Hz), 6.24 (dd, 2 H, J = 3.4 and 7.9 Hz), 6.51 (t, 2 H, J = 3.4 Hz), 7.36–7.52 (m, 3 H), 7.87–7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.42, 23.76, 38.31, 41.55, 47.61, 105.83, 126.21, 127.99, 128.57, 129.71, 132.98, 136.90, 199.91 and 201.11; HRMS calcd for $C_{19}H_{20}O_2$ 280.1463, found 280.1460.

The second fraction isolated was assigned as 1,14-diphenyl-7-tetradecane-1,6,9,14-tetrone (**39**) (14% yield): mp 135–136 °C; IR (KBr) 3420, 2970, 1685, 1690, 1640, 1620, 1390, 1270, and 1150 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.69–1.73 (m, 8 H), 2.65 (t, 4 H, J = 6.7 Hz), 2.95 (t, 4 H, J = 6.7 Hz), 6.81 (s, 2 H), 7.35–7.50 (m, 6 H), and 7.86–7.89 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.35, 23.54, 38.18, 41.43, 127.97, 128.58, 133.01, 136.20, 136.85, 199.72, and 200.12; HRMS calcd for $C_{26}H_{28}O_4$ 404.1987, found 404.1977.

Acknowledgment. We gratefully acknowledge support of this work by the National Institute of Health (CA-26751). The use of the high-field NMR spectrometer used in these studies was made possible through equipment grants from the NIH and NSF.

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra (75 MHz) for all compounds with high resolution mass spectra (9 pages). Ordering information is given on any current masthead page.

Regioselective ϵ-Alkylation of 5-Acetoxy-1,3-alkadienes by Organocopper–Magnesium Reagents

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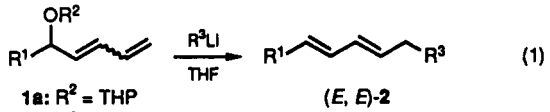
Treatment of the 5-acetoxy-1,3-alkadienes **1b** with dialkylcopper–magnesium complex $R_2Cu{\cdot}MgX$ prepared in tetrahydrofuran gave ϵ-alkylated products, i.e., conjugated (*E,E*)-alkadienes **2**, predominantly. In contrast, when **1b** was treated with the alkylcopper–magnesium reagent $RCuZ{\cdot}MgX$ prepared in diethyl ether, γ-alkylated 1,4-alkadienes **3** were the major products. The reaction of 6-acetoxy-2,4-tridecadiene (**14**) with *n*-BuMeCu·MgBr gave a 52:48 mixture of α- and ϵ-butylated products **15** and **16**, respectively. The conjugated (*E,E*)-alkadienes **21** possessing functional groups Y (Y = Br, AcO, Ac, HC≡C) at the ω-position were prepared in tetrahydrofuran by the same method.

Introduction

The regio- and stereoselective cross-coupling of allylic or dienylic derivatives with organometallic compounds to yield alkenes[1] and alkadienes[2] has been investigated. Earlier,[3] we reported the highly selective ϵ-alkylation of 5-(tetrahydropyranyloxy)-1,3-alkadienes **1a** by alkyllithiums (eq 1). Here, we report the results of a detailed study of similar ϵ-alkylations of 5-acetoxy-1,3-alkadienes **1b** by organocopper-mediated Grignard reagents.[4]



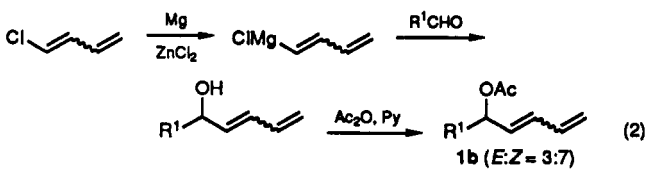
(1)

1a: R^2 = THP
1b: R^2 = Ac

(*E, E*)-**2**

Results and Discussions

Compound **1b** ($R^1 = n$-C_7H_{15}) was easily synthesized by acetylation of the alcohol obtained from the reaction of 1,3-butadienylmagnesium chloride[3,5] with *n*-octanal (eq 2).



(2)

1b (*E*:*Z* = 3:7)

The reaction of **1b** with organocopper–magnesium reagents, prepared in tetrahydrofuran (THF) or diethyl ether from Grignard reagents (RMgX) and either copper(I) iodide (CuI) or alkylcopper (RCu), was investigated (eq 3). The alkylation of **1b** by an organometallic reagent could, in theory, afford three sets of regioisomers, i.e., the products of α-, γ-, and ϵ-alkylation. A total of eight stereoisomers would be expected. The reaction products were separated by silica gel column chromatography. ^{1}H NMR analysis indicated that four isomeric products (*E,E*)-**2**, (*E,Z*)-**2**, (*E*)-**4**, and (*Z*)-**4**, were present (Table I). Neither α-alkylated products, i.e., (*E*)-**3** and (*Z*)-**3**, nor two of the possible ϵ-alkylated products, i.e., (*Z,E*)-**2** and (*Z,Z*)-**2** were

† Department of Industrial Chemistry.
‡ Department of Chemistry.

(1) (a) Fouquet, G.; Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 82. (b) Gendreau, Y.; Normant, J. F. *Tetrahedron* **1979**, *35*, 1517. (c) Claesson, A.; Sahlberg, C. *J. Organomet. Chem.* **1979**, *170*, 355. (d) Yamamoto, Y.; Maruyama, K. *Ibid.* **1978**, *156*, C9. (e) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 2320. (f) Goering, H. L.; Seitz, E. P., Jr.; Tseng, C. C. *J. Org. Chem.* **1981**, *46*, 5304. (g) Goering, H. L.; Kantner, S. S. *Ibid.* **1983**, *48*, 721. (h) Goering, H. L.; Singleton, V. D., Jr. *Ibid.* **1983**, *48*, 1531. (i) Goering, H. L.; Kantner, S. S. *Ibid.* **1984**, *49*, 422. (j) Tseng, C. C.; Paisley, S. D.; Goering, H. L. *Ibid.* **1986**, *51*, 2884. (k) Tseng, C. C.; Yen, S.-J.; Goering, H. L. *Ibid.* **1986**, *51*, 2892. (l) Sekiya, K.; Nakamura, E. *Tetrahedron Lett.* **1988**, *29*, 5155. (m) Nakamura, E.; Sekiya, K.; Arai, M.; Aoki, S. *J. Am. Chem. Soc.* **1989**, *111*, 3091.

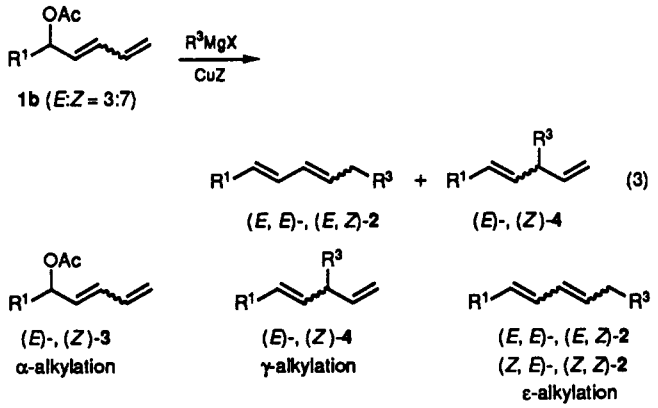
(2) (a) Samain, D.; Descoins, C. *Synthesis* **1978**, 388. (b) Decodts, G.; Dressaire, G.; Langlois Y. *Ibid.* **1979**, 510. (c) Underiner, T. L.; Goering, H. L. *J. Org. Chem.* **1988**, *53*, 1140. (d) Underiner, T. L.; Paisley, S. D.; Schmitter, J.; Lesheski, L.; Goering, H. L. *Ibid.* **1989**, *54*, 2369. (e) Underiner, T. L; Goering, H. L. *Ibid.* **1990**, *55*, 2757.

(3) Ishii, T.; Kawamura, N.; Matsubara, S.; Utimoto, K.; Kozima, S.; Hitomi, T. *Ibid.* **1987**, *52*, 4416.

(4) Presented in part at the Annual Meeting of the Chemical Society of Japan, April 1989. While this manuscript was in preparation, Goering's paper[2e] appeared in print.

(5) Kozima, S.; Ishii, T.; Tsuboi, T.; Kawanisi, M.; Mizuno, M.; Hitomi, T. *Chem. Express*, **1987**, *2*, 301.

0022-3263/91/1956-3278$02.50/0

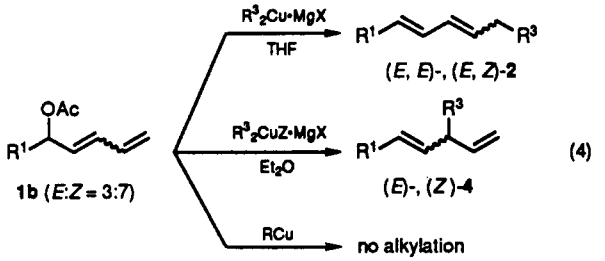


detected. The stereochemistry of compound **1b** had no influence on the product distribution.[6]

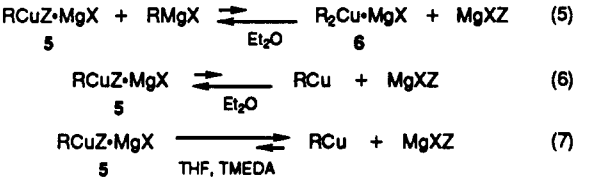
In the absence of copper(I) salts, no alkylation of **1b** by *n*-BuMgBr in THF took place at −30 °C. The acetate **1b** was recovered unchanged when the reaction mixture was quenched with aqueous NH_4Cl at −30 °C (run 1). Treatment of **1b** in THF at −30 °C with an equimolar mixture of *n*-BuMgBr and CuI, a grayish yellow dispersion prepared by mixing *n*-BuMgBr and CuI in THF at −78 °C and then warming the mixture to −30 °C over 10 min, gave ϵ-alkylated products **2** in 42% yield (run 2). Another equimolar mixture of *n*-BuMgX and CuI, a yellow dispersion prepared by slowly adding *n*-BuMgX to a suspension of CuI in THF at −30 °C and then maintaining the mixture at −30 °C with stirring for 1.5 h, was virtually unreactive at −30 °C toward **1b**. A very low yield (2%) of alkylated products was obtained. Most (78%) of acetate **1b** was recovered intact (run 3). Another equimolar mixture of *n*-BuMgBr and CuI in THF, a yellow dispersion prepared by adding CuI (1.5 equiv) at −30 °C to a grayish dispersion of *n*-BuMgBr (3.0 equiv) and CuI (1.5 equiv) in THF, was also unreactive at −30 °C toward **1b** (run 4). The grayish dispersion was prepared by mixing *n*-BuMgBr and CuI at −78 °C in THF. Dispersions prepared by mixing 2 or more equiv of *n*-BuMgBr and 1 equiv of CuI in THF at −78 °C gave, upon reaction with **1b** at −30 °C, products of ϵ-alkylation exclusively. (*E*,*E*)-**2** was produced in high yield (runs 5, 6).

In contrast, when **1b** was treated at −30 °C with an equimolar mixture of *n*-BuMgBr and CuI in diethyl ether, a pale yellow dispersion prepared by mixing the two compounds at −78 °C and then warming the mixture, γ-alkylation predominated (run 7). When 2 equiv of *n*-BuMgBr were used to prepare the reagent, γ-alkylation still predominated (run 8).[8] However, the use of 3 equiv of *n*-BuMgBr slightly increased the yield of ϵ-alkylated products (run 9). The regioselectivity of the alkylation was therefore remarkably solvent dependent.

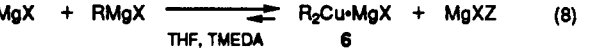
Thus, the grayish yellow dispersion in THF, presumably containing the dialkylcopper–magnesium reagent $R_2Cu{\cdot}MgX$ (**6**), reacted with **1b** to give, exclusively, ϵ-alkylated products **2**; whereas the pale yellow dispersion in diethyl ether, presumably containing the alkylcopper–magnesium reagent $RCuZ{\cdot}MgX$, reacted to give, preferentially, γ-alkylated products **4**. The yellow dispersions in THF, presumably containing the alkylcopper RCu, were unreactive toward **1b** (eq 4).



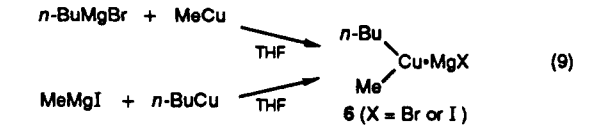
These interpretations were supported by the following experimental results: (1) In diethyl ether, the reaction of **1b** in the presence of excess *n*-BuMgBr led to a slight increase in the proportion of ϵ-alkylated products (runs 8, 9). In this instance, the formation of **6** and MgXZ from **5** and RMgX was not favored because diethyl ether is not sufficiently basic to induce dissociation of $RCuZ{\cdot}MgX$ by solvation of MgXZ (eq 5).[9] (2) When either THF or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was slowly added to an equimolar mixture of *n*-BuMgBr and CuI in diethyl ether at −30 °C, a yellow dispersion of *n*-BuCu, which was unreactive toward **1b** was produced (runs 10, 11). In this instance, the solvation of MgBrI by the more basic THF or TMEDA shifted the equilibrium (**7**) to favor the formation of unreactive RCu and MgXZ from **5**. On the other hand, in pure diethyl ether, the formation of reactive $RCuZ{\cdot}MgX$ was favored (eq 6). (3) When



THF, TMEDA, or dioxane was added to the dispersion prepared in diethyl ether from 2 equiv of *n*-BuMgBr and 1 equiv of CuI, ϵ-alkylation predominated in the subsequent reactions with **1b** (runs 12–15). In this instance, the reagent **6** was produced from **5** and RMgX by the solvation of MgXZ with a strong Lewis base (eq 8). (4) Regiospecific



ϵ-alkylation of **1b** by RMgX also occurred in THF in the presence of catalytic amounts of methylcopper (runs 16, 19, 20). Here, the alkylmethylcopper reagent $RMeCu{\cdot}MgX$ (**6**) may have been the reactive species.[9] (5) Treatment of **1b** with the *n*-butylmethylcopper reagent prepared in THF from an equimolar mixture of *n*-BuMgBr and MeCu gave ϵ-butylated products (run 17). Another *n*-butylmethylcopper reagent, prepared from MeMgI and *n*-BuCu, gave the same ϵ-butylated products in the same ratio (run 18). Therefore, both reagents must contain the same reactive species, presumably *n*-$BuMeCu{\cdot}MgX$ (**6**, eq 9). It



should be noted that the reaction of either *n*-butyl-

(6) When the reactions of **1b** with organocopper–magnesium reagents were quenched with aqueous NH_4Cl at various stages, no significant differences in the product distribution were found. The *E*/*Z* ratio of recovered **1b** was essentially the same (*E*:*Z* = 3:7) as that of the starting material.

(7) Lipshutz, B. H.; Parker, D. A.; Nguyen, S. L.; McCarthy, K. E.; Barton, J. C.; Whitney, S. E.; Kotsuki, H. *Tetrahedron* **1986**, *42*, 2873.

(8) A similar solvent effect was reported for an allylic substitution reaction of *n*-BuMgBr and CuI in THF and diethyl ether. See: (a) Westmijze, H.; Kleijn, H.; Vermeer, P. *Tetrahedron Lett.* **1977**, *23*, 2023. (b) Barsant, P.; Calo, V.; Lopez, L.; Marchese, G.; Maso, F.; Pesce, G. *J. Chem. Soc., Chem. Commun.* **1978**, 1085.

(9) The introduction of excess MeMgBr into the Et_2O solution apparently has no effect on the reaction of the yellow MeCu precipitate. See: Bergbreiter, D. E.; Whitesides, G. M. *J. Org. Chem.* **1975**, *40*, 779.

Table I. Alkylation of 5-Acetoxy-1,3-dodecadiene 1b (R^1 = n-C_7H_{15}, R^2 = Ac) in THF or Diethyl Ether[a]

run	R^3M (equiv)	CuZ (equiv)	solvent	product distribution (%) (E,E)-2	(E,Z)-2	(E)-4	(Z)-4	yield (%)	method
1	n-BuMgBr (1.5)	none	THF	0	0	0	0	0[b]	
2	n-BuMgBr (1.5)	CuI (1.5)	THF	51	24	20	5	42	A
3	n-BuMgBr (1.5)	CuI (1.5)	THF	64	23	11	2	2	E
4	n-BuMgBr (3.0)	CuI (3.0)	THF	51	24	19	6	4	F
5	n-BuMgBr (3.0)	CuI (1.5)	THF	84	15	<1	0	81	A
6	n-BuMgBr (1.5)	CuI (0.3)	THF	90	9	<1	0	83	A
7	n-BuMgBr (1.5)	CuI (1.5)	ether	7	1	83	9	63	C
8	n-BuMgBr (3.0)	CuI (1.5)	ether	10	3	77	10	77	C
9	n-BuMgBr (4.5)	CuI (1.5)	ether	30	26	40	4	61	C
10	n-BuMgBr (1.5)	CuI (1.5)	ether/THF[c]	0	0	0	0	0	D
11	n-BuMgBr (1.5)	CuI (1.5)	ether/TMEDA[d]	34	9	51	6	1	D
12	n-BuMgBr (3.0)	CuI (1.5)	ether/THF[c]	78	22	0	0	78	D
13	n-BuMgBr (3.0)	CuI (1.5)	ether/TMEDA[d]	54	41	5	1	60	D
14	n-BuMgBr (3.0)	CuI (1.5)	ether/TMEDA[e]	89	11	0	0	68	D
15	n-BuMgBr (3.0)	CuI (1.5)	ether/diox[f]	64	25	10	1	71	D
16	n-BuMgBr (1.5)	MeCu (0.3)	THF	93	7	0	0	72	B
17	n-BuMgBr (1.5)	MeCu (1.5)	THF	78	22	0	0	77	B
18	MeMgI (1.5)	n-BuCu (1.5)	THF	77	23	0	0	83	B
19	i-PrMgCl (1.5)	MeCu (0.3)	THF	84	16	0	0	60	B
20	t-BuMgCl (1.5)	MeCu (0.3)	THF	82	18	0	0	78	B
21	MeMgI (6.0)	CuI (3.0)	THF	95	5	0	0	71	A
22	n-BuMgBr (1.5)	(2-Th)CuCNLi[g]	THF	6	2	91	1	67	
23	n-BuMgBr (1.5)	(2-Th)CuCNLi[h]	THF	20	3	72	5	27	
24	n-BuMgBr (2.0)	CuCN (2.0)	THF[i]	20	8	63	9	81	
25	n-BuLi (2.0)	CuI (2.0)	THF	0	0	0	0	0	
26	n-BuLi (3.0)	CuI (1.5)	THF	87	13	0	0	78	

[a] 1 equiv of 1b was used. The reactions were performed at −30 °C for 2 h. General procedures (methods A–F) are described in the Experimental Section. [b] When the rection was quenched with aqueous NH_4Cl at −30 °C, 1b was recovered quantitatively. [c] THF (10 mL) was added before the introduction of 1b. [d] TMEDA (1.5 equiv) was added before the introduction of 1b. [e] TMEDA (3.0 equiv) was added before the introduction of 1b. [f] Dioxane (3.0 equiv) was added before the introduction of 1b. [g] (2-Thienyl)Cu(CN)Li[7] (2.0 equiv) was used. [h] (2-Thienyl)Cu(CN)Li[7] (0.3 equiv) was used. [i] The reagent was prepared in THF in a manner similar to that described in method C.

methylcopper reagent gave no methylated products, even when the reagent was prepared from MeCu (run 17).[10] (6) Because n-BuCu, prepared in THF from an equimolar mixture of n-BuLi and CuI, did not react with 1b (run 25), transfer of the alkyl group of RMgX to RCu to produce the dialkylcopper reagent 6 was essential for ϵ-alkylation to occur. (7) When an equimolar amount of CuI was added to $R_2Cu{\cdot}MgX$ (6) prepared in THF, RCu was produced (eq 10), and, subsequently, no alkylation of 1b occurred (run

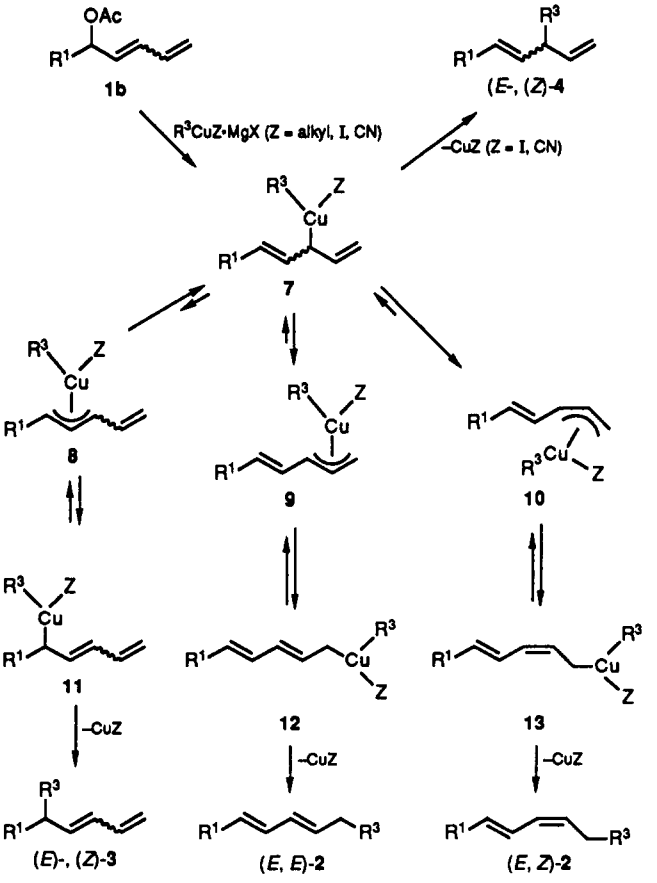
$$\underset{\mathbf{6}}{R_2Cu{\cdot}MgX} + CuI \underset{THF}{\rightleftharpoons} 2\,RCU + MgIX \qquad (10)$$

4). Vigorous mixing for 1.5 h at −30 °C was necessary to complete equilibration (eq 7) in THF and form the yellow dispersion of RCu (run 3). When an equimolar mixture of n-BuMgBr and CuI in THF was kept at −30 °C for 10 min, a heterogeneous mixture containing some 6 and CuI was produced (run 2).

The regiochemical outcome of the alkylation of 1b by organocopper–magnesium reagents is illustrated in Scheme I. The reaction of allylic or dienylic pivalates with organocopper reagents was reported to proceed by an analogous mechanism.[2e]

Initially, substitution might occur exclusively at the γ-position of 1b, via an S_N2' mechanism, to give the Cu(III) intermediate 7.[11] In the case of monoalkylcopper reagents $R^3CuZ{\cdot}MgX$ 5 (Z = I or CN), reductive elimination of CuZ from the γ-copper(III) intermediate 7 to yield the γ-alkylated products 4 must be fast (runs 7–9, 22–24) because an electron-attracting group Z would accelerate the reductive elimination.[12] However, with a dialkylcopper 6 (Z = alkyl), the electron-donating alkyl group would stabilize the intermediate 7 and the rate of the reductive elimination of CuR from 7 would decrease. Then isomerization of 7 to the more stable ϵ-dienylcopper(III) intermediates 12 and 13 via the π-allylcopper intermediates

Scheme I



(10) For the tendency of the substituent on the Cu atom to be transferred, see: Lipshutz, B. H. *Synthesis* **1987**, 325.
(11) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063.
(12) Bäckvall, J.-E.; Sellen, M. *J. Chem. Soc., Chem. Commun.* **1987**, 827.

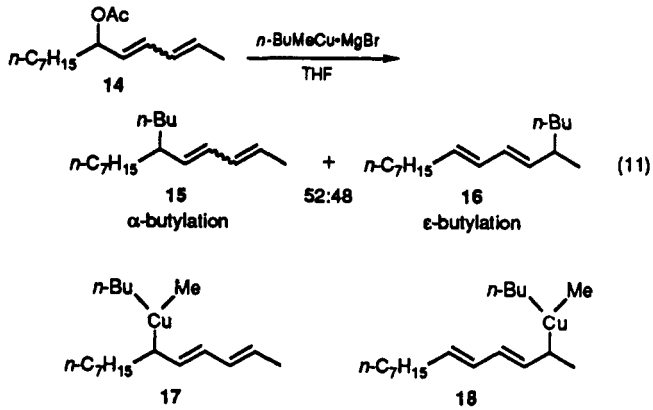
Table II. Preparation of Functionalized Conjugated Alkadienes 21[a]

substrate 20 $Y(CH_2)_n$	*n*-BuMgBr (equiv)	CuX (equiv)	products (*E*,*E*)-21	products (*E*,*Z*)-21	yield (%)
20a $Br(CH_2)_5$	1.5	MeCu (1.5)	86	14	78
20b $AcO(CH_2)_5$	1.5	MeCu (1.5)	83	17	69
20c $Ac(CH_2)_5$	3.0	CuI (1.5)[b]	92	8	49
20d $HC{\equiv}C(CH_2)_4$	1.5	MeCu (0.3)	88	12	50

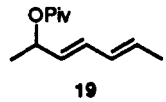
[a] All reactions were performed in THF on a 1 mmol scale. [b] MeCu gave a lower (20%) yield of 21c.

9 and 10 could occur. The relative stabilities of the four dialkylcopper(III) intermediates 7, and 11–13 would be reflected in the product distribution. For steric reasons, the isomerization of 7 to the α-dienylcopper (III) intermediate 11, via the π-allylcopper intermediate 8, would be thermodynamically less favored. That no isomerization of 7 to 11 took place might be the reason why no α-alkylated products 3 were obtained.

The reaction of 6-acetoxy-2,4-tridecadiene (14) with the *n*-butylmethylcopper reagent *n*-BuMeCu·MgBr (6) gave a 52:48 mixture of α- and ε-butylated products (15 and 16, respectively, eq 11). Thus, there might not be a significant difference between the stabilities of the respective α- and ε-dienylcopper(III) intermediates 17 and 18. It should also be noted that no γ-alkylated product was obtained from the reaction of 6 and 14.

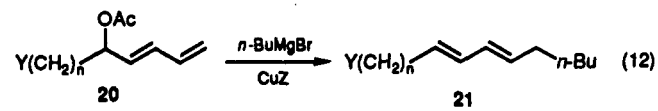


It was reported[2e] that the reaction of 3,5-heptadien-2-yl pivalate (19) with the di-*n*-butylcopper reagent *n*-Bu_2Cu·MgI in diethyl ether gave predominantly (76%) γ-butylated products. Minor amounts of α-butylated (21%) and ε-butylated (3%) products were also observed. This displayed high γ-regioselectivity could, however, be the result of the incomplete formation of *n*-Bu_2Cu·MgI in diethyl ether. *n*-BuCuI·MgI might thus be the major reactive species in this instance (eq 5). When *n*-Bu_2CuLi was treated in diethyl ether with 19, γ-cross-coupling was a minor side reaction.[2e] This is consistent with the result that no γ-alkylated product was obtained in the reaction of *n*-Bu_2CuLi with 1b (run 26) reported here.



Alkenyl and aryl groups could not be introduced into the acetates 1b and 14 in good yield by the methods described here. However, the related phenylation of the pivalate 19 was reported to occur in good yield.[2e]

Because organocopper reagents display high chemoselectivity,[13] the functionalized conjugated (*E*,*E*)-alkadienes 21 could be prepared by the method described here (eq 12). The results are shown in Table II. The compounds



a: Y = Br
b: Y = $CH_3C(O)O$
c: Y = $CH_3C(O)$
d: Y = $HC{\equiv}C$

20 could be easily prepared by the acetylation of the alcohols obtained from the reaction of 1,3-btuadienylmagnesium chloride[5] with aldehydes possessing unprotected functional groups.

Experimental Section

5-Acetoxy-1,3-dodecadiene (1b). To a CH_2Cl_2 solution of 1,3-dodecadien-5-ol[3] (9.10 g, 50 mmol) was added, drop by drop, a solution of acetic anhydride (10.2 g, 100 mmol) and pyridine (7.9 g, 100 mmol) at 0 °C. A catalytic amount (30 mg) of 4-(dimethylamino)pyridine was then added. The mixture was kept at room temperature for 1 h, and then it was concentrated under reduced pressure. The concentrate was diluted with water, and the solution was extracted with Et_2O. The extract was washed (saturated aqueous $CuSO_4$, aqueous $NaHCO_3$, and brine) and concentrated. The concentrate was purified by silica gel chromatography to give a mixture of (*E*)-1b and (*Z*)-1b (10.2 g, 91%, *E*:*Z* = 3:7): bp 100 °C (3 mmHg); IR (neat) 2924, 2854, 1740, 1370, 1238, 1019, 909 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 6.0 Hz, 3 H), 1.15–1.45 (b s, 10 H), 1.45–1.80 (m, 2 H), 2.03 (s, 2.1 H, the *E* isomer), 2.06 (s, 0.9 H, the *Z* isomer), 5.10–5.45 (m, 3 H), 5.55–5.80 (m, 1 H), 6.10 (dd, *J* = 11, 10 Hz, 0.7 H), 6.20–6.45 (m, 0.6 H), 6.75 (d, d, d, *J* = 17, 11, 10 Hz, 0.7 H); ^{13}C NMR δ 170.3, 136.1 (*E*), 133.0 (*E*), 132.0, 131.9 (*Z*), 129.7 (*Z*), 119.8 (*Z*), 118.3 (*E*), 74.3 (*E*), 70.4 (*Z*), 34.8 (*Z*), 34.4 (*E*), 31.8, 29.3, 29.2, 25.1 (*E*), 25.0 (*Z*), 22.6, 21.3, 14.1. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.12; H, 10.88.

General Procedure for the Alkylation of 1b by Organocopper–Magnesium Reagents. All reactions were performed under an Ar atmosphere.

Method A (RMgX:CuI = 2:1, in THF). To a suspension of CuI (286 mg, 1.5 mmol) in THF (3 mL) was added a THF solution of RMgX (1.25 M, 2.40 mL, 3.0 mmol) at −78 °C with stirring over 5 min. The mixture was slowly warmed to −30 °C and kept there for 10 min. A grayish dispersion formed. The dispersion was cooled to −78 °C, and a solution of 1b (1.0 mmol) and THF (2.0 mL) was added drop by drop. The mixture changed color to greenish gray. The mixture was then slowly warmed to −30 °C over 2 h. The mixture was treated with aqueous NH_4Cl and 3% aqueous NH_3 and was extracted with Et_2O. The extract was purified by column chromatography on silica gel, and the various fractions collected were analyzed by capillary GC (FS-WCOT, Silicone OV-1, Gasukuro Kogyo, 25 m × 0.35 mm).

Method B (RMgX:MeCu = 5:1 or 1:1; in THF). To a suspension of CuI (0.3 or 1.5 mmol) in THF (3 mL) at −78 °C was added an Et_2O solution of salt-free MeLi (0.3 or 1.5 mmol), prepared from Li metal and CH_3Br in Et_2O. The yellow precipitate of MeCu that formed dissolved when a THF solution of RMgX (1.5 mmol) was added. A grayish (0.3 mmol MeCu, run 16) or pale brownish purple solution (1.5 mmol MeCu, run 17) formed. The reaction of these solutions with 1b was performed at −30 °C in the manner described in method A.

Method C (RMgX:CuI = 1:1, 2:1, or 3:1; in Et_2O). To a suspension of CuI (1.5 mmol) in Et_2O was added an Et_2O solution of *n*-BuMgBr (1.5, 3.0, or 4.5 mmol) at −78 °C. The mixture was

(13) Posner, G. H. *Org. React.* **1975**, *22*, 253.

warmed to −30 °C and kept there for 10 min. An Et_2O solution of **1b** was then added drop by drop at −78 °C. The reaction was performed at −30 °C in the manner described in method A.

Method D (RMgX:CuI = 1:1 or 2:1, in Et_2O containing added Lewis bases). To a mixture of CuI (1.5 mmol) and *n*-BuMgBr (1.5 mmol or 3.0 mmol) in Et_2O (10 mL) was added either THF (10 mL; runs, 10, 12), TMEDA (1.5 mmol; runs 11, 13), TMEDA (3.0 mmol; run 14), or dioxane (3.0 mmol; run 15) at −78 °C. The mixture was then stirred at −30 °C for 1.5 h. The reaction of the reagent with **1b** was performed at −30 °C in the manner described in method A.

Method E (RMgX:CuI = 1:1, in THF). To a suspension of CuI (1.5 mmol) kept at −30 °C was very slowly added a THF solution of an equimolar amount of *n*-BuMgBr (1.25 M, 1.2 mL, 1.5 mmol) over 10 min. The mixture was stirred for 1.5 h. A yellow dispersion formed. The reaction of the dispersion with 1b was performed at −30 °C in the manner described in method A (run 3).

Method F ($R_2Cu{\cdot}MgX/CuI$, in THF). To a grayish dispersion prepared from *n*-BuMgBr (3.0 mmol) and CuI (1.5 mmol) in THF at −78 °C was slowly added a suspension of CuI (1.5 mmol) in THF. The mixture was warmed to −30 °C and kept there for 1.5 h with stirring. A yellow dispersion formed. The reaction of the dispersion with **1b** was performed at −30 °C in the manner described in method A (run 4).

The specrta and other physical properties of the alkylated products are reported in the following text.

(*E*,*E*)- and (*E*,*Z*)-6,8-hexadecadiene (2; R^1 = *n*-C_7H_{15}, R^3 = *n*-Bu) from *n*-BuMgBr/MeCu and 1b (run 16): (*E*,*E*):(*E*,*Z*) = 93:7; GC (column temperature = 140 °C, carrier gas pressure = 0.7 kg/cm²) t_R(retention time) = 10.75 (*E*,*E*), 9.29 (*E*,*Z*) min; IR (neat) 3010, 2912, 2852, 1466, 1378, 985, 722 cm⁻¹; ^{1}H NMR δ 0.88 (t, *J* = 6.0 Hz, 6 H), 1.20–1.50 (b s, 16 H), 2.00–2.25 (m, 4 H), 5.25–5.45 (m, 0.07 H, *E*,*Z*), 5.50–5.80 (m, 1.93 H, *E*,*E* and *E*,*Z*), 5.95–6.20 (m, 1.93 H, *E*,*E* and *E*,*Z*), 6.25–6.45 (m, 0.07 H, *E*,*Z*); ^{13}C NMR δ 134.7 (*E*,*Z*), 132.4 (*E*,*E*), 130.3 (*E*,*E*), 130.1 (*E*,*Z*), 128.7 (*E*,*Z*), 125.7 (*E*,*Z*), 32.6, 31.9, 31.5, 29.5, 29.4, 29.2, 22.7, 22.2, 14.1, 14.0. Anal. Calcd for $C_{16}H_{30}$: C, 86.41; H, 13.59. Found: C, 86.39; H, 13.80.

(*E*)-3-Butyl-1,4-dodecadiene (4, R^1 = *n*-C_7H_{15}, R^3 = *n*-Bu) from *n*-BuMgBr/CuI and 1b: GC (column temperature = 140 °C, carrier gas pressure = 0.7 kg/cm²) t_R = 5.47 min; IR (neat) 2954, 2922, 2852, 1466, 910 cm⁻¹; ^{1}H NMR δ 0.89 (t, *J* = 6.0 Hz, 6 H), 1.15–1.50 (b s, 16 H), 2.00 (dt, *J* = 7.5, 6.0 Hz, 2 H), 2.66 (ddt, *J* = 6.0, 6.0, 7.0 Hz, 1 H), 4.95 (d, *J* = 10.5 Hz, 1 H), 4.97 (d, *J* = 17.5 Hz, 1 H), 5.15–5.55 (m, 2 H), 5.75 (ddd, *J* = 7.0, 10.5, 17.5 Hz, 1 H); ^{13}C NMR δ 142.5, 132.8, 130.4, 113.2, 46.8, 34.6, 32.7, 31.9, 29.6, 29.5, 29.1, 22.7, 14.2. Anal. Calcd for $C_{16}H_{30}$: C, 86.41; H, 13.59. Found: C, 86.48; H, 13.64.

(*E*,*E*)- and (*E*,*Z*)-3,5-tridecadiene from MeMgI/CuI and 1b (run 18): (*E*,*E*):(*E*,*Z*) = 95:5; GC (column temperature = 100 °C, carrier gas pressure = 0.8 kg/cm²) t_R = 10.58 (*E*,*E*), 9.61 (*E*,*Z*) min; ^{1}H NMR δ 0.87 (t, *J* = 6.6 Hz, 3 H), 1.00 (t, *J* = 7.4 Hz, 3 H), 1.15–1.50 (b s, 10 H), 1.95–2.30 (m, 4 H), 5.25–5.45 (m, 0.05 H, *E*,*Z*), 5.50–5.80 (m, 1.95 H, *E*,*E* and *E*,*Z*), 5.95–6.20 (m, 1.95 H, *E*,*E* and *E*,*Z*), 6.25–6.45 (m, 0.05 H, *E*,*Z*); ^{13}C NMR of (*E*,*E*) δ 133.9, 132.6, 130.3, 129.4, 32.7, 31.9, 29.5, 29.2, 25.6, 22.7, 14.1, 13.7. Anal. Calcd for $C_{13}H_{24}$: C, 86.59; H, 13.41. Found: C, 86.73; H, 13.17.

(*E*,*E*)- and (*E*,*Z*)-2-methyl-4,6-tetradecadiene from *i*-PrMgCl/MeCu and 1b (run 19): (*E*,*E*):(*E*,*Z*) = 86:14; GC (column temperature = 140 °C, carrier gas pressure = 0.8 kg/cm²) t_R = 4.93 (*E*,*E*), 4.50 (*E*,*Z*) min; ^{1}H NMR 0.87 (d, *J* = 6.5 Hz, 6 H), 0.87 (t, *J* = 7.5 Hz, 3 H), 1.15–1.85 (m, 11 H), 1.90–2.25 (m, 4 H), 5.25–5.45 (m, 0.16 H, *E*,*Z*), 5.50–5.80 (m, 1.84 H, *E*,*E* and *E*,*Z*), 6.25–6.45 (m, 0.16 H, *E*,*Z*); ^{13}C NMR of (*E*,*E*) δ 132.5, 131.5, 131.0, 130.3, 42.1, 32.7, 31.9, 29.5, 29.2, 28.6, 22.7, 22.4, 14.1. Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.50; H, 13.82.

(*E*,*E*)- and (*E*,*Z*)-2,2-dimethyl-4,6-tetradecadiene from *t*-BuMgCl/MeCu and 1b (run 20): (*E*,*E*):(*E*,*Z*) = 82:18; GC (column temperature = 140 °C, carrier gas pressure = 0.8 kg/cm²) t_R = 6.17 (*E*,*E*), 5.92 (*E*,*Z*) min; ^{1}H NMR δ 0.8–1.1 (m, 12 H), 1.1–1.7 (m, 10 H), 1.93 (d, *J* = 7.4 Hz, 2 H), 2.06 (dt, *J* = 7.0, 7.0 Hz, 2 H), 5.25–5.45 (m, 0.18 H, *E*,*Z*), 5.50–5.80 (m, 1.82 H, *E*,*E* and *E*,*Z*), 5.90–6.20 (m, 1.82 H, *E*,*E* and *E*,*Z*), 6.25–6.45 (m, 0.18 H, *E*,*Z*); ^{13}C NMR of (*E*,*E*) δ 132.6, 132.5, 130.3, 129.3, 32.6, 31.9, 29.4, 29.2, 22.7, 14.1; ^{13}C NMR of (*E*,*Z*) δ 134.7, 130.1, 126.9, 125.9, 47.0, 32.8. Anal. Calcd for $C_{16}H_{28}$: C, 86.41; H, 13.59. Found: C, 86.49; H, 13.79.

6-*n*-Butyl-2,4-tridecadiene (15) and 5-Methyl-6,8-hexadecadiene (16). A 52:48 mixture of **15** and **16** was obtained from the reaction of **14** with the *n*-butylmethylcopper reagent **6** (method B): GC (column temperature = 170 °C, carrier gas pressure = 0.9 kg/cm²) t_R = 5.74 (**15**), 7.14 (**16**) min; ^{1}H NMR δ 0.80–0.95 (m, 6 H), 0.98 (d, *J* = 7 Hz, 1.44 H, **16**), 1.10–1.50 (m, 17.0, 4 H), 1.74 (dd, *J* = 7, 1 Hz, 1.56 H, **15**), 1.80–2.20 (m, 1.96 H, **15** and **16**), 5.20–6.40 (m, 4 H).

10-Bromo-5-acetoxy-1,3-decadiene (20a). Acetylation of 10-bromo-1,3-decadien-5-ol (4.66 g, 20 mmol; prepared from 1,3-butadienylmagnesium chloride[5] and 6-bromohexanal) gave **20a** (4.72 g, 86%): bp 140 °C (4 mmHg); IR (neat) 2932, 2854, 1736, 1460, 1433, 1370, 1237, 1019, 954, 912, 643, 604 cm⁻¹; ^{1}H NMR δ 1.2–2.0 (m, 8 H), 2.04 (s, 2.1 H), 2.06 (s, 0.9 H), 3.40 (t, *J* = 6.7 Hz, 2 H), 5.1–5.4 (m, 3 H), 5.5–5.8 (m, 1 H), 6.11 (d, d, *J* = 11, 10 Hz), 6.2–6.4 (m, 0.6 H), 6.6–6.8 (m, 0.7 H); ^{13}C NMR δ 170.3, 136.0 (*E*), 133.1 (*E*), 132.2 (*Z*), 131.7 (*Z*), 131.5 (*E*), 129.3 (*Z*), 120.0 (*Z*), 118.5 (*E*), 74.0 (*E*), 70.1 (*Z*), 34.5 (*Z*), 34.2 (*E*), 33.7, 32.6, 27.9, 24.3 (*E*), 24.2 (*Z*), 21.3. Anal. Calcd for $C_{12}H_{19}O_2Br$: C, 52.38; H, 6.96. Found: C, 52.33; H, 7.06.

5,10-Diacetoxy-1,3-decadiene (20b). Acetylation of 10-acetoxy-1,3-decadien-5-ol (4.25 g, 20 mmol; prepared from 1,3-butadienylmagnesium chloride[5] and 6-acetoxyhexanal) gave **20b** (3.76 g, 74%): bp 130 °C (4 mmHg); IR (neat) 3012, 2938, 2858, 1728, 1654, 1605, 1596, 1457, 1435, 1367, 1217, 1009, 961, 914 cm⁻¹; ^{1}H NMR δ 1.2–1.5 (m, 4 H), 1.5–1.8 (m, 4 H), 2.04 (s, 2.1 H, *Z*), 2.05 (s, 3 H), 2.06 (s, 0.9 H, *E*), 4.05 (t, *J* = 6.5 Hz, 2 H), 5.1–5.4 (m, 3 H), 5.5–5.8 (m, 1 H), 6.11 (d, d, *J* = 11, 11 Hz, 0.7 H), 6.2–6.4 (m, 0.6 H), 6.6–6.9 (m, 0.7 H); ^{13}C NMR δ 171.2, 170.3, 136.0 (*E*), 133.1 (*E*), 132.1 (*Z*), 131.7 (*Z*), 131.6 (*E*), 129.3 (*Z*), 120.0 (*Z*), 118.4 (*E*), 74.0 (*Z*), 70.1 (*E*), 64.4, 34.6 (*Z*), 34.3 (*E*), 28.4, 25.7, 24.8 (*E*), 24.7 (*Z*), 21.3, 21.0. Anal. Calcd for $C_{12}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.92; H, 8.96.

11-Acetoxy-12,14-pentadecadien-2-one (20c). Acetylation of 11-hydroxy-12,14-pentadecadien-2-one (2.38 g, 10 mmol; prepared from 1,3-butadienylmagnesium chloride[5] and 2-oxoundecanal) gave **20c** (1.92 g, 68%): bp 150 °C (4 mmHg); IR (neat) 2926, 2852, 1737, 1717, 1370, 1239, 1019 cm⁻¹; ^{1}H NMR δ 1.2–1.4 (b s, 10 H), 1.4–1.7 (m, 4 H), 2.04 (s, 2.1 H), 2.06 (s, 0.9 H), 2.14 (s, 3 H), 2.42 (t, *J* = 6.3 Hz, 2 H), 5.1–5.4 (m, 3 H), 5.5–5.8 (m, 1 H), 6.12 (d, d, *J* = 11, 11 Hz, 0.7 H), 6.2–6.4 (m, 0.6 H), 6.6–6.9 (m, 0.7 H); ^{13}C NMR δ 170.3, 136.0 (*E*), 132.0, 131.8 129.6 (*Z*), 119.9 (*Z*), 118.3 (*E*), 74.2 (*E*), 70.3 (*Z*), 43.8, 34.7 (*Z*), 34.3 (*E*), 29.9 (*Z*), 29.7 (*Z*), 29.3, 29.1, 25.1, 25.0, 23.8, 21.3. Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.90; H, 10.25.

5-Acetoxy-1,3-decadien-9-yne (20d). Acetylation of 1,3-decadien-9-yn-5-ol (1.20 g, 8 mmol; prepared from 1,3-butadienylmagnesium chloride[5] and 5-hexynal) gave **20d** (1.07 g, 69%): bp 95 °C (4 mmHg); IR (neat) 3296, 2946, 2864, 1739, 1457, 1435, 1371, 1240, 1185, 1018, 967, 953, 912 cm⁻¹; ^{1}H NMR δ 1.4–1.6 (m, 2 H), 1.6–1.9 (m, 2 H), 1.97 (t, *J* = 2.6 Hz, 1 H), 2.04 (s, 2.1 H), 2.07 (s, 0.9 H), 2.22 (d, t, *J* = 2.6, 6.8 Hz, 2 H), 5.1–5.4 (m, 3 H), 5.5–5.8 (m, 1 H), 6.12 (d, d, *J* = 11, 11 Hz, 0.7 H), 6.2–6.4 (m, 0.6 H), 6.6–6.9 (m, 0.7 H); ^{13}C NMR δ 170.3, 135.9 (*E*), 133.2 (*E*), 132.3 (*Z*), 131.7 (*Z*), 131.3 (*E*), 129.1 (*Z*), 120.1 (*Z*), 118.6 (*E*), 83.8, 73.7, 69.7, 68.8, 33.7 (*Z*), 33.4 (*E*), 24.1 (*E*), 24.0 (*Z*), 21.2, 18.2. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.04; H, 8.53.

1-Bromo-6,8-tetradecadiene (21a): GC (column temperature = 170 °C, carrier gas pressure = 0.85 kg/cm²) t_R = 5.20 (*E*,*E*), 4.64 (*E*,*Z*) min; IR (neat) 3008, 2952, 2924, 2852, 1459, 987 cm⁻¹; ^{1}H NMR of (*E*,*E*):(*E*,*Z*) = 78:22) δ 0.88 (t, *J* = 7.5 Hz, 3 H), 1.20–1.60 (m, 10 H), 1.65–2.00 (m, 2 H), 2.00–2.25 (m, 4 H), 3.41 (t, *J* = 6.8 Hz, 2 H), 5.20–5.40 (m, 0.22 H, *E*,*Z*), 5.45–5.80 (m, 1.78 H, *E*,*E* and *E*,*Z*), 5.90–6.20 (m, 1.78 H, *E*,*E*), 6.20 (m, 0.22 H, *E*,*Z*); ^{13}C NMR of (*E*,*E*) δ 132.8, 131.6, 130.7, 130.1, 33.8, 32.7, 32.6, 32.3, 31.4, 29.1, 28.5, 27.7, 22.5, 14.1; HRMS calcd for $C_{14}H_{25}{}^{79}Br$ 272.1140, found 272.1092.

1-Acetoxy-6,8-tetradecadiene (21b): (*E*,*E*):(*E*,*Z*) = 78:22; GC (column temperature = 170 °C, carrier gas pressure = 0.85 kg/cm²) t_R = 6.02 (*E*,*E*), 5.37 (*E*,*Z*) min; IR (neat) 3012, 2924, 2852, 1742, 1458, 1437, 1387, 1365, 1237, 1045, 987 cm⁻¹; ^{1}H NMR 0.88 (t, *J* = 5.0 Hz, 3 H), 1.20–1.55 (m, 10 H), 1.55–1.88 (b s, 2 H), 1.95–2.30 (m, 4 H), 2.05 (s, 3 H), 4.05 (t, *J* = 6.7 Hz, 2 H), 5.25–5.80 (m,

2 H, *E,E* and *E,Z*), 5.90–6.15 (m, 1.78 H, *E,E* and *E,Z*), 6.20–6.45 (m, 0.22 H, *E,Z*); ^{13}C NMR of (*E,E*) δ 171.2, 132.7, 131.7, 130.6, 130.1, 64.5, 32.5, 32.4, 31.4, 29.1, 29.0, 28.4, 25.4, 22.5, 21.0, 14.0. Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 75.93; H, 11.27.

11,13-Nonadecadien-2-one (21c): (*E,E*):(*E,Z*) = 92:8; GC (column temperature = 170 °C, carrier gas pressure = 1.45 kg/cm²) t_R = 11.12 (*E,E*), 9.69 (*E,Z*) min; IR (neat) 3008, 2926, 2850, 1718, 1465, 1370, 986 cm⁻¹; ^1H NMR δ 0.88 (t, *J* = 6.0 Hz, 3 H), 1.10–1.70 (m, 17 H), 1.90–2.10 (m, 4 H), 2.14 (s, 3 H), 2.41 (t, *J* = 7.3 Hz, 2 H), 5.25–5.40 (m, 0.08 H, *E,Z*), 5.45–5.80 (m, 1.92 H, *E,E* and *E,Z*), 5.90–6.10 (m, 1.92 H, *E,E* and *E,Z*), 6.25–6.40 (m, 0.08 H, *E,Z*); HRMS calcd for $C_{19}H_{34}O$ 278.2611, found 278.2677.

6,8-Tetradecadien-1-yne (21d): (*E,E*):(*E,Z*) = 88:12; GC (column temperature = 140 °C, carrier gas pressure = 0.75 kg/cm²) t_R = 8.40 (*E,E*), 7.35 (*E,Z*) min; IR (neat) 3306, 3012, 2924, 2854, 1437, 1433, 987 cm⁻¹; ^1H NMR δ 0.88 (t, *J* = 6.0 Hz, 3 H), 1.15–1.50 (m, 6 H), 1.50–1.80 (m, 2 H), 1.95 (t, *J* = 2.5 Hz, 1 H), 1.90–2.40 (m, 4 H), 2.16 (dt, *J* = 2.5, 7.5 Hz, 2 H), 5.25–5.40 (m, 0.12 H, *E,Z*), 5.40–5.80 (m, 1.88 H, *E,E* and *E,Z*), 5.90–6.20 (m, 1.88 H, *E,E* and *E,Z*), 6.25–6.40 (m, 0.12 H, *E,Z*); ^{13}C NMR of (*E,E*) δ 14.1, 17.8, 22.6, 28.2, 29.1, 31.5, 32.6, 68.4, 84.4, 130.1, 130.6, 131.4, 133.1. Anal. Calcd for $C_{14}H_{22}$: C, 88.35, H, 11.65. Found: C, 88.47, H, 11.91.

Cobalt(II)-Catalyzed Reaction between Polycyclic Aromatic Aldehydes and Acetic Anhydride. Formation of Acylals, Not 1,2-Diketones

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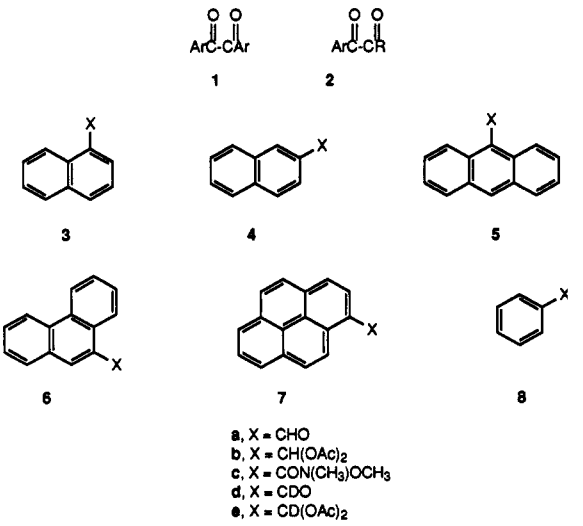
Several polycyclic aromatic aldehydes were found to react with acetic anhydride in acetonitrile in the presence of excess $CoCl_2$ to afford the corresponding acylals [$ArCH(OAc)_2$]. The results are not consistent with the literature report (Ahmad, S.; Iqbal, J. *J. Chem. Soc., Chem. Commun.* **1987**, 692) that substituted benzaldehydes afford 1,2-diketones under similar conditions. The cobalt(II) chloride probably promotes acylal formation through its weakly Lewis acid character.

In connection with other work,[1] we needed a series of diaryl and aryl alkyl 1,2-diketones (**1** and **2**). The literature contains a variety of methods for the synthesis of such substances.[2] However, it happened that our need for these compounds coincided with a report by Ahmad and Iqbal[3] concerning the reaction between acetic anhydride (Ac_2O) and a number of substituted benzaldehydes in acetonitrile in the presence of anhydrous cobalt(II) chloride ($CoCl_2$). They indicated that the reaction could be made to produce either **1** or **2** (Chart I), depending upon the ratio of Ac_2O to aldehyde employed in the reaction. In view of the apparent simplicity and versatility of this reaction, we decided to use it with a series of polycyclic aromatic aldehydes to prepare the corresponding diketones. In our hands, using somewhat different conditions, the reaction takes a considerably different course.

Results

Syntheses of Acylals. When we subjected either benzaldehyde or 4-nitrobenzaldehyde to the conditions of ref 3, we isolated only unreacted starting aldehyde. However, when 1-naphthaldehyde (**3a**) was allowed to react for 24 h at room temperature with acetic anhydride in dry CH_3CN containing excess $CoCl_2$, in the proportion Ac_2O/aldehyde/$CoCl_2$ = 3:1:1.5 (we refer to these proportions, temperature, and time throughout the following discussion as our "standard conditions"), a reaction did take place. The product was a white crystalline solid, mp 105 °C. It was clearly not the diketone 1,1′-naphthil, which is a yellow substance, mp 188–189 °C.[4] The white solid was identified as the acylal α,α-diacetoxy-1-methylnaphthalene (**3b**) by its ^1H NMR spectrum (s, δ 2.15, 6 H and mult δ 7.4–8.3, 8 H), mass spectrum (peaks at 258 [parent], 156 (base), and 127), IR spectrum(1745 and 1760 cm⁻¹), and combustion analysis. This structural assignment was confirmed through an independent synthesis by the reaction between **3a** and Ac_2O under BF_3 catalysis.[5]

Chart I



The generality of this acylal-forming reaction was then tested by subjecting a series of polycyclic aromatic aldehydes to similar conditions. The other aldehydes examined were 2-naphthaldehyde (**4a**), 9-anthraldehyde (**5a**), 9-phenanthraldehyde (**6a**), and 1-formylpyrene (**7a**). While **3a** and **4a** reacted completely in 24 h at room temperature under the standard conditions, the other aldehydes were only partly converted under these conditions and required higher temperatures and/or longer reaction times to go to completion. In every case, the product was the corresponding acylal (**3–7b**). There was no evidence for the

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