of this adduct will be much smaller than the ^1H and ^{13}C T_1 values of quinuclidine in this adduct. Under these circumstances the relaxation rate enhancement, RE_i, of a certain quinuclidine nucleus i is given by[30]

$$RE_i = T_1^{-1}{}_i - T_1^{-1}(0)_i - T_1^{-1}(\text{inter}) = K/R_i^6 \quad (7)$$

$T_1^{-1}{}_i$ and $T_1^{-1}(0)_i$ are the relaxation rates of nucleus i in the presence and absence of $Gd(fod)_3$, $T_1^{-1}(\text{inter})$ is the contribution of Gd^{3+} ions to the relaxation of nucleus i, other than the intra $Gd(fod)_3$ quinuclidine adduct contributions. For the determination of this quantity see the Experimental Section. K is a constant containing gyromagnetic ratios and reduced spectral density functions,[30] R_i is the internuclear Gd-i distance. In Table II the relaxation rate enhancements relative to the enhancements of proton 2 or carbon 2 are given. After substituting the geometry of quinuclidine,[21] the Gd-N distance was found by determing the best fit of the calculated relaxation rates to the experimental ones, using eq 7. Gd-N distances of 2.56 and 2.50 Å were found from the ^1H and ^{13}C results, respectively. As show before[6] the Gd-N distance obtained is rather insensitive to random variations in the relaxation rate enhancements but very sensitive to the value of T_1(inter). A variation of 10% in T_1(inter) varied the Gd-N distance by 0.08 Å. Comparing the values of 2.50 and 2.56 Å with the Yb-N distance of 2.63 Å obtained from the bound shifts, the agreement is very good, contrary to what was found previously,[6] when shift measurements in the fast-exchange region were applied. The values of 2.50, 2.56, and 2.63 Å are also in very good agreement with the Eu-N distance of 2.50 Å in the $Eu(dpm)_3$ quinuclidine adduct as determined by x-ray analysis.[21] This once again emphasizes that bound shifts obtained in the slow-exchange region and relaxation rate enhancements give reliable structural information, whereas shifts obtained in the fast-exchange region might give unreasonable results. Unfortunately, it is often difficult or even impossible to reach the slow-exchange region. In these cases it may be useful to check structural data based on LIS measurements via measurements of ^1H and ^{13}C spin-lattice relaxation rate enhancements induced by $Gd(fod)_3$. These experiments can be performed under conditions where self-association is negligible ($L_0/S_0 < 10^{-2}$).

(30) Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1964**, *40*, 2686.
(31) Raber, D. J.; Janks, C. M.; Johnston M. D., Jr.; Raber, N. K. *Org. Magn. Reson.* **1981**, *15*, 57.

Conclusions

(1) Exchange of quinuclidine between the free and bound state takes place via an associative mechanism. (2) Except for Bleaney's T^{-2} term there are considerable contributions of higher order T^{-n} ($n \geq 3$) terms to the experimental pseudocontact shifts. (3) Pseudocontact shifts obtained from the slow-exchange region of NMR spectra are preferable to fast-exchange data in order to get structural information about the complex. (4) Ln-N distances determined from shift and ^1H and ^{13}C relaxation data agree well.

Registry No. S, 100-76-5; LS, 80327-79-3.

Supplementary Material Available: Tables with the bound shifts of the 2, 3, and 4 protons as a function of temperature, with the longitudinal relaxation and average lifetimes of free and bound quinuclidine as a function of temperature, and with the average lifetimes of bound quinuclidine as determined from the line widths of the 2 and 3 protons of bound S (3 pages). Ordering information is given on any current masthead page.

Reaction of (9-Anthryl)arylmethyl Chlorides with Grignard and Lithium Reagents

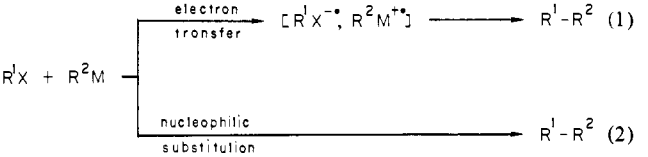
Masato Takagi, Masatomo Nojima,* and Shigekazu Kusabayashi

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan. *Received August 14, 1981*

Abstract: We have investigated the reaction of (9-anthryl)arylmethyl chlorides **1a-d** (para substituent = MeO, Me, H, and Cl) with Grignard and lithium reagents. The variables are the structures of the alkyl group of Grignard and lithium reagents (alkyl group = *tert*-butyl, isopropyl, ethyl, methyl, and phenyl), solvent (diethyl ether and tetrahydrofuran), and presence or absence of additive (*p*-dinitrobenzene and $FeCl_3$). The products were a mixture of two alkylation products, **3** (coupling at C-α) and **4** (coupling at C-10), and three dimerization products, **5** (C_α-C_α coupling), **6** (C_α-C_{10} coupling), and **7** (C_{10}-C_{10} coupling), the composition being determined for each reaction.

Introduction

The reaction of alkyl halides with magnesium and lithium reagents has received attention lately with regard to mechanism.[1] Using stereochemistry and CIDNP as the most definitive indicators of mechanism, it has been confirmed that at least two reaction mechanisms, i.e., electron transfer (eq 1) and direct



nucleophilic substitution (eq 2), are possible. Evidence is available for both mechanisms in individual cases. However, a delicate balance must exist between these mechanistic alternatives, and

(1) (a) Bank, S.; Bank, J. F. "Organic Free Radicals", ACS Symposium Series No. 69; Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; p 343. (b) Guthrie, R. D. "Comprehensive Carbanion Chemistry", Part A; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1980; Chapter 5. (c) Negishi, E. "Organometallics in Organic Chemistry"; Wiley: New York, 1980; Vol. 1, Chapter 4. (d) Creary, X. *J. Am. Chem. Soc.* **1977**, *99*, 7632. (e) Sauer, J.; Braig, W. *Tetrahedron Lett.* **1969**, 4275. (f) Allen, R. B.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1973**, *95*, 1692.

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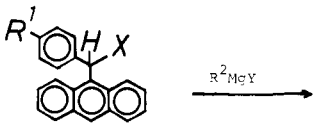
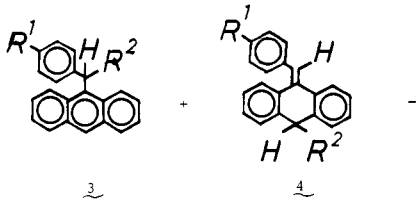
a minor change of reaction conditions may alter the extent of each process.[2,3]

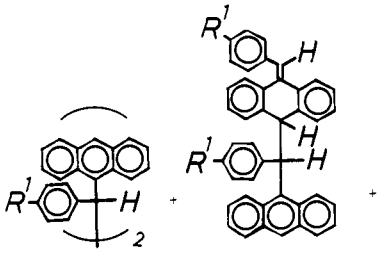
We have investigated the reaction of chlorides **1a–d** with a series of Grignard and lithium reagents, and determined the ratio of **3** (cross-coupling at C-α) to **4** (cross-coupling at C-10) for each reaction (eq 3). The variables are the structure of alkyl groups



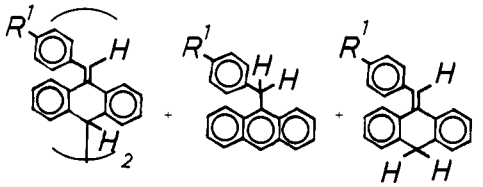
1a; R^1=OMe, X=Cl 2b; R^1=Me , X=Br
1b; R^1=Me, X=Cl 2c; R^1=H , X=Br
1c; R^1=H, X=Cl 2d; R^1=Cl, X=Br
1d; R^1=Cl, X=Cl



3 4 (3)



5a; R^1=OMe 6a; R^1=OMe
5b; R^1=Me 6b; R^1=Me
5c; R^1=H 6c; R^1=H
5d; R^1=Cl 6d; R^1=Cl



7a; R^1=OMe 8a; R^1=OMe 9a; R^1=OMe
7b; R^1=Me 8b; R^1=Me 9b; R^1=Me
7c; R^1=H 8c; R^1=H 9c; R^1=H
7d; R^1=Cl 8d; R^1=Cl 9d; R^1=Cl

of Grignard and lithium reagents (alkyl group = *tert*-butyl, isopropyl, ethyl, methyl, and phenyl), solvent (diethyl ether and tetrahydrofuran), and presence or absence of additives (*p*-dinitrobenzene and $FeCl_3$). If the para substituent of the halide affects the composition of two isomeric cross-coupling products **3** and **4** in a significantly different fashion depending on mechanism, this approach might serve to elucidate the reaction paths participating in these reactions and the factors affecting the extent of each path.

(2) The existence of a delicate balance between nucleophilic addition and one-electron transfer reduction has also been demonstrated in the reaction of Grignard reagents with ketones. In this case, a trace amount of transition metal impurities in magnesium is known to accelerate the electron transfer route.

(3) (a) Ashby, E. C.; Wiesemann, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 189. (b) Ashby, E. C.; Bowers, J. R., Jr. *Ibid.* **1981**, *103*, 2242.

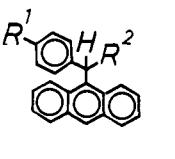
Table I. Reaction of (9-Anthryl)arylmethyl Chlorides 1a-d with Grignard Reagents in Ether[a]

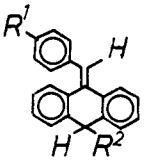
RMgBr R	substrate	% alkylation[b] [3:4][c]	% dimerization[b] [6:7][c]	% reduction[b] [8:9][c]
t-Bu	1a	40 [35:65]	42 [59:41][d]	18 [80:20]
t-Bu	1b	48 [30:70]	36 [58:42][d]	16 [68:32]
t-Bu	1c	42 [29:71]	37 [50:50]	21 [67:33]
t-Bu	1d	43 [27:73]	39 [51:49]	18 [67:33]
i-Pr	1a	66 [50:50]	25 [50:50][a]	9 [66:34]
i-Pr	1b	68 [34:66]	26 [53:47][d]	6 [67:33]
i-Pr	1c	66 [33:67]	26 [52:48]	8 [55:45]
i-Pr	1d	64 [33:67]	25 [50:50]	10 [55:45]
Et	1a	88 [84:16]	9 [61:39][d]	3 [62:38]
Et	1b	90 [54:46]	6 [58:42][d]	4 [62:38]
Et	1c	85 [49:51]	12 [56:44]	3 [55:45]
Et	1d	75 [44:56]	18 [52:48]	7 [59:41]
Ph	1a	96 [68:32]	4 [60:40]	
Ph	1b	100 [42:58]		
Ph	1c	92 [23:77]	8 [56:44]	
Ph	1d	96 [22:78]	4 [60:40]	
Me	1a	100 [92:8]		
Me	1b	75 [62:38]	25 [59:41][d]	
Me	1c	66 [41:59]	34 [50:50]	
Me	1d	33 [46:54]	67 [50:50]	

[a] The reaction with 5 equiv of Grignard reagent at 0 °C for 2 h. [b] The given total yield was 90%, normalized; 100 % = % alkylation + % dimerization + % reduction. [c] The ratio of products was determined by NMR spectroscopy; average values of duplicate runs. The errors were of the order of 2% for alkylation products and 5% for dimerization products. [d] Dimer **5** was also obtained; its proportion in dimeric products was ca. 5%.

Results and Discussion

Reaction with Grignard Reagents in Diethyl Ether. The reaction of chlorides **1a–d** with a series of Grignard reagents gave a mixture of two alkylation products, **3** and **4**, three dimerization products,





3a; R^1=OMe, R^2=t-Bu 4a; R^1=OMe, R^2=t-Bu
3b; R^1=Me, R^2=t-Bu 4b; R^1=Me, R^2=t-Bu
3c; R^1=H, R^2=t-Bu 4c; R^1=H, R^2=t-Bu
3d; R^1=Cl, R^2=t-Bu 4d; R^1=Cl, R^2=t-Bu
3e; R^1=OMe, R^2=i-Pr 4e; R^1=OMe, R^2=i-Pr
3f; R^1=Me, R^2=i-Pr 4f; R^1=Me, R^2=i-Pr
3g; R^1=H, R^2=i-Pr 4g; R^1=H , R^2=i-Pr
3h; R^1=Cl, R^2=i-Pr 4h; R^1=Cl, R^2=i-Pr
3i; R^1=OMe, R^2=Et 4i; R^1=OMe, R^2=Et
3j; R^1=Me, R^2=Et 4j; R^1=Me, R^2=Et
3k; R^1=H, R^2=Et 4k; R^1=H, R^2=Et
3l; R^1=Cl, R^2=Et 4l; R^1=Cl, R^2=Et
3m; R^1=OMe, R^2=Ph 4m; R^1=OMe, R^2=Ph
3n; R^1=Me, R^2=Ph 4n; R^1=Me, R^2=Ph
3o; R^1=H, R^2=Ph 4o; R^1=H, R^2=Ph
3p; R^1=Cl, R^2=Ph 4p; R^1=Cl, R^2=Ph
3q; R^1=OMe, R^2=Me 4q; R^1=OMe, R^2=Me
3r; R^1=Me, R^2=Me 4r; R^1=Me, R^2=Me
3s; R^1=H, R^2=Me 4s; R^1=H, R^2=Me
3t; R^1=Cl, R^2=Me 4t; R^1=Cl, R^2=Me

5 (C_α–C_α coupling), **6** (C_α–C_{10} coupling, a mixture of two conformational isomers), and **7** (C_{10}–C_{10} coupling, a mixture of two conformational isomers), and two reduction products, **8** (anthracene hydrocarbon) and **9** (9,10-dihydroanthracene) (eq 3 and Table I),[4,5] In all the reactions dimers **5** were obtained in yields

of less than 3%, and, therefore, the yields are not listed in Tables I–VII.

Examination of the data in Table I reveals certain trends. First, in the reaction of chlorides **1a–d** with *tert*-butyl- and isopropylmagnesium reagents, the product compositions were found to be insensitive to the para substituent electronic effects of the chlorides. In the case of EtMgBr the para substituent has a slight effect on the composition. Steric factors of the alkyl group of Grignard reagents seem to be important with increasing hindrance leading to small amounts of alkylation products. Conversely, both the yields of dimers and those of reduction products increase with increase in steric bulk of the alkyl moieties. Second, a change of para substituent has little influence on **3**/**4** ratios. The structure of the organic part of Grignard reagents exerts a small, but meaningful influence on **3**/**4** ratios; the ratios are around 3:7 for *tert*-butyl, 1:2 for isopropyl, and 1:1 for ethyl. The exceptions are the reactions of **1a** with isopropyl- and ethylmagnesium reagents, the ratios being 1:1 for isopropyl and 4:1 for ethyl. Finally, both the para substituents of chlorides and the alkyl groups of Grignard reagents do not affect the compositions of dimers **6** and **7**, the ratio being ca. 5:4 in all the reactions.

Phenylmagnesium bromide behaves in a significantly different manner. The reaction of **1a–d** with this reagent gave almost exclusively a mixture of the alkylation products **3** and **4**, the ratio being substantially increased as the substituent became increasingly electron-donating. The **3**/**4** ratios were well correlated with Brown σ^+ constants (Figure 1). The behavior of MeMgBr is also characteristic. The reaction of **1a–d** with this reagent gave both the alkylation products **3** and **4** and the dimers **5–7**. The **6**/**7** ratio (ca. 5:4) is insensitive to the para substituent. In direct contrast, the **3**/**4** ratio is a marked function of the electronic effects of the para substituent. A plot of the **3**/**4** ratio vs. σ^+ gives, however, a curved line, the **3**/**4** ratio being a minimum when the substituent is hydrogen (Figure 1). The alkylation/dimerization ratio was also affected by the para substituent, the ratio being increased with the increase of electron-donating ability of the substituent. In some reactions the purity of Mg or the presence of $FeCl_3$ was found not to exert a significant effect on the product composition (Table V).

How can we explain these apparently complicated results? Dimers **5–7** are reasonably expected to be a result of coupling of two (9-anthryl)arylmethyl radicals **10**.[1b] The fact that the composition of the dimers is insensitive to both the para substituents of chlorides and the alkyl groups of Grignard reagents seems to be consistent with the above hypothesis. It is well known that the distribution of odd electrons in para substituted benzyl radicals is perturbed by the para substituent only to a small extent,[6] and addition of CCl_3Br to substituted stilbenes does not show significant para substituent effects on orientation.[7] To assure that intermediacy of (9-anthryl)arylmethyl radical **10** in the formation of dimers **5–7**, we have examined the reactions of **1a** and **2b–d** with silver in THF (Table II and eq 4). The para substituent

$$\textbf{1a and 2b–d} \xrightarrow{\text{Ag in THF, } N_2} \textbf{5} + \textbf{6} + \textbf{7} \qquad (4)$$

independent composition of dimers (**6**:**7** = 5:4) is exactly the same as that observed in the reaction with Grignard reagents. This fact leads to an important conclusion that (9-anthryl)arylmethyl radicals **10** have two reaction sites, the ratio of attack at C-α to that at C-10 not being affected by the para substituents of **10**.

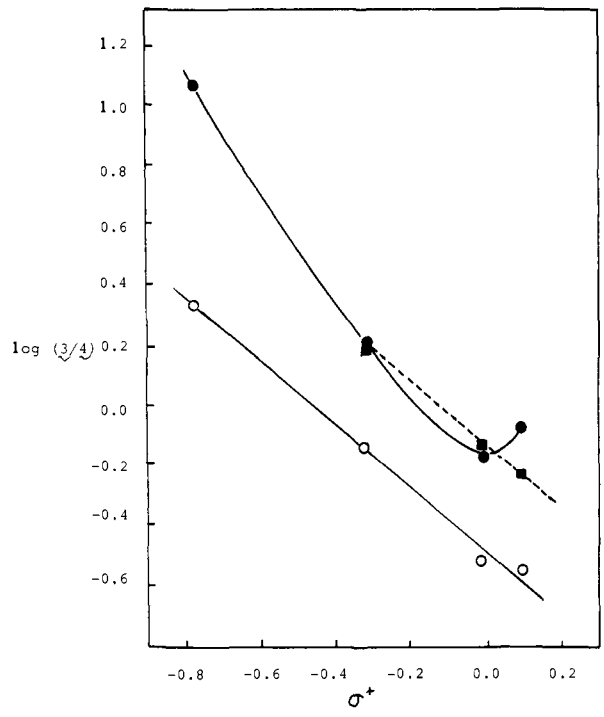


Figure 1. Plot of log (**3**/**4**) vs. σ^+ constants for the reactions of **1a–d** with phenyl- and methylmagnesium reagents in diethyl ether at 0 °C: (○) PhMgBr, (●) MeMgBr, (■) MeMgBr in the presence of *p*-DNB.

Table II. Reaction with Silver in THF[a]

substrate	conversion %	product[b,c] 6:7
1a	53	55:45
2b	59	56:44
2c	59	53:47
2d	72	50:50

[a] The reaction with 5 equiv of silver at 20 °C for 2 h under a nitrogen atomosphere. [b] The ratio of products was determined by NMR. [c] Dimer 5 was also obtained; its proportion in dimeric products was ca. 5%.

When no substantial para substituent effect on the **3**/**4** ratios in the reactions with *tert*-butyl-, isopropyl-, and ethyl-magnesium reagents is seen, the alkylation products in these reactions are most probably produced by the cross-coupling between (9-anthryl)-arylmethyl radicals **10** and the alkyl radicals derived from the alkylmagnesium reagents.[8] Thus, as far as reaction with *tert*-butyl-, isopropyl-, and ethylmagnesium reagents is concerned, a mechanism involving single electron transfer (SET) is reasonably proposed. Path a in Scheme I illustrates that a radical pair, formed from R^1Cl and R^2MgY by electron transfer, couples in the cage to afford a mixture of **3** and **4**, while radicals **10** which escape from the cage dimerize to yield a mixture of dimers **5–7**.

If the reactions proceed by a rate-determining SET, the relative rates must be determined by the donor power of the Grignard reagent;[9] the donor power of organomagnesium reagents increases in the order Ph < Me < Et < Me_2CH < Me_3C, as established from the oxidation potential of alkylmagnesium halides.[10] With the above in mind, some competitive experiments between two

(4) The reaction of 9-α-chloromethylanthracene with MeMgI has been reported to afford 1,2-bis(9-anthryl)ethane (C_α–C_α coupling) and lepidopterin (C_α–C_{10} coupling). We reinvestigated the reaction with MeMgBr to give 9,9′-dimethylene-9,9′,10,10′-tetrahydro-10,10′-anthracenyl [mp 200 °C dec (from ether); *m/e* 382 (M^+); NMR δ 4.20 (s, 2 H, 10 position), 5.12 (s, 4 H, methylene). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.79. Found: C, 94.50; H, 5.48.] (C_{10}–C_{10} coupling) along with the above C_α–C_α and C_α–C_{10} coupling products in a molar ratio of 1:1:4.

(5) Felix, G.; Lapouyade, R.; Castellan, A.; Bouas-Laurent, H.; Gaultier, J.; Hauw, C. *Tetrahedron Lett.* **1975**, 409.

(6) Gey, E. *Z. Chem.* **1974**, *14*, 279.

(7) Gadogan, J. I. G.; Duell, E. G.; Inwald, P. W. *J. Chem. Soc.* **1962**, 4164.

(8) To explain the results, a referee has suggested that the following, alternative mechanism may be possible. (9-Anthryl)-arylmethyl radical **10** reacts with RMgX to give a radical ion and produce a short kinetic chain. As he suggests, the substitution product distribution in such a case would be relatively independent of substituents on the phenyl ring. Further work is required to distinguish between this mechanism and the proposed one (path a in Scheme I).

(9) (a) Nugent, A. W.; Bertini, F.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 4945. (b) Chen, J. Y.; Gardner, H. C.; Kochi, J. K. *Ibid.* **1976**, *98*, 6150. (c) Gough, R. G.; Dixon, J. A. *J. Org. Chem.* **1968**, *33*, 2148. (d) Berti, C.; Greci, L.; Marchetti, L. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 233.

(10) Holm, T.; Crossland, I. *Acta Chem. Scand.* **1971**, *25*, 59.

Table III. Competition Reaction between Two Grignard Reagents for 1b in Ether[a]

R^1MgX	R^2MgX	product[b]
t-BuMgCl	*i*-PrMgBr	(**3b** + **4b**):(**3f** + **4f**) = 77:23
i-PrMgBr	EtMgBr	(**3f** + **4f**):(**3j** + **4j**) = 65:35
EtMgBr	MeMgBr	(**3j** + **4j**):(3r + 4r) = 88:12
MeMgBr	PhMgBr	(3r + **4r**):(3n + 4n) = 47:53

[a] The reaction with 5 equiv of each Grignard reagent at 0 °C for 10 min. [b] The ratio of products was determined by NMR.

Grignard reagents were examined (Table III). The results demonstrate the following reactivity order of Grignard reagents: Me_3C > Me_2CH > Et > Me ≃ Ph. This sequence supports the hypothesis that the reaction with *tert*-butyl-, isopropyl-, and ethylmagnesium reagents proceeds by a mechanism involving SET, but the same sequence suggests that at least the reaction with PhMgBr proceeds by a different mechanism. The SET mechanism (path a in Scheme I) explains well the fact that both the product compositions and the **3**/**4** ratios vary in considerable amounts depending on the steric bulk of the alkyl moieties of the Grignard reagents. The most voluminous *tert*-butyl radical is reasonably expected to attack predominantly the less hindered C-10 of (9-anthryl)arylmethyl radicals **10** to yield the alkylation products **4** with a quinoidal structure in preference to **3** or allow easy abstraction of hydrogen by **10** to yield reduction products **8** and **9**.[11]

What is the mechanistic origin for the appearance of large para substituent effects on **3**/**4** ratios, which is only observed in the reaction with PhMgBr or MeMgBr? If it is noticed that the charge density of a chloride **1** at C-10 increases as the substituent becomes increasingly electron withdrawing, the following may explain the results. Phenylmagnesium bromide with a relatively higher ionization potential attacks both the C-α and the C-10 of a chloride **1** in different ratios depending on variable charge distribution (path b in Scheme I), with the **3**/**4** ratio being decreased as the substituent becomes increasingly electron withdrawing.[12,13]

An apparently complicated behavior of MeMgBr may now be rationalized in terms of competitive participation of two processes; alkylation products being formed by a nucleophilic substitution mechanism (path b in Scheme I) and dimers being formed by a mechanism involving SET (path a in Scheme I). A main factor which determines the ratio of alkylation to dimerization, i.e., nucleophilic substitution vs. SET, seems to be para substituent electronic effects, the reaction of highly ionizable **1a** proceeding mainly by the former path, while that of poorly ionizable **1d** is likely to proceed by the latter path. Not consistent with a nucleophilic mechanism, the **3t**/**4t** ratio (46;54) obtained in the reaction of **1d** is larger than the **3s**/**4s** ratio (41;59) from **1c**. This sequence suggests that in the case of **1d** a part of the alkylation products may come from cross-coupling between **10d** and methyl radical (as will be discussed in a later section, this process gives a mixture of **3t** and **4t** in a ratio of approximately 1:1). The **3**/**4** ratio obtained in the reaction of bromides **2b–d** follows, however, a sequence expected from a nucleophilic substitution mechanism: Me (7:3) > H (1;1) > Cl (4:6) (Table IV). Good leaving efficiency of the bromide ion must be the reason. The reaction of **1a–c** with MeMgI gives dimers **5–7** in higher yields compared with the reaction with MeMgBr. This fact indicates that MeMgI, which is expected to have a lower ionization potential,[14,15] favors a SET mechanism.

Scheme I

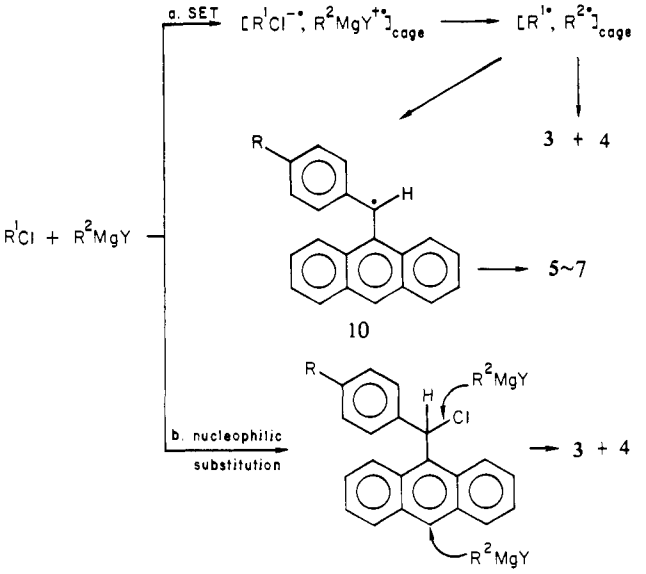


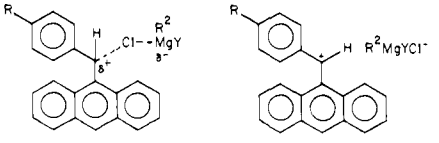
Table IV. Reaction with Methyl Grignard Reagents in Ether[a]

RMgX X	substrate	reaction time (min)	% alkylation[b,c] [3:4]	% dimerization[b,c] [6:7]
Br	1a	120	100 [92:8]	
Br	1b	120	75 [62:38]	25 [59:41][d]
Br	1c	10	69 [41:59]	31 [50:50]
Br	1c	60	66 [42:58]	34 [53:47]
Br	1c	120	66 [41:59]	34 [53:47]
Br	**1d**	120	33 [46:54]	67 [50:50]
Br	2b	120	88 [66:34]	12 [58:42][d]
Br	2c	120	70 [43:57]	30 [53:47]
Br	2d	120	46 [37:63]	54 [48:52]
I	1a	120	65 [96:4]	35 [57:43][d]
I	1b	120	15 [63:47]	85 [51:49][d]
I	1c	120	15 [38:82]	85 [50:50]

[a] The reaction with 5 equiv of MeMgX at 0 °C. [b] Normalized 100% = % alkylation + % dimerization. [c] The ratio of products was determined by NMR spectroscopy; average values of duplicate runs. The errors were of the order of 2% for alkylation products and 5% for dimerization products. [d] Dimer **5** was also obtained; its proportion in dimeric products was ca. 5%.

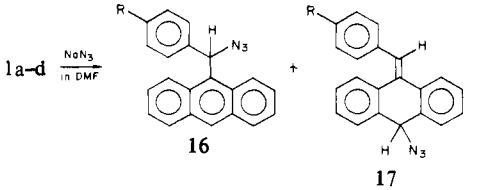
(11) (a) Takagi, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc. Perkin Trans. 1* **1979**, 2941. (b) Takagi, M.; Ogata, F.; Nojima, M.; Kusabayashi, S. *Ibid.* **1979**, 2948.

(12) Under the reaction conditions chloride **1** may exist as a charge-developed species. A Grignard reagent is able to coordinate through Mg to the leaving group of **1** and weakens the C–Cl bond to produce **18**. The limiting case is a carbenium ion **18′**.



18 18′

In connection with this, the following fact may be suggestive. The reaction of **1a–d** with sodium azide under solvolytic conditions gives a mixture of **16** and **17**, the ratio being substantially varied from 8:2 for the *p*-methoxy derivatives to 3:7 for the *p*-chloro derivatives.[13]



16 17

(13) Ogata, F.; Takagi, M.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1981**, *103*, 1145.

(14) There are no reliable data for ionization potentials of RMgX and R_2Mg. However, first vertical ionization potentials of binary mercury(II) derivatives are known to follow the sequence MeHgCl (10.88 eV) > MeHgBr (10.16) > Me_2Hg (9.33) > MeHgI (9.25), and therefore it may be reasonable to speculate that the same sequence holds for MeMgBr, Me_2Mg, and MeMgI.

(15) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; p 454.

Table V. Effect of Additives (*p*-Dinitrobenzene and $FeCl_3$) on the Reaction with Grignard Reagents[a]

RMgX	substrate	solvent	additive	% alkylation[b] [3:4][c]	% dimerization[b] [6:7][c]	% redn[b,c]	% unreacted[b,c] chloride[j]
MeMgBr	1b	Et_2O	*p*-DNB[d,e]	90 [62:38]	10 [55:45][h]		
MeMgBr	1c	Et_2O	*p*-DNB[d,e]	96 [43:57]	4 [50:50]		
MeMgBr	1d	Et_2O	*p*-DNB[d,e]	89 [38:62]	6 [55:45]		5
MeMgI	1b	Et_2O	*p*-DNB[d,e]	65 [55:45]	35 [54:46][h]		
EtMgBr	1b	Et_2O	*p*-DNB[d,e]	84 [51:49]	10 [52:48][h]	6[i]	
EtMgBr	1d	Et_2O	*p*-DNB[d,e]	74 [40:60]	21 [53:47]	5[i]	
i-PrMgBr	1b	Et_2O	*p*-DNB[d,e]	54 [42:58]	39 [68:32][h]	7[i]	
MeMgBr[f]	1c	Et_2O	none	58 [44:56]	42 [52:48]		
MeMgBr	1d	Et_2O	$FeCl_3$[g]	29 [38:62]	71 [50:50]		
MeMgBr	1d	THF	$FeCl_3$[g]		97 [60:40]	3[i]	

[a] The reaction with the Grignard reagent prepared from Grignard grade magnesium turnings (99.5%) at 0 °C for 2 h unless otherwise noted. [b] Normalized; 100% = % alkylation + % dimerization + % redn + % unreacted chloride. [c] The ratio of products was determined by NMR. [d] *p*-Dinitrobenzene. [e] As 4 mol of MeMgBr is known to be consumed by each mole of *p*-DNB, 9 equiv of RMgX was treated with a mixture of 1 equiv of chloride and 1 equiv of *p*-DNB. [f] Prepared from high-grade magnesium turnings (99.99%). [g] $FeCl_3$ (1000 ppm) was doped. [h] Dimer **5** was also obtained; its proportion in dimeric products was ca. 5%. [i] The crude products were treated with KOBu-*t* in *t*-BuOH to isomerize 9 to 8. [j] After workup the reaction mixture was treated with methanol to convert the unreacted chloride to the corresponding methyl ether.

Table VI. Reaction with Grignard Reagents in THF[a]

RMgBr R	substrate	reaction time (min)	% alkylation[b] [3:4][c]	% dimerization[b] [6:7][c]	% redn[b,c]	% 11[b]	% unreacted chloride[b,c,f]
Me	1a	60	79 [83:17]	21 [63:37][e]			
Me	1b	120	46 [52:48]	37 [50:50][e]		17	
Me	1c	10	10 [44:56]	10 [50:50]		10	69
Me	1c	60	19 [42:58]	19 [50:50]		19	41
Me	1c	120	27 [44:56]	25 [50:50]		25	23
Me	1d	120	14 [39:61]	14 [52:48]		35	37
Me	2b	120	24 [52:48]	71 [54:46][e]		5	
Et	1a	60	77 [69:31]	23 [69:31][e]			
Et	1b	60	30 [50:50]	70 [48:52][e]			
Et	1c	60	13 [41:59]	87 [47:53]			
Et	1d	60	23 [36:64]	77 [54:46]			
i-Pr	1a	60	71 [39:61]	27 [55:45][e]	2[d]		
i-Pr	1b	60	60 [21:79]	35 [52:48][e]	5[d]		
i-Pr	1c	60	60 [21:79]	38 [50:50]	2[d]		
i-Pr	1d	60	60 [22:78]	37 [48:52]	3[d]		

[a] The reaction with 5 equiv of Grignard reagent at 0 °C. [b] Normalized; 100% = % alkylation + % dimerization + % redn + % 11 + % unreacted chloride. [c] The ratio of products was determined by NMR spectroscopy. [d] The products were treated with KOBu-*t* in *t*-BuOH to isomerize 9 to 8. [e] Dimer **5** was also obtained; its proportion in dimeric products was ca. 5%. [f] After workup the reaction mixture was treated with methanol to convert the unreacted chloride to the corresponding methyl ether.

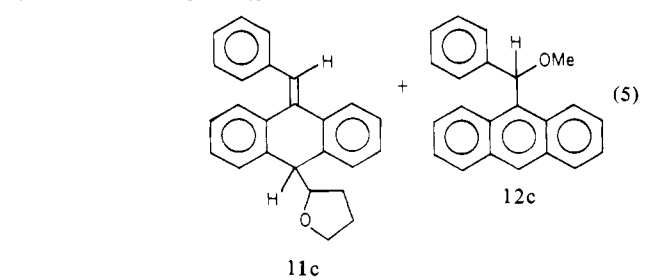
Table VII. Reaction with Alkyllithium[a]

RLi R	substrate	% alkylation[b] [3:4][c]	% dimerization[b] [6:7][c]	% redn[b,c]	% 15[b]
Me	1a	53 [54:46]	31 [50:50][d]		16
Me	1b	32 [46:54]	34 [61:39][d]		34
Me	1c	29 [47:53]	46 [51:49]		25
Me	1d	30 [51:49]	51 [53:47]		19
Me	2b	40 [52:48]	60 [61:39][d]		
Et	1a	70 [46:54]	29 [43:57][d]	1[e]	
Et	1b	68 [52:48]	32 [51:49][d]		
Et	1c	67 [51:49]	30 [54:46]	3[e]	
Et	1d	66 [56:44]	30 [54:46]	4[e]	

[a] The reaction with 5 equiv of alkyllithium at 0 °C for 2 h. [b] Normalized; 100% = % alkylation + % dimerization + % redn + % 15. [c] The ratio of products was determined by NMR. [d] Dimer **5** was also obtained; its proportion in dimeric products was ca. 5%. [e] The crude products were treated with KOBu-*t* in *t*-BuOH to isomerize 9 to 8.

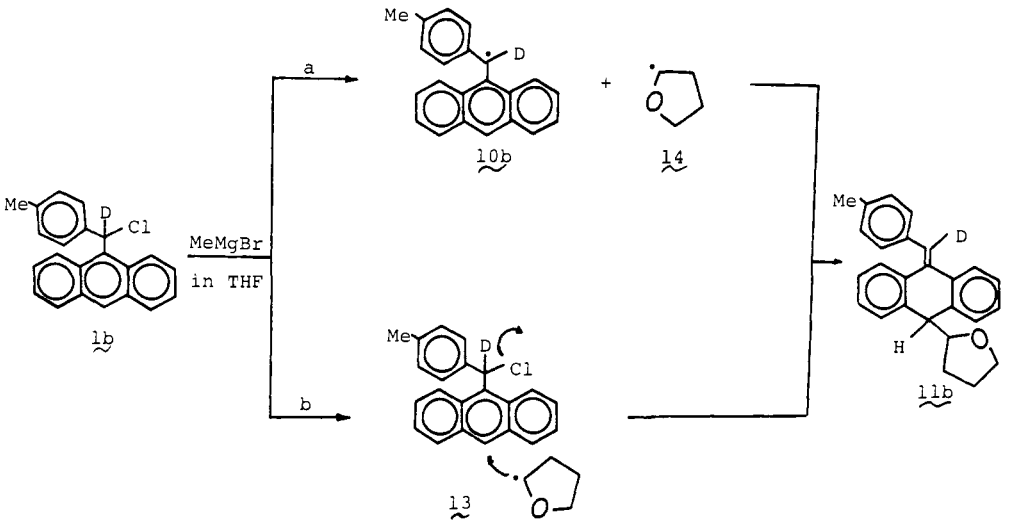
Addition of *p*-dinitrobenzene (p-DNB), which is well known to work as a "trapping agent" of organometallic reagents and radical anions,[16] exerts a pronounced influence on product composition. In the reaction with MeMgBr, addition of p-DNB results in a remarkable increase of the alkylation products (Table V). In addition, the **3**/**4** ratios decrease by the sequence expected from a nucleophilic substitution mechanism: MeO > Me > H > Cl (Figure 1). The same trends were observed in the reaction with MeMgI. In the reaction of **1b** with isopropyl- and ethylmagnesium reagents, however, addition of p-DNB has no influence on the product composition.

Reaction with Grignard Reagents in Tetrahydrofuran. Tetrahydrofuran (THF) as a solvent exerts remarkable effects both on reaction rate and on product composition (Table VI). The reaction of **1c** with 5 equiv of a methylmagnesium reagent in THF for 2 h, followed by treatment with methanol, gave a mixture of the solvent participated product **11c**, the alkylation products, **3s** and **4s**, the dimers **5**–**7c**, and the methyl ether **12c** in approximately equal amounts (eq 5). The methyl ether **12c** is believed to be



(16) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

Scheme II



formed from the unreacted chloride **1c**. A series of reactions of **1a–d** with a methylmagnesium reagent reveal the following. First, the reaction in THF, a relatively polar solvent, is significantly slower than that in ether; the latter reaction is completed in 10 min (Table V). This result is not consistent with a reasonable expectation that in a solvent with higher polarity both SET and nucleophilic substitution might be accelerated. Second, para substituents again affect both **3**/**4** ratios and alkylation/dimerization ratios in trends observed in the reaction in ether. These trends suggest that alkylation products are formed by a nucleophilic substitution mechanism even in this slow reaction in THF. Finally, solvent participated products **11b–d** are formed from chlorides **1b–d**, the yield being increased with the increase of electron-withdrawing ability of the substituent. In harmony with this, a reactive chloride **1a** does not give the corresponding ether **11a**, and from **2b** the ether **11b** is obtained in a yield of only 5%.

What is the mechanistic origin of the solvent participated products **11**? Two mechanisms are considered (Scheme II). The first mechanism (path a) illustrates that a radical **14**, which is formed from THF by hydrogen abstraction, couples with **10b** at C-10. The second one (path b) illustrates attack of a radical **14** on the less hindered C-10 of a chloride,[17,18] followed by elimination of the leaving group Cl. To assure the possibility of the latter mechanism, chloride **1c** was treated with benzoyl peroxide in refluxing THF for 18 h. The expected product **11c** was obtained in a yield of 24% along with a complex mixture containing 9-benzoylanthracene. The facts that the ether **11c** with a quinoidal structure is the sole isomer isolated in both reactions and, by contrast, that cross-coupling between **10c** and voluminous *tert*-butyl radical affords a mixture of **3c** and **4c** in a ratio of ca. 3:7, may demonstrate that the latter mechanism is more probable. If the former mechanism is operating, the solvent participated product with an anthracene structure, together with **11c**, should have been formed.

In marked contrast to the reaction in ether, added $FeCl_3$ accelerates remarkably the reaction of **1d** in THF, with the dimers **5–7d** being formed almost exclusively (Table V). This result is reasonably interpreted as the significant participation of a process involving organoiron species in the reaction in THF. Organoiron species favor SET, with the rate being accelerated and the yield of dimers being increased significantly.[3a]

The reaction of **1b–d** with isopropylmagnesium reagent did not afford the solvent participated products **11b–d**. This may be interpreted as the relatively stable isopropyl radical finds it difficult to abstract hydrogen from THF.

(17) Anthracene is known to be susceptible to addition by some stable radicals ($PhCH_2$· and PhCO·, etc.).[18]

(18) (a) Beckwith, A. L. J.; Waterd, W. A. *J. Chem. Soc.* **1957**, 1001. (b) Bass, K. C.; Bass, P.; Nababsing, P. *Ibid.* **1965**, 4396. (c) Beckwith, A. L. J.; Leydon, R. J. *Aust. J. Chem.* **1968**, *21*, 817.

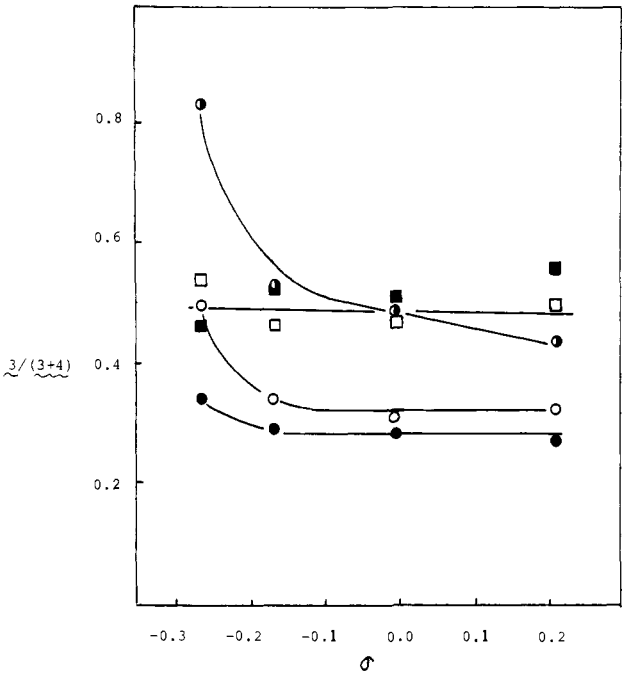


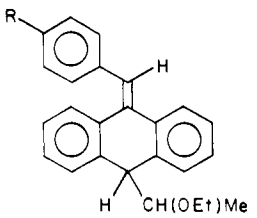
Figure 2. Plot of 3/(3 + 4) vs. σ constants for the reactions of **1a–d** with Grignard reagents and alkyllithiums in diethyl ether at 0 °C: (●) *t*-BuMgBr, (○) *i*-PrMgBr, (◑) EtMgBr, (■) EtLi, (□) MeLi.

Reaction with Alkyllithium. The reaction of **1a–d** with EtLi in ether gave both the alkylation products **3** and **4** and the dimerization products **5–7** (Table VII). The substituent independent **3**/**4** ratios (ca. 1:1) are exactly the same as those observed in the reaction of ethylmagnesium reagent in ether. It should be noticed that the reaction of the reactive chloride **1a** also gave the same **3**/**4** ratio. The alkylation/dimerization ratios (ca. 7:3) were also independent of chlorides **1a–d**. These results are consistent with a mechanism involving SET. Surprisingly, the same trends in **3**/**4** ratios and in alkylation/dimerization ratios were observed in the reaction with MeLi (see Figure 2). These results are in marked contrast to those for the reaction with MeMgBr and suggest that MeLi favors a SET mechanism.

A solvent participated product **15** with a quinoidal structure was also obtained in the reaction with MeLi.

Conclusion

As a tool to differentiate the change of the reaction processes in a series of reactions of chlorides **1a–d** with organometallic reagents, we have used the composition of alkylation products and their dependence (or independence) upon para substituents. This



15a, R = OMe; b, R = Me; c, R = H; d, R = Cl

approach has enabled us to propose that the following two mechanisms competitively participate in different extents depending on some variable factors. The first one is a single electron transfer, radical coupling mechanism (path a in Scheme I). The second one involves nucleophilic attack by organometallic reagents on a chloride (path b in Scheme I). Donor power of organometallic reagents is the largest single factor which determines the extent of each path. Easily oxidizable *tert*-butyl-, isopropyl-, and ethylmagnesium reagents and also methyl-, and ethyllithium reagents favor the first path, while phenylmagnesium bromide, having a high ionization potential, favors the second one. In the reaction with methylmagnesium reagent which has an intermediate ionization potential, these two processes competitively participate. The electron-donating para substituent facilitates the occurrence of a nucleophilic substitution mechanism. An additive p-DNB exerts a remarkable influence on product composition. Solvent THF slows down the reaction with a Grignard reagent to a remarkable extent.

Thus, we have examined and interpreted the somewhat complicated data in terms of participation of two mechanistic alternatives (paths a and b in Scheme I). It must be noted, however, that additional examination is necessary for a full understanding.

Experimental Section

^{1}H NMR spectra were obtained with a JNM-PS-100 spectrometer in $CDCl_3$. Mass spectral data were obtained with a Hitachi RMU-6H spectrometer, infrared spectra with a Hitachi 215 spectrometer, and UV spectra with a Varian Techron 635 spectrometer in dioxan.

Materials. Grignard reagent solutions were prepared by standard procedure from the following grades of magnesium: Wako Grignard grade turnings (99.5%) and Mituwa turnings (99.99%). Grignard reagents in THF were prepared by removing the ether from the Grignard reagents under vacuum and adding THF. Grignard reagents were analyzed by hydrolyzing an aliquot with distilled water, adding excess standard HCl, and back-titrating standard NaOH to a phenolphthalein end point. Methyllithium and ethyllithium were synthesized from methyl bromide and ethyl bromide in ether solution, respectively.[19] Concentrations of organolithium reagent solutions were determined by Eastmann's method.[20] Silver and $FeCl_3$ were reagent grade and used without purification. (9-Anthryl)arylmethyl chlorides **1a–d** and bromides **2b–d** were prepared by the reported method.[13] *p*-Dinitrobenzene was commercial grade and used without purification.

Reaction in General. The following procedure for the reactions of **1a–d** and **2b–d** with Grignard reagents and organolithiums is representative. Into a 200-mL flask, equipped with a magnetic stirrer and maintained under N_2, a solution of organometallic reagent was syringed and cooled to 0 °C. A solution of halide was dropped into the solution, and the mixture was stirred at 0 °C under a slow stream of N_2. Then the mixture was decomposed by methanol and/or hydrolyzed with aqueous NH_4Cl solution. The ether layer was separated and dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The crude products were chromatographed on silica gel to give two fractions. The first fraction (eluted with 1:1 and 1:5 benzene–light petroleum for *p*-methoxy derivatives and others, respectively) was composed of a mixture of **3**, **4**, **8**, and **9**. The second fraction (eluted with benzene and 1:1 benzene–light petroleum) contained **5**, **6**, and **7**. The compositions of the products were then determined by ^{1}H NMR spectroscopy.

Reaction with *tert*-Butylmagnesium Bromide in Ether. To 15.9 mmol of *tert*-butylmagnesium bromide in 30 mL of ether was added an ether solution of **1b** (1.0 g, 3.2 mmol). After 2 h, the reaction mixture was decomposed by methanol and extracted with ether. The crude products were chromatographed on silica gel to give two fractions. The first fraction (0.66 g) contained α-*tert*-butyl-10-*p*-methylbenzylanthracene (**3b**: 0.46 mmol, 14%), 9-*tert*-butyl-10-*p*-methylbenzylidene-9,10-dihydroanthracene (**4b**: 1.06 mmol, 32%), 9-*p*-methylbenzylanthracene (**8b**: 0.33 mmol, 10%) [NMR δ 4.95 (s, 2 H)], and 9-*p*-methylbenzylidene-9,10-dihydroanthracene (**9b**: 0.17 mmol, 5%) [NMR δ 4.00 (s, 2 H)]. The second fraction (0.30 g) consisted of 1,2-di-*p*-methylbenzyl-1,2-bis(9-anthracenyl)ethane (**5b**: 0.03 mmol, 2%), 10-(9′-anthryl-*p*-methylbenzyl)-9-*p*-methylbenzylidene-9,10-dihydroanthracene (**6b**: 0.31 mmol, 19%), and 9,9′-di-*p*-methylbenzylidene-9,9′,10,10′-tetrahydro-10,10′-bianthracene (**7b**: 0.23 mmol, 14%).

By column chromatography on silica gel and fractional recrystallizations of the first fraction, were isolated **3b** [mp 165–166 °C (from methanol); UV 390 nm (log ε 3.89), 370 (3.90) 350 (3.75), 334 (3.37); NMR δ 1.20 (s, 9 H), 2.22 (s, 3 H), 5.70 (s, 1 H). Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.40; H, 7.68.] and **4b** [mp

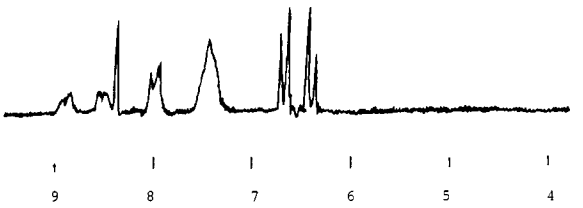


Figure 3. 100-MHz ^{1}H NMR spectrum of dimer **5b** in $CDCl_3$.

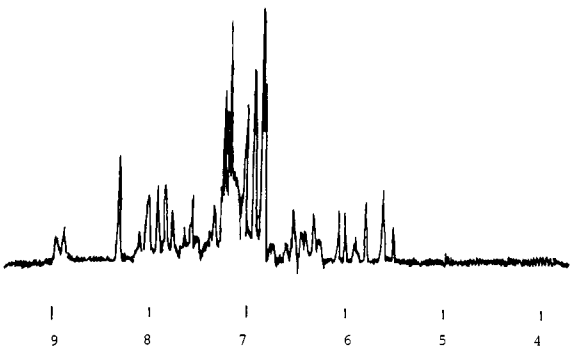


Figure 4. 100-MHz ^{1}H NMR spectrum of dimer **6b** in $CDCl_3$.

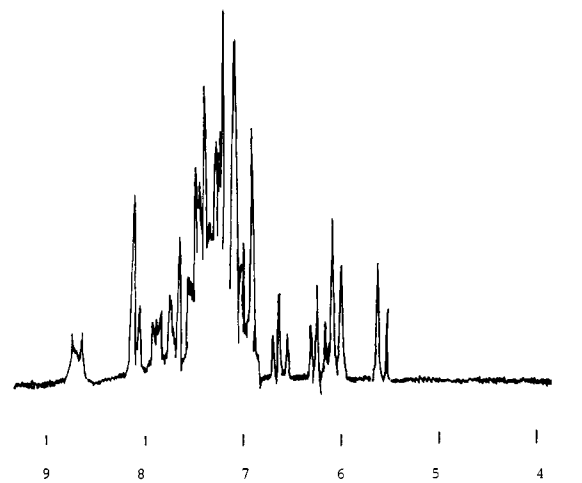


Figure 5. 100-MHz ^{1}H NMR spectrum of dimer **6b′** in $CDCl_3$.

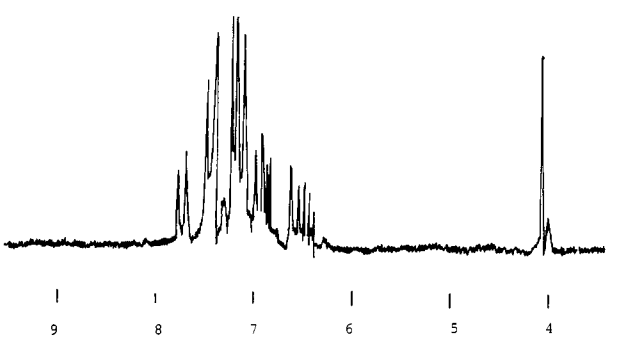


Figure 6. 100-MHz ^{1}H NMR spectrum of dimer **7b** in $CDCl_3$.

(19) "Organic Synthesis", Collect. Vol. V; Wiley: New York, 1973; p 859.
(20) Watson, S. C.; Eastmann, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

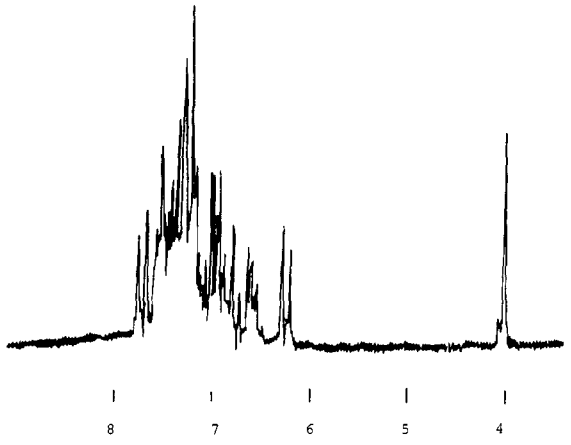


Figure 7. 100-MHz ^1H NMR spectrum of dimer **7b′** in $CDCl_3$.

150–151 °C (from benzene–methanol); UV 317 nm (log ε 4.13); NMR δ 0.97 (s, 9 H), 2.30 (s, 3 H), 3.69 (s, 1 H). Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.35; H, 7.62] in pure states. Column chromatography on silica gel and fractional recrystallizations of the second fraction gave pure **5b** [mp 244–245 °C (from ether); *m/e* 562 (M^+); UV 395 nm (log ε 4.41), 374 (4.38), 354 (4.15), 337 (3.84); NMR δ 1.89 (s, 3 H, methyl) (Figure 3). Anal. Calcd for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.96; H, 6.01], **6b** [mp 209–212 °C (from ether–light petroleum); *m/e* 562 (M^+); UV 393 nm (log ε 3.97), 372 (4.01), 320 (4.18); NMR δ 2.16 (s, 3 H, methyl), 2.31 (s, 3 H, methyl), 5.60 (d, 1 H) (Figure 4). Anal. Calcd for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.78; H, 5.93.], the conformational isomer **6b′** [mp 217–220 °C (from ether–light petroleum); *m/e* 562 (M^+); UV 393 nm (log ε 4.01), 372 (4.05), 318 (4.19); NMR δ 2.19 (s, 3 H, methyl), 4.04 (s, 3 H, methyl), 5.60 (d, 1 H) (Figure 5). Anal. Calcd for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.66; H, 5.96.], **7b** [mp 242–245 °C (from CH_2Cl_2–ether); *m/e* 562 (M^+); UV 317 nm (log ε 4.37); NMR δ 2.19 (s, 6 H, methyl), 4.04 (s, 2 H, 10 position) (Figure 6). Anal. Calcd for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.94; H, 6.01.], and the conformational isomer **7b′** [mp 226–228 °C (from benzene–methanol); UV 317 nm (log ε 4.35); NMR δ 2.19 (s, 6 H, methyl), 4.00 (s, 2 H, 10 position) (Figure 7)].

Reaction with Methylmagnesium Bromide in THF. To 16.5 mmol of methylmagnesium bromide in 30 mL of THF was added a THF solution of **1c** (1.0 g, 3.3 mmol). After 2 h, the reaction mixture was decomposed by methanol, hydrolyzed with aqueous NH_4Cl solution, and extracted with ether. The crude products were chromatographed on silica gel to give three fractions. The first fraction (0.17 g) contained **3s** (0.40 mmol, 12%) and **4s** (0.50 mmol, 15%). The second fraction (0.43 g) consisted of α-(9-anthryl)benzyl methyl ether (**12c**: 0.73 mmol, 22%) [NMR δ 3.30 (s, 3 H)], **6c** (0.18 mmol, 11%), and **7c** (0.18 mmol, 11%). The third fraction (eluted with benzene; 0.26 g) contained 9-tetrahydrofuryl-10-benzylidene-9,10-dihydroanthracene (**11c**: 0.8 mmol, 24%).

By column chromatography on silica gel and fractional recrystallizations of the first fraction were isolated **3s** [mp 158–159 °C (from methanol); UV 388 nm (log ε 3.88), 368 (3.97), 349 (3.89), 333 (3.49), 316 (3.11); NMR δ 1.97 (d, 3 H, J = 7 Hz), 5.79 (q, 1 H, J = 7 Hz). Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.42. Found: C, 93.25; H, 6.42.] and **4s**[13] [mp 120–121 °C (from benzene–methanol); NMR δ 1.52 (d, 3 H, J = 8 Hz), 4.07 (q, 1 H, J = 8 Hz)] in pure states. Fractional recrystallizations of the third fraction gave pure **11c** [mp 145–148 °C (from methanol); *m/e* 338 (M^+); IR 1060 cm^{-1}; UV 318 nm (log ε 4.30); NMR δ 1.62–1.86 (m, 4 H), 3.54–4.20 (m, 4 H). Anal. Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.51; H, 6.50.].

Reaction with Methylmagnesium Bromide in the Presence of *p*-Dinitrobenzene. To 13.7 mmol of methylmagnesium bromide in 30 mL of ether was added a mixture of **1b** (0.5 g, 1.5 mmol) and *p*-dinitrobenzene (0.26 g, 1.5 mmol) in 50 mL of ether. After 10 min the reaction mixture was decomposed by methanol, hydrolyzed with aqueous NH_4Cl solution, and extracted with ether. The crude products were chromatographed on silica gel. The first fraction (0.38 g) contained **3r** (0.78 mmol, 52%) and **4r** (0.48 mmol, 32%). The second fraction consisted of **6b** (0.04 mmol, 5%) and **7b** (0.03 mmol, 4%).

Reaction with Methylmagnesium Bromide in the Presence of $FeCl_3$. To a mixture of 7.4 mmol of methylmagnesium bromide and $FeCl_3$ (0.07 mmol) in 30 mL of THF was added a THF solution of **1d** (0.5 g, 1.5 mmol). After 2 h, the reaction mixture was decomposed by methanol, hydrolyzed with aqueous NH_4Cl solution, and extracted with ether. The crude products were chromatographed on silica gel to give two fractions. The first fraction (0.01 g) was heated with potassium *tert*-butoxide in *tert*-butyl alcohol unde reflux, extracted with ether, and shown by ^1H NMR spectroscopy to contain **8d** (0.05 mmol, 3%). The second fraction (0.39 g) consisted of **6d** (0.39 mmol, 52%) and **7d** (0.26 mmol, 35%).

Reaction with Methyllithium. To 16.5 mmol of methyllithium in 30 mL of ether was added an ether solution of **1c** (1.0 g, 3.3 mmol). After 2 h, the reaction mixture was decomposed by methanol and extracted with ether. The crude products were chromatographed on silica gel to give three fractions. The first fraction (0.25 g) contained **3s** (0.43 mmol, 13%) and **4s** (0.46 mmol, 14%). The second fraction (0.38 g) consisted of **6c** (0.36 mmol, 22%) and **7c** (0.35 mmol, 21%). The third fraction (eluted with benzene; 0.27 g) consisted of 9-α-ethoxyethyl-10-benzylidene-9,10-dihydroanthracene (**15c**: 0.76 mmol, 23%) [mp 144–146 °C (from methanol); *m/e* 340 (M^+); IR 1100 cm^{-1}; UV 317 nm (log ε 4.31); NMR δ 1.05 (m, 6 H), 3.00–3.72 (m, 3 H), 3.93 (m, 1 H). Anal. Calcd for $C_{25}H_{24}O$: C, 88.20; H, 7.10. Found: C, 87.95; H, 7.02.].

Reaction with Silver. In a 100-mL flask maintained under N_2, was placed silver powder (0.75 g, 6.9 mmol). A THF solution of **2b** (0.5 g, 1.4 mmol) was added while a current of N_2 was bubbled through. The bubbling was contained with stirring for 30 min at room temperature. After filtration of silver, the solvent was removed under vacuum and the crude products were treated with methanol. Analysis by NMR indicated that the crude products consisted of **5b**, **6b**, **7b**, and **12b** in a molar ratio of 3:31:25:41.

Thermal Decomposition of Benzoyl Peroxide in the Presence of 1c in THF. In a 100-mL flask maintained under N_2 were placed benzoyl peroxide (0.75 g, 1.7 mmol), **1c** (0.5 g, 1.7 mmol), and 50 mL of THF. This mixture was heated under reflux for 18 h under a slow stream of N_2. After the mixture was cooled to room temperature, triphenylphosphine (0.43 g, 1.65 mmol) was added and the solution was stirred for 1 h. The crude products were treated with methanol and extracted with ether. Column chromatography on silica gel of the crude products gave **12c** (0.10 g, 22%) (elution with 1:1 benzene–light petroleum), 9-benzoylanthracene (0.06 g, 13%), and **11c** (0.14 g, 24%) (elution with benzene).

Registry No. 1a, 77032-88-3; **1b**, 77032-89-4; **1c**, 72948-51-7; **1d**, 77032-90-7; **2b**, 77032-92-9; **2c**, 77032-93-0; **2d**, 77032-94-1; **3a**, 80502-92-7; **3b**, 80502-93-8; **3c**, 80502-94-9; **3d**, 80502-95-0; **3e**, 80502-96-1; **3f**, 80502-97-2; **3g**, 80502-98-3; **3h**, 80502-99-4; **3i**, 80503-00-0; **3j**, 80503-01-1; **3k**, 80503-02-2; **3l**, 80503-03-3; **3m**, 72948-35-7; **3n**, 80514-62-1; **3o**, 67856-20-6; **3p**, 80514-63-2; **3q**, 80503-04-4; **3r**, 80503-05-5; **3s**, 80503-06-6; **3t**, 80503-07-7; **4a**, 80503-08-8; **4b**, 80503-09-9; **4c**, 72948-68-6; **4d**, 80503-10-2; **4e**, 80503-11-3; **4f**, 80503-12-4; **4g**, 77033-37-5; **4h**, 80503-13-5; **4i**, 80503-14-6; **4j**, 80503-15-7; **4k**, 80503-16-8; **4l**, 80503-17-9; **4m**, 80503-18-0; **4n**, 80503-19-1; **4o**, 72948-69-7; **4p**, 80503-20-4; **4q**, 80503-21-5; **4r**, 80503-22-6; **4s**, 77033-38-6; **4t**, 80503-23-7; **5a**, 80503-24-8; **5b**, 80503-25-9; **5c**, 80503-26-0; **5d**, 80503-27-1; **6a**, 80503-28-2; **6b**, 80503-29-3; **6c**, 80503-30-6; **6d**, 80503-31-7; **7a**, 80503-32-8; **mb**, 80503-33-9; **7c**, 80503-34-0; **7d**, 80503-35-1; **8a**, 17407-24-8; **8b**, 1498-79-9; **8c**, 1498-71-1; **8d**, 17407-22-6; **9a**, 63650-30-6; **9b**, 77033-25-1; **9c**, 63650-28-2; **9d**, 63650-32-8; **11c**, 80503-36-2; **12c**, 2026-30-4; **15a**, 80503-37-3; **15b**, 80503-38-4; **15c**, 80503-39-5; **15d**, 80503-40-8; **16** (R = MeO), 77033-14-8; **16** (R = Cl), 80503-41-9; **17** (R = MeO), 80503-42-0; **17** (R = Cl), 77033-18-2; 9-benzoylanthracene, 1564-53-0; 9,9′-dimethylene-9,9′,10,10′-tetrahydro-10,10′-anthracenyl, 80503-43-1; tetrahydrofuran, 109-99-9; t-BuMgBr, 2259-30-5; i-PrMgBr, 920-39-8; EtMgBr, 925-90-6; PhMgBr, 100-58-3; MeMgBr, 75-16-1; MeLi, 917-54-4; EtLi, 811-49-4.

Supplementary Material Available: Table VIII, physical properties of the products (4 pages). Ordering information is given on any current masthead page.