dissolved in dry toluene (5 ml). Deactivated Raney nickel (ca. 2 g) was added using a few milliliters of toluene (gas evolution was noticed) and the mixture was stirred (magnet) at room temperature. When the reaction was complete (ca. 10 min, TLC: SiO_2/ethyl acetate–light petroleum; 1:2 for monosaccharides and 3:2 for the disaccharide) the mixture was filtered by suction through a pad of Celite. The residue was washed several times with ether and the filtrate was evaporated. This gave pure (TLC, NMR) thioglycoside as a colorless oil that crystallized (except for the lacto derivative) on addition of a few drops of ethanol.

***p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside.** Yield 83%. Recrystallization from ethanol gave an analytical sample. For melting point, optical rotation, IR, ^{1}H NMR, ^{13}C NMR, and MS data, see ref 7.

***p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-galactopyranoside.** Yield 94%. Recrystallization from ethanol gave an analytical sample: mp 117–118 °C; $[\alpha]^{24}_{578}$ +5.0° (*c* 1.0; $CHCl_3$) (lit.[8] mp 113–115 °C; $[\alpha]^{23}_D$ +4.4°); IR 1740, 804 cm^{-1}; NMR δ 7.37, 7.09 (rough AB q, 2 H each, J_{AB} = 8.4 Hz, aromatic H), 3.70–5.50 (m, 7 H, OCH), 2.34 (s, 3 H, C**H**$_3$Ph), 2.10 (s, 6 H, CH_3COO), 2.03, 1.96 ppm (s, 3 H each, CH_3COO); mass spectrum *m/e* (rel intensity) 454 (M$^+$, 0.1, $C_{21}H_{26}O_9S$), 331 (60), 271 (1), 229 (3), 187 (2), 169 (100, base peak), 127 (30), 109 (73).

Anal. Calcd for $C_{14}H_{19}O_9$: mol wt, 331.1029. Found: mol wt, 331.0998 (M − C_7H_7S).

***p*-Methylphenyl 2,3,4-Tri-*O*-acetyl-1-thio-β-D-xylopyranoside.** Yield 95%. Recrystallization from ethanol gave an analytical sample: mp 108–109 °C; $[\alpha]^{24}_{578}$ −68.4° (*c* 2.0; $CHCl_3$); IR 1747, 803 cm^{-1}; NMR δ 7.37, 7.13, (rough AB q, 2 H each, J_{AB} = 8.4 Hz, aromatic H), 3.10–5.35 (m, 6 H, OCH), 2.35 (s, 3 H, C**H**$_3$Ph), 2.09 (s, 3 H, CH_3COO), 2.03 ppm (s, 6 H, CH_3COO); mass spectrum *m/e* (rel intensity) 382 (M$^+$, 0.4, $C_{18}H_{22}O_7S$), 259 (50), 199 (37), 157 (79), 139 (84), 97 (100, base peak).

Anal. Calcd for $C_{18}H_{22}O_7S$: mol wt, 382.1085. Found: mol wt, 382.1059. Calcd: C, 56.5; H, 5.8; S, 8.4. Found: C, 56.4; H, 5.8; S, 8.3.

***p*-Methylphenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside.** Yield 80%. Column chromatography (SiO_2, 15 g, ethyl acetate–light petroleum, 3:2) gave an analytical sample: syrup; $[\alpha]^{24}_{578}$ −17.6° (*c* 1.7; $CHCl_3$); IR 1754, 809 cm^{-1}; NMR δ 7.34, 7.08 (rough AB q, 2 H each, J_{AB} = 8.2 Hz, aromatic H), 3.53–5.35 (m, 14 H, OCH), 2.33 (s, 3 H, C**H**$_3$Ph), 2.12, 2.07, 2.01, 1.94 ppm (s, 21 H, CH_3COO); mass spectrum *m/e* (rel intensity) 742 (M$^+$, 0.05, $C_{33}H_{42}O_{17}S$), 619 (50), 559 (37), 457 (14), 397 (2), 395 (6), 331 (70), 169 (100, base peak).

Anal. Calcd for $C_{26}H_{35}O_{17}$: mol wt, 619.1873. Found: mol wt, 619.1868 (M − C_7H_7S). Calcd for $C_{33}H_{42}O_{17}S$: S, 4.3. Found: S, 4.3.

***p*-Methylphenyl 2,3,4-Tri-*O*-acetyl-1-thio-β-D-glucopyranuronic Acid (Methyl Ester).** Yield 89%. Recrystallization from ethanol gave an analytical sample: mp 127–128 °C; $[\alpha]^{24}_{578}$ −25.0° (*c* 0.9; $CHCl_3$); IR 1763, 1744, 804 cm^{-1}; NMR δ 7.40, 7.14 (rough AB q, 2 H each, J_{AB} = 8.4 Hz, aromatic H), 3.87–5.50 (m, 5 H, OCH), 3.76 (s, 3 H, OCH_3), 2.35 (s, 3 H, C**H**$_3$Ph), 2.08 (s, 3 H, CH_3COO), 1.98 ppm (s, 6 H, CH_3COO); mass spectrum *m/e* (rel intensity) 440 (M$^+$, 0.4, $C_{20}H_{24}O_9S$), 317 (19), 257 (20), 215 (9), 197 (15), 155 (100, base peak), 127 (64).

Anal. Calcd for $C_{13}H_{17}O_9$: mol wt, 317.0872. Found: mol wt, 317.0877 (M − C_7H_7S). Calcd for $C_{20}H_{24}O_9S$: C, 54.5; H, 5.5. Found: C, 54.4; H, 5.6.

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Registry No.—*p*-Methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside, 28244-94-2; *p*-methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside, 28244-99-7; *p*-methylphenyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside, 61025-08-9; *p*-methylphenyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside, 29019-41-8; *p*-methylphenyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-glucopyranuronic acid methyl ester, 61025-09-0; *p*-methylphenyl peracetyl-α-D-glucopyranosethio ortho ester isomer A, 60426-93-9; *p*-methylphenyl peracetyl-α-D-glucopyranosethio ortho ester isomer B, 60410-57-3; *p*-methylphenyl peracetyl-α-D-galactopyranosethio ortho ester isomer A, 60410-58-4; *p*-methylphenyl peracetyl-α-D-galactopyranosethio ortho ester isomer B, 60439-00-1; *p*-methylphenyl peracetyl-α-D-xylopyranosethio ortho ester isomer A, 60410-59-5; *p*-methylphenyl peracetyl-α-D-xylopyranosethio ortho ester isomer B, 60410-60-8; *p*-methylphenyl peracetyl-4-*O*-(β-D-galactopyranosyl)-α-D-glucopyranosethio ortho ester isomer A, 61091-25-6; *p*-methylphenyl peracetyl-4-*O*-(β-D-galactopyranosyl)-α-D-glucopyranosethio ortho ester isomer B, 60410-61-9; *p*-methylphenyl peracetyl-α-D-glucopyranuronic acid methyl ester thio ortho ester isomer A, 60410-62-0; *p*-methylphenyl peracetyl-α-D-glucopyranuronic acid methyl ester thio ortho ester isomer B, 60410-63-1; *p*-methylthiophenol, 106-45-6.

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Metal Catalysis in Organic Reactions. 3. Nickel-Promoted Reaction of Triisobutylaluminum with Terminal Acetylenes as a Synthetic Route to (*E*)-2,4-Dialkyl-1,3-butadienes and/or Trialkylbenzenes

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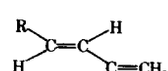
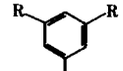
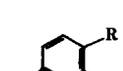
Recently we reported that the reaction of triisobutylaluminum with terminal acetylenes affords products which correspond to metalation, reduction, and carbalumination of the substrate.[1] In connection with studies on nickel-catalyzed organic reactions,[2] we have now investigated the influence of soluble nickel(II) complexes, such as bis(*N*-methylsalicylaldimine)nickel [Ni(mesal)$_2$],[3] on the selectivity of the above reaction.[1]

The stoichiometric reaction of triisobutylaluminum with terminal alkynes, at 25 °C and in the absence of solvent, is accelerated by the presence of catalytic amounts of Ni(mesal)$_2$ and a "head-to-tail" dimer [(*E*)-2,4-dialkyl-1,3-butadiene] and trialkylbenzenes are formed as main products (Table I). Thus, 1-hexyne is completely converted by this procedure into a mixture containing (*E*)-5-methylene-6-undecene (**5**),[4] 1,3,5-tri-*n*-butylbenzene (**6**), and 1,2,4-tri-*n*-butylbenzene (**7**), together with those products whose formation occurs even in the absence of the nickel complex[1] and minor amounts of linear trimers and C_{16} dienes[5] (Table I). The yields both of the dimer and the cyclotrimers are dependent on the molar ratio (i-C_4H_9)$_3$Al to Ni(mesal)$_2$, at least in the stoichiometric reaction of 1-alkynes with triisobutylaluminum. In fact, decreasing the molar ratio (i-C_4H_9)$_3$Al to Ni(mesal)$_2$ up to 60 substantially depresses the formation of the metalation (**1**) and reduction (**2**) products whereas it increases the yields of **5**, **6**, and **7** (entries 1–4). The use of higher nickel concentrations is not advisable because of the increasing formation of the by-products.

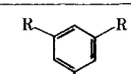
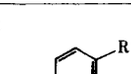
The extremely high selectivity in the dimerization of 1-hexyne had prompted us to explore the validity of the nickel-catalyzed reaction between 1-alkynes and triisobutylaluminum as a synthetic route to preparing 2,4-dialkyl-1,3-butadienes, whose preparation cannot be easily achieved using conventional methods.[6] For this purpose, some 3-alkyl-,

Table I. Reactions of RC≡CH with $(i\text{-}C_4H_9)_3Al$ in the Presence of $Ni(mesal)_2$[a]

Entry	R	$[(i\text{-}C_4H_9)_3Al]$[b] / $[Ni(mesal)_2]$	Products, yields %[c, d]						
			RC≡CH[e] 1	RCH=CH₂ 2	 3	 4	 5	 6	 7
1	$n\text{-}C_4H_9$	240	27 (693-02-7)[f]	35 (592-41-6)	5 (52763-10-7)	6 (25127-82-4)	10 (61063-95-4)	5 (841-07-6)	3 (14800-16-9)
2	$n\text{-}C_4H_9$	120	28	26	4	4	15	9	5
3	$n\text{-}C_4H_9$	60	12	13	3	1	29	18	10
4	$C_2H_5CH(CH_3)$	60	2 (922-59-8)	7 (760-20-3)	Traces	2 (52763-12-9)	66 (61063-96-5)	14 (6565-55-5)	3 (61064-05-9)
5	$i\text{-}C_3H_7CH(CH_3)$	60	1 (61064-08-2)	5 (7385-78-6)		1 (61116-94-7)	76 (61063-97-6)	9 (61064-01-5)	3 (61139-52-4)
6	$t\text{-}C_4H_9CH(CH_3)$	60	26 (52763-16-3)	(564-03-4)			59 (61063-98-7)	9 (61064-02-6)	
7	$C_2H_5CH(CH_3)CH_2$	60	5 (52713-81-2)	7 (3769-23-1)	2 (61063-92-1)	Traces	27 (61063-99-8)	44 (61064-03-7)	3 (61064-06-0)
8	$C_2H_5CH(CH_3)(CH_2)_2$	60	11 (61064-09-3)	26 (13151-04-7)	3 (61063-93-2)	2 (61063-94-3)	27 (61064-00-4)	14 (61064-04-8)	8 (61064-07-1)

[a] The reactions were carried out in the absence of solvents, at 25 °C for 40 h. [b] $[RC{\equiv}CH]/[(i\text{-}C_4H_9)_3Al] = 1$. [c] By GLC (SE-301) of the reaction mixtures upon hydrolysis, other products being dienes containing the isobutyl group and traces of linear trimers. [d] For the data of the uncatalyzed reaction, see ref 1. [e] Present as alkynylalane before hydrolysis. [f] Registry no.

Table II. Oligomerization of RC≡CH by the $(i\text{-}C_4H_9)_3Al/Ni(mesal)_2$ System

Entry	R	$\frac{[RC{\equiv}CH]}{[(i\text{-}C_4H_9)_3Al]}$	$\frac{[RC{\equiv}CH]}{[Ni(mesal)_2]}$	Temp, °C	Recovered RC≡CH, %[a]	Products, yields %[b]					
						RCH=CH₂ 2	 5	 6	 7	Linear trimers	Tetramers
9[c]	$n\text{-}C_4H_9$	0.5	60	25	3	24	37	13	7	6	
10[c]	$n\text{-}C_4H_9$	2.0	60	25	15	21	29	20	12	6	Traces
11[c]	$n\text{-}C_4H_9$	3.0	60	25	36	17	28	20	12	9	Traces
12[d]	$n\text{-}C_4H_9$	4.0	60	25	30	5	19	32	20	14	2
13[d]	$n\text{-}C_4H_9$	10.0	60	25	57		11	36	21	14	14
14[e]	$n\text{-}C_4H_9$	6.0	100	80	11	1	8	26	16	20	18
15[e]	$n\text{-}C_4H_9$	15.0	100	80	24		5	32	20	16	21
16[e]	$C_2H_5CH(CH_3)$	6.0	100	80	10	2	13	41	9	9	16
17[e]	$C_2H_5CH(CH_3)$	15.0	100	80	26	4	4	48	8	12	23

[a] Partially as alkynylalane. [b] By GLC (SE-301) of the hydrolyzed reaction mixtures. [c] Hydrolysis after 40 h. [d] Hydrolysis after 80 h. [e] In benzene as solvent, alkyne molar concentration 4 M, hydrolysis after 6 h.

4-alkyl-, and 5-alkyl-1-alkynes were used as substrates. The inspection of Table I show that the yields in the diene (**5**) are very improved, while the formation of trialkylbenzenes is substantially hindered, when the alkyne has the substituent alkyl group in the α position with respect to the triple bond. Thus, the reaction of 3-methyl-1-pentyne with $(i\text{-}C_4H_9)_3Al$ under the reported experimental conditions (Table I, entry 4), followed by successive hydrolysis, give a 45% isolated yield of (*E*)-3,7-dimethyl-4-methylene-5-nonene (**5**), having a satisfactory chemical purity (>90%). Unfortunately, the yields in the dimer drop when the substituent alkyl group of the alkyne is in the β or γ position with respect to the triple bond.

It is noteworthy that the increasing size of the alkyl group attached to the 3 position of the 1-alkyne results in a progressive decreasing of the yields of the aromatic products (Table I, entries 3–6). This result seems to indicate that the competitive aromatizing reaction has greater steric requirements than the dimerization reaction. The improved yields in the trialkylbenzenes when 4-methyl-1-hexyne and 5-methyl-1-heptyne are used are consistent with this consideration. Reasonably steric factors may be responsible for the prevailing formation of the symmetrical over the unsymmetrical trialkylbenzene too.[7]

In exploring more widely the influence of some variables on the reaction, we have found that the molar ratio 1-alkyne to $(i\text{-}C_4H_9)_3Al$ is important to determine the direction of the reaction toward dimerization or cyclotrimerization of the terminal acetylenes (Table II). In fact, while increasing the molar ratio 1-hexyne to $(i\text{-}C_4H_9)_3Al$ from 1.0 to 3.0 has little effect on the product yields, probably because of the intervention of the other two isobutyl groups of the organoaluminum compound,[8] the excess of $(i\text{-}C_4H_9)_3Al$ with respect to the acetylenic substrate results in an increase of the diene (**5**) yields with respect to those of the aromatic products (entry 9).[9] At molar ratio 1-alkyne to $(i\text{-}C_4H_9)_3Al$ higher than 3.0, the yields of the aromatic products are strongly improved, even if the rate of the reaction decreases appreciably and tetramerization may occur as a side reaction (Table II). The reaction rate is increased and comparable results are obtained when the reaction is carried out in refluxing benzene; thus, 3-methyl-1-pentyne may be converted into 1,3,5-tri-*sec*-butylbenzene (48% GLC yield) (Table II, entry 17).

The preparative possibilities of these nickel-catalyzed reactions should be borne in mind. In fact 2,4-dialkyl-1,3-butadienes of trans configuration, not otherwise available, can be prepared in satisfactory or excellent yields in relation to the structure of the 1-alkyne. Moreover, the highly selective cyclotrimerization of the monoalkylacetylenes we observed suggests the use of these reactions as an alternative method for the synthesis of benzene derivatives having bulk alkyl substituents in the 1,3,5 positions of the aromatic ring.[7,10]

Experimental Section[11]

Triisobutylaluminum and 1-hexyne were commercial products (Fluka A. G. Co., Buchs) which were carefully distilled before use. The other 1-alkynes (**1**) employed were prepared through the corresponding α olefins by published methods.[12] Bis(*N*-methylsalicylaldimine)nickel was prepared and purified as reported elsewhere.[3] All the reaction products were recovered by preparative GLC and were identified by analysis of NMR, IR, and mass spectra.

General Procedure. In a typical run (Table I, entry 4) a weighed amount of $(i\text{-}C_4H_9)_3Al$ (5.94 g, 30 mmol) was transferred from a sealed capillary glass vial to a two-necked flask (100 ml), equipped with a magnetic stirrer, a Versilic silicone cap, and a glass stopcock, containing the nickel complex (0.163 g, 0.5 mmol) cooled at 0 °C. 3-Methyl-1-pentyne (**1**, 2.46 g, 30 mmol) was injected by hypodermic syringe through the cap and then the flask was placed in a thermostated bath at 25 ± 0.3 °C. After 40 h and removal of the volatile products (isobutane, isobutene, and unreacted **1**), the residual reaction mixture was cautiously hydrolyzed with dilute sulfuric acid, extracted with ether, and analyzed by GLC (silicone SE 301, 50–190 °C). Removal of the solvent and careful distillation gave (*E*)-3,7-dimethyl-4-methylene-5-nonene (**5**, 1.12 g, 45% yield) in addition to a high-boiling fraction. By preparative GLC (butanediol succinate LAC 6R-860, 100–170 °C) pure **5**, bp 81 °C(17 mmHg), $n^{25}D$ 1.4575, IR (neat) 3090, 880 (C=CH_2), 1610, and 965 cm^{-1} (trans -CH=CH-), and pure 1,3,5-tri-*sec*-butylbenzene (**6**,[13] 0.09 g) were recovered.

Registry No.—$(i\text{-}C_4H_9)_3Al$, 100-99-2; $Ni(mesal)_2$, 14322-02-2.

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Correlation of the Gas Phase Basicities of Primary Amines with the New Gas Phase Alkyl Inductive Substituent Constants

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Precise measurements of the intrinsic base strengths of an extended series of amines have recently become available from ion cyclotron resonance spectroscopic equilibrium constants.[1] Brauman and Blair[2] interpreted their striking observation that alkyl groups increase both acidity and basicity in the gas phase as due primarily to the polarization of R by a nearby ionic center. That is, polarizable alkyl groups stabilize both positive and negative charge centers which are in close proximity. This polarizability effect, in the simple electrostatic model, falls off very rapidly (r^{-4}) with distance between the centers of polarizability and of charge.[2,3] Distant alkyl groups,