.5-55.5 (55.5) <sup>j</sup>	$({ m CC1}_4)$ 2 d 2.42 (1 H), 2 q 2.83 (1 H), d 3.85 (1 H) $(J_{BY}=11, J_{T6}=14, J_{P-{ m CH}_3}=\sim 1$ Hz), s 6.24 $(J_{P-{ m CH}_3}=\sim 1$ Hz), s 6.24
<ul> <li>(E)-1-Iodo-1-hexene (20).</li> <li>(16644-98-7)</li> </ul>	Methyl acrylate (25)	25	¥	38 <sup>6</sup>	Methyl $(E, E)$ -2,4-nonadienoate (45) <sup>6, k</sup> (54354-51-7)		$(CCI_4)$ m 2.65 m 2.9 (1 H), m 3.70-3.95 (2 H), d 4.25 (J = 15) (1 H), s 6.30 (3 H), m 7.60-8.05 (2 H), m 8.35-8.84, m 8.95-9.35 (peak at 9.08) (7 H)
					Methyl ( $E,Z$ )-2,4-nonadienoate (8) <sup>6,1</sup> (39924-44-2)		$\begin{array}{l} ({\rm CCI}_4) \ 2 \ d \ 2.43 \ (1 \ {\rm H}), \ {\rm m} \\ 3.65-4.35 \ (J_{\alpha\beta}=15, \ J_{76}=11 \ {\rm Hz}) \ (3 \ {\rm H}), \ {\rm s} \ 4.30 \\ (3 \ {\rm H}), \ {\rm m} \ 7.45-7.90 \ (2 \ {\rm H}), \ {\rm m} \ 8.30-8.85, \ {\rm m} \ 8.90^- \\ 9.25 \ (7 \ {\rm H}) \end{array}$

(Z)-1-Iodo-1-hexene (10) (16538-47-9)	Methyl acrylate (12.5)	12.5	A	$15^{b}$	Dimethyl $(E, Z)$ -2,4-nonadi- enoate $(30)^c$ Dimethyl $(E, E)$ -2,4-nonadi- enoate $(51)^c$		
(Z)-1-Iodo-1-hexene (10)	Methyl acrylate (12.5)	12.5	A	150 <sup>m</sup>	Dimethyl $(E,Z)$ -2,4-nonadi- enoate $(44)^c$ Dimethyl $(E,E)$ -2,4-nonadi- enoate $(39)^c$		
(Z)-1-Bromo-1-hexene (5) (13154-12-6)	Methyl acrylate (6.25)	6.25	а	$21^b$	Dimethyl $(E,Z)$ -2,4-nonadi- enoate $(40)^{\circ}$ Dimethyl $(E,E)$ -2,4-nonadi- enoate $(18)^{\circ}$		
(Z)-1-Bromo-1-hexene (5)	Methyl acrylate (6.25)	6.25	$\mathrm{B}$ + 6 mol % $\mathrm{Ph}_3\mathrm{P}$	$19^{b}$	Dimethyl $(E,Z)$ -2,4-nonadi- enoate $(71)^{\circ}$ Dimethyl $(E,E)$ -2,4-nonadi- Dimethyl $(E,E)$ -2,4-nonadi-		
(Z)-1-Bromo-1-hexene (5)	Methyl acrylate (12.5)	6.25	$\begin{array}{l} \mathbf{B} + 6 \ \mathrm{mol} \ \% \\ \mathbf{P} \mathbf{h}_3 \mathbf{P} \end{array}$	$21^{b}$	Dimethyl $(E, Z)$ -2,4-nonadi- enoate $(79)^c$ Dimethyl $(E, E)$ -2,4-nonadi- enoate $(13)^c$		
(Z)-1-Bromo-1-hexene (5)	Methyl acrylate (6.25)	12.5	$\begin{array}{l} \mathrm{B} + 6 \mod \% \\ \mathrm{Ph_3P} \end{array}$	19 <sup>b</sup>	Dimethyl $(E,Z)$ -2,4-nonadi- enoate $(82)^{\circ}$ Dimethyl $(E,E)$ -2,4-nonadi- Dimethyl $(E,E)$ -2,4-nonadi-		
1-Bromo-2-methyl- propene (50)	Styrene (100)	62.5	U	300 <sup>b</sup>	(E)-1-Phenyl-4-methyl-1,3- pentadiene $(57,9)^n$ (39491- 73-1)	bp 78–80 (1.2 mm)	(neat) m 2.77, d 3.18 (6 H), d 4.07 (1 H), 2 m 4.05 (1 H) $(J_{\alpha\beta} = 16, J_{\beta\gamma} = 11$
Methyl (E)-3-Bromo-2- methylpropenoate (20)	Styrene (40)	25	В	$21^{b}$	Methyl $(E,E)$ -2-methyl-5- phenyl-2,4-pentadienoate (78) (20414-95-3)	mp 86.5-87 (86-87)°	нz', s (ргоад) 6.33 (р. н) (С <sub>6</sub> D <sub>6</sub> ) m 2.33-2.95, 3.01, 3.21, 3.30, 3.54 (8 H), s 6.46 (3 H), s 8.03 (3 H)
(E)-2-Bromostyrene (30) (582-79-7)	Styrene (60)	37.5	В	$135^{b}$	(E,E)-1,4-Diphenyl-1,3-buta-diene (40) (538-81-8)	$ \substack{ \text{mp } 150-151 \ (150-151)^p } $	
1-Bromo-2-methyl- propene (80)	(E)- and $(Z)$ -Cro- tononitrile (100) (627-29-6, 1190-76-7)	100	ш	340 <sup>b</sup>	(E) - and (Z) -1-Cyano-2,4- dimethyl -1,3-pentadiene $(26,5)^{4,4}$ (54354-52-8, 54354-53-9)	bp 92–94 (23 mm)	<i>E</i> (CCl <sub>4</sub> ) s (broad) 4.28 (1 H), s (broad) 4.97 (1 H), s 7.89 (3 H), s 8.16 (6 H)
							Z (CCl <sub>4</sub> ) s (broad) 4.10 (1 H), s (broad) 4.95 (1 H), s $8.02$ (3 H), s $8.10$ (3 H), s $8.18$ (3 H)
Methyl ( <i>E</i> )-3-Bromo-2- methylpropenoate (40)	Methyl methacry- late (50)	20	ц	48°	Dimethyl $(E, E)$ -2,5-dimethyl- 2,4-hexadienedioate (33.4) <sup><math>r</math></sup> (23119-30-4) Dimethyl $(E, Z)$ -2,5-dimethyl- 2,4-hexadienedioate (28.3) <sup><math>t</math></sup> (54354-54-0)	mp 101.5-102.5 (99-100) <sup>s</sup>	$(CCI_4)$ s 2.55 (2 H), s 6.22 (6 H), s 8.03 (6 H) $(CCI_4)$ d 2.19 (1 H), d 3.48 (1 H) ( $J = 12$ Hz), s 6.28 (6 H), s (broad) 8.12 (6 H)

				<b>L</b> 0()	'able I ntinued)	
Vinylic halide (mmol) (registry no.)	Olefinic reactant (mmol) (registry no.)	Ét3N, mmol	Catalyst <sup>a</sup>	Reaction time, hr	Products (% yield) (registry no.)	Bp or nip teported), <sup>o</sup> C NMR spectrum, ד
(Z)-1-Iodo-1-hexene (5)	Ethylene (74-85-1)	6.25	В	139 <sup>"</sup>	1,3-Octadiene (13.5) <sup>c</sup>	
(Z)-1-Bromo-1-hexene (10)	Ethylene	12.5	В	38 <sup>"</sup>	4,4-Octadiene (02.2) 1,3-Octadiene (36.1) <sup>c</sup>	
<i>(E)</i> -1-Iodo-1-hexene (10)	Ethylene	12.5	В	88	2,4-Octadiene (56.9) <sup><math>c</math></sup> 1,3-Octadiene (5.9) <sup><math>c</math></sup> 2,4-Octadiene (67.8) <sup><math>c</math></sup>	
<ul> <li><sup>a</sup> A, 1 mol % Pd(OAc)<sub>2</sub>, 2 mc</li> <li>C, 1 mol % (Ph<sub>3</sub>P)<sub>2</sub>Pd(OAc)<sub>2</sub> t determined by VPC. <sup>a</sup> Pure sam</li> <li>H, 7.78. / Calcd: C, 70.81; H, 6</li> <li>C, 70.68; H, 7.01. <sup>b</sup> Reaction ca</li> <li>capped tube at 100° required 2</li> </ul>	al % Ph <sub>3</sub> P based on vinylic then 0.5 mol % after 170 ht pales isolated by VPC. <sup>e</sup> Cal :99. Found: C, 70.90; H, 7. rried out in an open system the to reach completion an	halide; B, - <sup>b</sup> Reactic led: C, 62.3 10. <sup>g</sup> Calcu a under re a under re	1 mol % (Ph <sub>3</sub> P) m temperature 1 25; H, 7.60. Foun d: C, 70.81; H, 6 flux. A similar r as approximatel	<sup>2</sup> Pd(OAc) <sup>2</sup> ; 00°. <sup>c</sup> Yield d: C, 62.75; .99. Found: eaction in a v the same.	168115. <sup>4</sup> Calcd mol wt: 168115. Found: 168 158110. Found: 158107. <sup>6</sup> G. Pattendon and <sup>p</sup> W. P. Weber, R. A. Felix, A. K. Willard, <sup>q</sup> Calcd mol wt (E): 121089. Found: 121088. mol wt: 198.089. Found: 198.087. <sup>s</sup> J. A. Ellvic 1026 (1953). <sup>4</sup> Calcd mol wt: 198.089. Found	8.115. "Reaction temperature 70°. "Calcd mol wt: d B. C. L. Weedon, J. Chem. Soc. C, 1997 (1968). and K. E. Koenig, <i>Tetrahedron Lett.</i> , 4701 (1971). Calcd mol wt (Z): 121.089. Found: 121.088. "Calcd dge, R. P. Linstead, and J. F. Smith, J. Chem. Soc. d: 198.089. "Reaction temperature 130°. "Reaction

temperature 155°

capped tube at 100° required 2 hr to reach completion and yield was approximately the same. <sup>•</sup> Calcd mol wt: 184.073. Found: 184.074. <sup>•</sup> M. Ohno, Y. Inoue, and T. Sugita, Bull. Inst. Chem. Res., Kyoto Univ., **38**, 8 (1960); Chem. Abstr., **56**, 333i (1962). <sup>\*</sup> Calcd mol wt: 168.115. Found:

diene. Both vinyl iodide and 2-bromopropene react with excess methyl acrylate to form only Diels-Alder adducts with none of the expected dienes being isolable even when only equivalent amounts of the ester were used. The vinyl iodide reaction was complicated further by the problem that the initially formed Diels-Alder product partially underwent a rearrangement of the double bond catalyzed by the triethylamine present. The related methyl derivative



formed from 2-bromopropene and methyl acrylate does not rearrange under the same conditions. The stereochemistry of the initial adduct formed in the vinyl iodide reaction was established by hydrogenating it to the known dimethyl *cis*-1,2-cyclohexanedicarboxylate. A similar result was observed in the reaction of 2-bromopropene with styrene, and a high molecular weight, apparently Diels-Alder, product was formed. This product was not identified; however, the intermediate conjugated diene could be captured with dimethyl maleate if it was added to the reaction mixture, since it is a better dienophile than either of the reactants,  $CH_3$ 



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and it is relatively unreactive in the vinylation reaction. Two isomeric products were obtained in this example. These are likely formed by endo and exo Diels-Alder additions, since the other possible isomers involve isomerization at the carbons  $\alpha$  to the ester groups. This isomerization would not be expected to occur because it did not in the closely related dimethyl cyclohexenedicarboxylates described above under the same conditions.

The yields of dienes obtained and the rates at which the dienes are formed depend on the structures of both the vinylic halides and the olefinic compounds. The reactivities of vinylic bromides and iodides are rather similar. In the reactions of the 1-halo-1-hexenes, the bromide is apparently somewhat more reactive with ethylene, while the iodide is a little more reactive with methyl acrylate. Substituents  $\beta$  to the halo group exert a significant effect; electronsupplying groups (alkyl) decrease reactivity, while electron-withdrawing groups (carbomethoxyl, aryl) increase it. The methyl substituent on the  $\alpha$  carbon in 2-bromopropene has much less effect than the two  $\beta$ -methyls in 1bromo-2-methyl-1-propene. Replacement of one of the two  $\beta$ -methyls in the last compound by a carbomethoxyl group led to about a tenfold increase in the reaction rate with methyl acrylate.

The reactivity of disubstituted olefinic compounds in the vinylic halide reaction is considerably lower than that of the related monosubstituted olefinic compounds, as has been noted previously.<sup>3</sup> Thus, methyl (E)-3-bromo-2-methylpropenoate reacts with methyl acrylate about eight times faster than it does with methyl methacrylate. Croto-nonitrile reacts very slowly with 1-bromo-2-methyl-1-propene, giving only a 26.5% yield of the expected two isomeric dienes after 340 hr at 100°, when all of the bromide had disappeared.

The relatively low reactivity of ethylene compared with methyl acrylate or styrene is unexpected in view of the reverse order of reactivity found at room temperature in the addition of "phenylpalladium chloride" to the same olefins.<sup>3</sup> The explanation may be that in the present reactions all or part of the rearrangement proceeds by way of a  $\pi$ -allylic palladium intermediate (formed by metal hydride elimination-readdition steps). The  $\pi$ -allylic complex then must be decomposed thermally to regenerate the catalyst while the decomposition would be much easier in the arylpalladium halide-olefin reactions. The less substituted  $\pi$ -allylic complex from the ethylene reaction would be expected to be more stable thermally than the more substituted products expected from methyl acrylate or styrene. Of course, the 2,4-diene is thermodynamically favored in the ethylene reaction, while the unrearranged 2,4-dienoic ester is favored in the acrylate reaction. In any case, the arylpalladium-olefin reactions were carried out competitively and stoichiometrically and are not strictly comparable to the approximate individual reaction rates estimated in the present examples.

(Z)-1-Iodo-1-hexene reacts about twice as fast as the (E)-iodo compound with methyl acrylate. We have looked at the stereochemistry of this reaction in some detail, since we expected that the results would be typical of those that would be obtained in many other related reactions. The two expected products were readily obtained in good yields by the reactions of the (Z)- and (E)-1-hexenylboronic acids with stoichiometric amounts of palladium acetate in the presence of methyl acrylate at 0°. The Z compound produced methyl (E,Z)-2,4-nonadienoate in 70% yield and the E boronic acid gave the E,E ester in 82% yield. The more practical synthesis from the vinylic halides, which is catalytic in palladium, is not so stereospecific.



Under our usual reaction conditions, i.e.,  $100^{\circ}$  with 1 mol % of Pd(OAc)<sub>2</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> or its equivalent, 1 mol % of Pd(OAc)<sub>2</sub> with 2 mol % of P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> as catalyst, (*E*)-1-iodo-1-hexene and methyl acrylate produced methyl (*E*,*E*)-2,4-nonadienoate in 45% yield and the *E*,*Z* isomer in 8% yield in 38 hr, by which time the vinylic iodide had all reacted. The *Z* iodide under the same conditions reacted in about 15 hr, forming 51% of the *E*,*E* ester and 30% of the *E*,*Z* isomer. Lowering the reaction temperature to 70° in the last reaction improved the selectivity some; 39% *E*,*E* and 44% *E*,*Z* esters were now produced, but 150 hr was required for complete reaction. Very similar results were obtained from CH (CH)



the cis iodide without triphenylphosphine being present. The reaction proceeded only about half as fast, however, but the products were essentially identical.

The stereochemistry of the addition also depended upon the halide used and some other reaction conditions. The reaction of (Z)-1-bromo-1-hexene with methyl acrylate gave 40% E,Z and 18% E,E ester compared with 30 and 51%, respectively, with the Z iodo compound after all of the halide had reacted (31 hr for the bromide and 15 hr for the iodide). A very substantial improvement in the selectivity occurred when more than 2 mol % of triphenylphosphine per mole of vinylic halide was present per mole percent of palladium in the bromide reaction. With 8 mol % of the phosphine, after 15 hr at 100°, there was obtained 72% E,Zand only 10% E,E ester. Initially, almost pure E,Z isomer was formed. Longer reaction times lead to a slow formation of the E,E ester at the expense of the E,Z isomer. After 51 hr the yields were 27% E,Z and 56% E,E, for example. Increasing the methyl acrylate concentration relative to the bromide (from 1:1 to 2:1) had little effect upon the reaction, but increasing the triethylamine concentration from 1:1 to 2:1 relative to the bromide improved the reaction with the 8 mol % triphenylphosphine still further to give 83% E,Z and 11% E,E ester in 19 hr. Again, the relative amount of the E, E ester increased slowly with longer reaction times, but the initial more rapid diene isomerization was significantly decreased. Thus, it appears that there are at least three different mechanisms by which isomerization is occurring in this reaction. There are (1) the isomerization which is inhibited by excess triphenylphosphine, (2) an initial diene product isomerization which becomes less rapid with time and which is inhibited by diluting the reaction mixture with excess amine, and (3) a residual slow product



isomerization which continues after the first two isomerization reactions have stopped or are inhibited.

The excess triphenylphosphine may be stopping one kind of isomerization by displacing diene from palladium in complex I. This would prevent internal readdition of the hydridopalladium group in the opposite direction and the formation of a  $\pi$ -allylic intermediate which ultimately would eliminate again, possibly forming a different isomeric diene than was originally produced.

The initial diene product isomerization appears to be a second-order palladium hydride or a phosphinepalladium hydride catalyzed isomerization, since it stops when the reaction is over and is inhibited by dilution with the amine, a reagent which presumably (slowly) reconverts the hydrides into the palladium(0) catalysts.

The slow residual isomerization also appears to be palladium catalyzed, since the pure esters are stable at the reaction temperature. The esters also are stable at 100° in the presence of 5% Pd on carbon,  $Pd[P(C_6H_5)_3]_4$ , and  $Pd(OAc)_2$ . We have no idea what reaction is responsible for this slow isomerization, unless it is due to addition-elimination reactions of a small equilibrium amount of metal hydride formed from Pd(0) compounds and the amine salt formed.

Whatever the reasons are for the isomerization, quite high stereospecificity can be obtained under the proper conditions.

The experiments carried out indicate fairly broad utility for the vinylic halide-olefin reaction, although some limitations are also apparent. Aside from the problem that Diels-Alder reactions may occur with the less substituted dienes when the olefinic reactant is a good dienophile, there are limitations when too many substituents are present in the olefinic reactant. Apparently, the vinylic halides undergo some unknown decomposition reaction by themselves, and, if the olefinic compounds are not very reactive, the halides decompose without adding to the olefins. Poor yields also are to be expected with vinylic halides deactivated with electron-supplying substituents when they are treated with olefinic compounds of only moderate reactivity. Still, many useful combinations remain which should allow this reaction to be of considerable utility in the synthesis of various types of substituted conjugated dienes.

### **Experimental Section**

(*E*)-1-Iodo-1-hexene. This compound was prepared by the method of Zweifel and Steele:<sup>4</sup> NMR (CDCl<sub>3</sub>)  $\tau 2 t$ , 3.47, 3.72 (1 H) (*J* = 7 Hz); d, 4.16 (*J* = 15 Hz) (1 H); m 7.80-8.31 (2 H); m 8.49-8.98 (4 H), m 8.98-9.35 (3 H).

1-Iodo-1-hexyne. 1-Hexyne (36 g, 0.44 mol) in 200 ml of ether was placed in a dry 1-l. three-necked flask equipped with a pressure-equalizing dropping funnel, a reflux condenser, and a mechanical stirrer. The system was flushed with argon and maintained under argon throughout the course of the reaction. Then 300 ml (0.5 mol) of 1.67  $\dot{M}$  methyllithium in ether (commercial) was added through the dropping funnel at such a rate as to cause gentle refluxing. After the addition, the mixture was stirred for 1 hr at room temperature. After cooling in an acetone–Dry Ice bath, 127 g (0.5 mol) of iodine was added. The bath was allowed to come gradually to room temperature (ca. 2 hr) and the reaction was continued overnight at room temperature. Water (200 ml) was added and the entire mixture was combined with 300 ml more water in a separatory funnel. The phases were separated and the aqueous phase was extracted with two 100-ml portions of ether. The ether phases were combined, washed with 300 ml of a saturated aqueous sodium thiosulfate solution, dried over magnesium sulfate, and filtered. The ether was removed under reduced pressure and the residue was distilled, yielding 77 g (84%) of 1-iodo-1-hexyne, bp 75° (20 mm).<sup>5</sup>

(Z)-1-Iodo-1-hexene. Our attempts to prepare this compound via dicyclohexylborane reduction of 1-iodo-2-hexyne<sup>5</sup> resulted in a product containing about 15% of the *E* isomer. Diimide reduction, on the other hand, was much more specific.

Dipotassium azodicarboxylate was prepared by adding 90 g (0.77 mol) of azodicarbonamide to a mechanically stirred 40% aqueous potassium hydroxide solution (270 ml), cooled by an external acetone-ice bath at a rate such that the temperature of the reaction mixture did not exceed 10° (~30 min). After the addition the mixture was stirred for an additional 45 min (below 10°) and then filtered and washed with 300 ml of cold methanol.

## A Palladium-Catalyzed Conjugated Diene Synthesis

The solid potassium salt was placed in a 1-l. flask with 400 ml of methanol and 20 g (0.096 mol) of 1-iodo-1-hexyne was added. The mixture was stirred magnetically while a solution of 75 ml of acetic acid in 200 ml of methanol was added at such a rate as to cause gentle boiling. After the addition, the mixture was colorless. The reaction mixture was transferred to a separatory funnel containing 2 l. of water and extracted with three 250-ml portions of pentane. The pentane fractions were combined, washed with two 1-l. portions of water, dried over magnesium sulfate, and filtered. The pentane was removed under reduced pressure. VPC examination of the residue showed that all of the 1-iodo-1-hexyne had reacted, but that in addition to the desired (Z)-1-iodo-1-hexene, a significant amount of 1-iodohexane had also been formed. The residue was dissolved in 75 ml of n-butylamine and the solution was allowed to stand at room temperature. After 45 min, VPC analysis showed that all of the 1-iodohexane had reacted. The solution was diluted with 200 ml of pentane and washed with two 300-ml portions of water, 300 ml of cold 10% HCl (aqueous), and then with 300 ml more of water. The organic phase was dried over magnesium sulfate and filtered and the pentane was removed under reduced pressure, leaving 11.2 g (55.5%) of (Z)-1-iodo-1-hexene as a colorless liquid which was shown to be pure by VPC and NMR: NMR (neat)  $\tau$  m, 3.72–4.17, s 3.89 (2 H), m 7.68–8.15 (2 H), m 8.33-8.78 (4 H), m 8.78-9.32 (3 H).

(Z)-1-Hexene-1-boronic Acid. A solution of 20 ml (44 mmol) of 2.2 M n-butyllithium (commercial) in hexane and 10 ml of anhydrous ether was placed in a dry, argon-filled, 250-ml, three-neck flask equipped with a pressure equalizer, a dropping funnel, and a magnetic stirring bar. The mixture was cooled in an acetone-Dry Ice bath and 6.3 g (30 mmol) of (Z)-1-iodo-1-hexene in 15 ml of ether was added over a 15-min period. The mixture was stirred for 3 hr at  $-78^{\circ}$  and then 15 g (76 mmol) of tri-*n*-butyl borate was added over a 10-min period. The acetone-Dry Ice bath was allowed to come gradually to room temperature (ca. 3 hr) and the mixture was stirred at room temperature overnight (ca. 16 hr). The reaction mixture was diluted with 200 ml of water and extracted with three 50-ml portions of ether which were then combined and extracted with two 100-ml portions of 10% aqueous sodium hydroxide. The aqueous fractions were combined, washed with 50 ml of ether, made acidic with cold 5% HCl, and extracted with four 50-ml portions of ether. The ether phases were combined, dried over anhydrous magnesium sulfate, and filtered. The ether was removed under reduced pressure, leaving a clear, colorless oil which was presumed to be the boronic anhydride. The addition of 20 ml of water caused almost instantaneous formation of a white solid. The mixture was stirred for 30 min at room temperature and then at 5° for 30 min. The solid was filtered and allowed to air dry, giving 1.01 g (26%): mp 62-63°; NMR (acetone- $d_6$ )  $\tau$  s (broad), 3.16 (2 H); 2 t, 3.57, 3.79 (J = 7 Hz) (1 H), d, 4.63 (J = 13 Hz) (1 H); m, 7.30-7.75 (2 H); m, 8.38-8.80 (4 H); m, 8.80-9.26 (3 H).

(*E*)-1-Hexene-1-boronic Acid. This compound was prepared by the method of Brown and Gupta:<sup>6</sup> NMR (acetone- $d_6$ )  $\tau$  s (broad), 3.08 (2 H); 2 t, 3.29, 3.59 (J = 7 Hz) (1 H); 2 t, 4.48, 4.78 (J= 1 Hz) (1 H); m, 7.70-8.12 (2 H); m, 8.41-8.90 (4 H); m, 8.90-9.35 (3 H).

(Z)-1-Bromo-1-hexene. This material was prepared essentially by the method of Brown et al.<sup>7</sup> A solution of 25.6 g (0.2 mol) of *trans*-1-hexene-1-boronic acid in 200 ml of methylene chloride and 100 ml of ether was cooled to  $-20^{\circ}$ , while 32 g (0.2 mol) of bromine was added keeping the reaction temperature below  $-20^{\circ}$ . The reaction mixture was stirred for 1 hr at  $-20^{\circ}$  and then 10.8 g (0.2 mol) of sodium methoxide in 200 ml of methanol was added while still maintaining the reaction temperature below  $-20^{\circ}$ . After the addition, the mixture was stirred at  $-20^{\circ}$  for 45 min and then warmed to room temperature, and shaken with 400 ml of water. The organic phase was separated and washed with saturated aqueous sodium thiosulfate and then dried over magnesium sulfate. Distillation yielded 16.5 g (50.7%) of (Z)-1-bromo-1-hexene: bp 47-48° (25 mm); NMR<sup>8</sup> (neat)  $\tau$  m, 3.80-4.17, s 3.89 (2 H); m, 3.68-2.15 (2 H); m, 8.33-8.78 (4 H); m, 8.78-9.32 (3 H).

Methyl (E)-3-Bromo-2-methylpropenoate. This material was prepared by the method of Caubere:<sup>9</sup> NMR (neat)  $\tau$ -q, 2.64 (J = 1.6 Hz) (1 H); s, 6.32 (3 H); d, 8.11 (J = 1.6 Hz) (3 H).

General Method for the Reaction of Vinylic Halides with Olefins. The indicated quantities (see Table I) of vinylic halide, olefin, amine, and catalyst were placed in a heavy-walled Pyrex reaction tube which was flushed with argon and capped with a selfsealing rubber-lined cap. The mixture was shaken well and heated at the indicated temperature.

In reactions where yields were determined by VPC analysis, an

internal standard was added initially and the reactions were run until the yields of products no longer increased.

In cases where products were isolated, the reactions were run until VPC analysis showed that all of the starting halide had reacted. The tubes were then opened and the reaction mixtures were extracted several times with ether. The extracts were filtered, the ether was removed under reduced pressure, and the residue was either distilled (see Table I) or purified as described below.

**1,4-Diphenyl-1,3-butadiene.** The residue from the ether solution was first sublimed and then recrystallized from methanol.

(E,E)- and (E,Z)-Dimethyl 2,5-Dimethyl-2,4-hexadienoate. The residue from the ether solution was placed in the bottom of a sublimator. An aluminum foil dish was placed above the residue and under the cold finger. Cold water was run through the cold finger and the sublimator was heated on a steam bath overnight at 0.2 mm. A light yellow solid identified as the E,E isomer was deposited on the cold finger. This was recrystallized from hexane. The aluminum foil dish contained the E,Z isomer as a pale yellow oil.

Dimethyl 1-Methyl-3-phenylcyclohexene-4,5-dicarboxylate. 2-Bromopropene (2.42 g, 20 mmol), styrene (2.60 g, 25 mmol), dimethyl maleate (3.60 g, 25 mmol), triethylamine (2.52 g, 25 mmol), and diacetatobis(triphenylphosphine)palladium (0.149 g, 0.2 mmol) were placed in a heavy-walled Pyrex reaction tube. The tube was flushed with argon, capped, and then heated on a steam bath. After 96 hr, all of the 2-bromopropene had reacted (VPC). The mixture was cooled to room temperature and extracted several times with ether. The ether extracts were combined, treated with decolorizing carbon, and filtered. Ether was removed under reduced pressure, leaving a pale yellow oil. The residue was distilled at 0.15 mm; most of the material was distilled at 138-150° (0.15 mm). Addition of a small amount of ether to the distillate caused precipitation of a colorless solid which was filtered and air dried, mp 107-109.5°C, 1.39 g (24.2%). A NMR spectrum was consistent with that expected for the desired product. Recrystallization from ether gave material of mp 111-112°.

The ether-soluble portion was purified further by chromatography on silica gel. Elution with benzene and removal of the solvent yielded 1.61 g (28.0%) of a colorless liquid which was shown by NMR to be a second isomer of the above expected diester. An analytical sample of this material was obtained by preparative VPC (15 ft  $\times$  0.25 in., 20% SE-30, 325°, retention time 470 sec).

(E,E)-Dimethyl 2-Methyl-2,4-hexadienoate. Methyl (E)-3bromo-2-methylpropenoate (35.8 g, 200 mmol), 21.4 g (250 mmol) of methyl acrylate, 25.2 g (250 mmol) of triethylamine, 0.448 g (2.0 mmol) of palladium acetate, and 1.04 g (4.0 mmol) of triphenylphosphine were placed in a 250-ml three-necked flask equipped with a mechanical stirrer and a reflux condenser. The flask was flushed with argon and maintained under an argon atmosphere throughout the course of the reaction. The reaction mixture was heated with stirring on a steam bath for 8 hr, after which time all of the starting bromide had reacted (VPC). The mixture was diluted with 300 ml of ether and filtered through a sintered glass funnel. The residue on the filter was washed well with about 500 ml more of ether. The ether, excess methyl acrylate, and triethylamine were removed under reduced pressure and the residue was distilled at 0.65 mm. A forerun boiling at less than  $89^\circ$  of 2.5 g was obtained, then the bulk of material distilled at 89°. This was then recrystallized from hexane, yielding 22 g (59.8%) of pure product.

Hydrogenation of Dimethyl Cyclohexenedicarboxylates. A mixture of 0.1 g of the distilled product from the reaction of vinyl iodide and methyl acrylate, 1 ml of tetrahydrofuran, and 0.075 g of  $PtO_2$  was placed in a small bomb equipped with a magnetic stirring bar. The system was flushed several times with hydrogen, pressured to 700 psi with hydrogen, and heated with magnetic stirring in a steam bath for 16 hr. The bomb was cooled to room temperature and opened and the reaction mixture was filtered through cotton. A VPC examination showed that the two peaks for the starting cyclohexenes had disappeared and that a single new product had been formed. This was shown to be dimethyl cis-cyclohexane-1,2-dicarboxylate by VPC comparison with an authentic sample on three different columns (5 ft  $\times$  0.25 in., 20% SE-30, 175°, retention time ~230 sec; 10 ft × 0.25 in., 20% Carbowax 20M, 215°, retention time  $\sim$ 710 sec; 5 ft  $\times$  0.25 in., 20% DEGS, 185°, retention time  $\sim 160$  sec). The authentic ester was obtained by reaction of diazomethane with the cis acid, mp 189–190° (reported mp 192° 10).

**Reaction of 1-Halo-1-hexenes with Ethylene.** The olefinic halide (10 mmol), triethylamine (12.5 mmol), diacetatobis(triphenylphosphine)palladium (0.1 mmol), and *n*-nonane (2.5 mmol) were placed in a 60-ml Teflon-lined bomb with a magnetic stirring bar. The system was flushed several times with ethylene and then

pressured to 700 psi with ethylene and heated with magnetic stirring at the indicated temperatures. The extent of reaction was measured by VPC until no more of the starting olefinic halide remained. Yields were determined by using the n-nonane as the internal standard (10 ft  $\times$  0.25 in., 20% DC-550, 140°). Products were identified by comparison of their VPC retention times with those of authentic samples and by mass spectral and NMR analyses of samples isolated by VPC.

Reaction of (E)-1-Hexene-1-boronic Acid with Methyl Acrylate. (E)-1-Hexene-1-boronic acid (0.64 g, 5 mmol), 10 ml of methyl acrylate, and 2 ml of triethylamine were stirred magnetically at 0° in an ice bath and 1.12 g (5 mmol) of Pd(OAc)<sub>2</sub> was added. The bath was allowed to gradually come to room temperature and the reaction mixture was stirred overnight at room temperature.

The mixture was then centrifuged and the residue was washed several times with ether. The supernatant liquids were combined and put through an alumina column, eluting with 1 l. of ether. Removal of the ether, methyl acrylate, and triethylamine under reduced pressure left 0.697 g of a pale yellow oil which was identified by its NMR spectrum as essentially pure methyl (E,E)-2,4-nonadieneoate (82%).

Reaction of (Z)-1-Hexene-1-boronic Acid with Methyl Acrylate. (Z)-1-Hexene-1-boronic acid (0.256 g, 2 mmol), 5 ml of methyl acrylate, 1 ml of triethylamine, and 0.448 g (2 mmol) of  $Pd(OAc)_2$  were allowed to react and the product was isolated as in

the preceding experiment. There was obtained 0.282 g of product which, by NMR and VPC analysis, was found to be mainly (E,Z)-2,4-hexadienoate (no E,E ester was present). The residue was dissolved in ether with 0.154 g (1 mmol) of biphenyl and the yield of the E,Z ester was determined by VPC (5 ft  $\times$  0.25 in., 20% DEGS, 140°) to be 70%. A pure sample of the ester was isolated by VPC.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Registry No.-1-Iodo-1-hexyne, 1119-67-1; (Z)-1-hexene-1boronic acid, 54354-55-1; tri-n-butyl borate, 688-74-4; (E)-1-hexene-1-boronic acid, 42599-18-8; Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>(OAc)<sub>2</sub>, 14588-08-0.

#### **References and Notes**

- (1) R. F. Heck and J. P. Nolley, Jr., J. Org. Chem., 37, 2320 (1972).
- H. A. Dieck and R. F. Heck, J. Am. Chem. Soc., 96, 1133 (1974).
   R. F. Heck, J. Am. Chem., Soc., 90, 5518 (1968).
   G. Zweifel and A. B. Steele, J. Am. Chem. Soc., 89, 2753 (1967).
- (5)
- (6)
- G. Zwelfel and H. Arzoumanian, J. Am. Chem. Soc., 89, 5086 (1967).
   H. C. Brown and S. K. Gupta, J. Am. Chem. Soc., 94, 4370 (1972).
   H. C. Brown, T. Hamaoka, and N. Ravindran, J. Am. Chem. Soc., 95, 6456 (1973).
- G. J. Martin and M. L. Martin, *Bull. Soc. Chim. Fr.*, 1636 (1936).
   P. Caubere, *Bull. Soc. Chim. Fr.*, 144 (1964).
- (10)G. E. Ficken, H. France, and R. P. Linstead, J. Chem. Soc., 3730 (1954).

# Organosilicon Compounds. XX. Synthesis of Aromatic Diamines via Trimethylsilyl-Protecting Aniline Intermediates

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#### Received September 12, 1974

A synthetic approach using a trimethylsilyl protecting group was employed to produce silicon- and diketo-containing diamines. Thus, the halogen-metal interchange of  $N_{\cdot}N_{\cdot}$  bis(trimethylsilyl) bromoanilines with n-butyllithium in ether produced the corresponding lithium derivatives, which were treated with dichloro-substituted silanes or dinitriles to afford the N,N-bis(trimethylsilyl)silicon-containing dianilines or the corresponding lithioimines, respectively. Hydrolysis removed the trimethylsilyl-protecting groups and converted the lithioimines to the corresponding carbonyl compounds to afford the free diamines.

Two investigators<sup>2,3</sup> have reported the synthesis of substituted anilines by treating, e.g., p-bromo-N,N-bis(trimethylsilyl)aniline with n-butyllithium, followed by treating the resulting lithium derivative with chlorotrimethylsilane to afford p-trimethylsilyl-N,N-bis(trimethylsilyl)aniline. The trimethylsilyl moieties blocked the amine nitrogen atom to the effects of n-butyllithium, since this silicon-nitrogen bond was inert to n-butyllithium under the reaction conditions, vet allowed the more selective halogen-metal interchange to produce a highly reactive organolithium reagent. After the reaction with chlorotrimethylsilane, hydrolysis of the trimethylsilyl protecting groups afforded p-trimethylsilylaniline. This same technique was employed by Greber<sup>4</sup> to prepare several bis(paminophenyl)methylsiloxane oligomers. The need for aromatic diamines containing flexiblizing groups for the synthesis of thermally stable polyamides and polyimides led to the expansion of this protecting technique to prepare silicon- and diketo-containing diamine precursors.

Scheme I describes the preparation of both meta and para isomers of several silicon-containing diamines. p- or m-Bromo-N,N-bis(trimethylsilyl)aniline (1 or 5) was prepared by treating the corresponding bromoaniline (1 mol) with n-butyllithium (2.3 mol) in THF at room temperature, followed by chlorotrimethylsilane (2.3 mol). A maximum yield of reproducibly pure product was obtained when this excess of *n*-butyllithium-chlorotrimethylsilane was utilized. Without this excess an azeotrope, e.g., of 1 and p-bromo-N-trimethylsilylaniline, was invariably formed.

A halogen-metal interchange of the bromine atoms of 1 or 5 with *n*-butyllithium in ether at  $0^{\circ}$  was found to produce the lithium derivatives 2 or 6 most readily. These lithio species were treated in situ with the appropriately substituted dichlorosilanes to form the fully silvlated diamines 3 or 7. The attempted preparation of 2 (and subsequent conversion to 3b) in THF-ether (1:1) at room temperature afforded 4-(n-butyl)-N,N-bis(trimethylsilyl)aniline (2a) in 42% yield.



The fully trimethylsilylated diamines (3 and 7) were readily hydrolyzed to their silicon-containing free diamines (4 and 8) in wet acetone or with a saturated solution of an-