Heterophilic Additions to Carbonyls and Thiocarbonyls. Scope and Stereochemistry

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The heterophilic additions of *Z* and *E* 1-propenyl organometallics to thiobenzophenone (**1**) and phenanthraquinone (**25**) proceed primarily with retention of configuration. These results may be used to rule out predominant reaction via a free 1-propenyl radical but do not distinguish between mechanisms involving a caged radical and direct nucleophilic addition. However, the latter process is provisionally preferred for addition of lithium reagents to **1** and organomagnesium bromides to **25**, since the yields of heterophilic addition products appear to be inversely proportional to the ability of a series of organometallics to transfer an electron. It is suggested that the small amount of isomerization which is observed in the additions of (*Z*)- and (*E*)-1-propenylmagnesium bromides to **1** and **25** is due to different rates of reaction of the isomeric Grignard reagents. Attempts to observe heterophilic addition of organometallics to carbonyl and imine functions substituted by sulfur on carbon reveal only carbophilic products. Furthermore, heterophilic additions are not observed in the reactions of phenyllithium with dimethyl thiobenzamide, of benzhydryl and benzyl organometallics with aromatic thioketones, and of vinyllithium with tetraphenylcyclopentadienone.

Heterophilic additions have been reported for reactions of organometallics with a variety of carbon–heteroatom multiple bonds. Products of thiophilic addition are obtained from aromatic and aliphatic thioketones,[1,5] dithio esters,[2b-6] and trithiocarbonates.[2b-7] In the cases of many thioketones, processes after formation of the initial α-thiaorganometallic are postulated to lead to radicals,[3a-d] episulfides,[8] olefins,[6,8,9] enethiol esters,[3b,c,e,4a-c] and novel double addition products.[3d,e,4c,10] A 2,3-sigmatropic rearrangement of the initial adduct has been suggested to rationalize the ultimate carbon–carbon bond formation by an allylic organometallic with thioadamantanone,[5] and related processes could account for the carbophilic products observed on reaction of pyrrolemagnesium bromide with thiocarbonates.[11] The extent of thiophilic addition has been found to be a function of the thioketone, organometallic, and solvent and some results have been rationalized in HSAB terms.[3d] Recently it has been suggested that addition of vinyl Grignard to thiobenzophenone occurs initially at carbon and is followed by migration to sulfur,[12] although an analogous rearrangement has been definitively ruled out for the thiophilic reaction of thiobenzophenone and phenyllithium.[2b] Additions of Grignard reagents to a dithio ester,[11] a thio ester,[13] a thio amide,[14] and thio acid chlorides,[10,15] and of benzhydrylsodium to thiobenzophenone[16] are reported to give products expected for carbophilic addition, although not all products have been characterized for those cases. It is interesting that alkyl Grignard reagents react with ethyl 2,2-dimethyl thioacetoacetate exclusively at sulfur,[4d] suggesting that thiophilic addition to sulfur can even be preferred over normal addition to a carbonyl.

Addition of an organometallic to the oxygen of a carbonyl group has been reported by at least three groups. However, the fact that ethers are formed only from phenanthraquinone,[17] tetraphenylcyclopentadienone,[18] and quinol acetates[19] or an analogous cation[18] suggests that this reaction path may be limited to carbonyl functions which can provide especially stable radicals or anions on oxophilic addition.

Carbon–nitrogen bond formation between an imine and a formal carbanion can be observed if the imine is conjugated with a carbonyl group[20] or another imine.[21] Azophilic additions to oximes,[22] an oxime tosylate,[23] and azo bonds[24] have been reported.

We wish to report a product study of heterophilic additions to thiocarbonyl and carbonyl groups which provides information about the question of whether such reactions proceed by one- or two-electron processes. We also have somewhat defined the scope of heterophilic additions by failing to find this reaction path for a variety of cases.

Results

Additions of Vinyllithium, 1-Propenyllithium, Vinylmagnesium Bromide, 1-Propenylmagnesium Bromide, and Phenyl-d_5-magnesium Bromide to Thiobenzophenone. Treatment of thiobenzophenone (**1**) with vinyllithium in ether or vinylmagnesium bromide[12] in tetrahydrofuran gives vinyl benzhydryl sulfide (**2**) in 40 and 36% yields, respectively. The reaction of (*Z*)- and (*E*)-1-propenyllithium and -magnesium bromide in ether and tetrahydrofuran, respectively, give the thiophilic products (*Z*)- and (*E*)-1-propenyl benzhydryl sulfides (**3**) in ca. 40% yields. Isomerically pure (*E*)-**3** and ca. 95% pure (*Z*)-**3** were obtained by chromatography of the crude products obtained from the reaction of **1** with (*E*)- and (*Z*)-1-propenyllithium, respectively. The stereochemistry for the isomers of **3** was determined by the characteristic couplings of the propenyl group: J_E = 15.0 and J_Z = 9.4 Hz.

When the reaction of (*Z*)- and (*E*)-1-propenyllithium with **1** was quenched with deuterium oxide, the NMR spectra of the crude product showed the expected vinyl hydrogens and no detectable benzhydryl protons, indicating that the product is **3**-d_1 as expected from the carbanion resulting from thiophilic addition.[2] Other products obtained from the reaction of vinyl- and 1-propenyllithium and the corresponding Grignard reagents with **1** include 24–35% benzophenone, which may arise from oxidation or hydrolysis of **1**, and in the case of Grignard reagents, ca. 10% of benzhydryl mercaptan.

$$(C_6H_5)_2C{=}S + RCH{=}CHM \longrightarrow (C_6H_5)_2CHSCH{=}CHR$$

1 R = H, CH_3; M = Li, MgBr — **2**, R = H; **3**, R = CH_3

The stereochemical results of the reactions of (*Z*)- and (*E*)-1-propenyllithium and (*Z*)- and (*E*)-1-propenylmagnesium bromide with thiobenzophenone, as summarized in Table I, show that these additions occur with a high degree of retention of stereochemistry.[25] However, the results do reveal an apparent isomerization of up to 15% of the product from (*E*)-1-propenylmagnesium bromide.

The (*Z*)- and (*E*)-1-propenyllithiums were found to maintain geometrical integrity under the reaction condi-

Table I
Retention of Stereochemistry of the 1-Propenyl Group in 1-Propenyl Benzhydryl Sulfides (3) Obtained from Reactions of Thiobenzophenone (1) with *cis*- and *trans*-1-Propenyllithium and -magnesium Bromide at 0° in Ether and Tetrahydrofuran

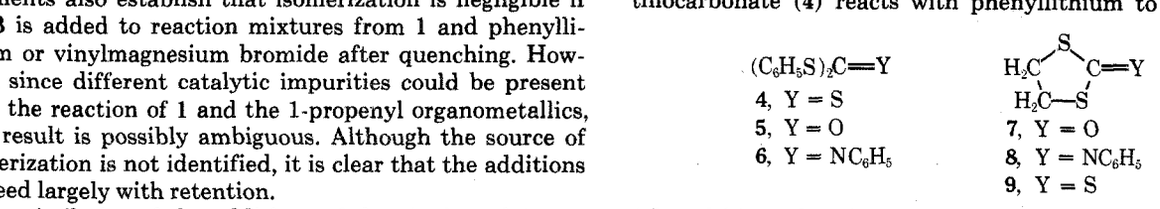
Organometallic	Isomeric purity, % Organometallic[a,b]	Isomeric purity, % Sulfide (3)[a-d]	Retention of stereochemistry, %[e]
(*E*)-CH_3CH=$CHLi$	94.7 ± 1.5	86.9 ± 2.1[f]	92
	(95.8 ± 1.9)[g]	(85.9 ± 1.8)	
	90.4 ± 0.7	84.3 ± 2.7[f]	94
	81.7 ± 0.9	73.8 ± 1.6[f]	90
	95.5 ± 0.5	91.4 ± 0.5	96
		(91.5 ± 0.8)	
	95.5 ± 0.5	91.8 ± 2.5	96
		(90.7 ± 1.1)	
	95.5 ± 0.5	91.9 ± 0.7	96
		(91.6 ± 2.0)	
(*Z*)-CH_3CH=$CHLi$	98.3 ± 0.9	94.6 ± 0.9[f]	96
	(97.0 ± 0.6)[g]		
	97.4 ± 1.0	95.1 ± 1.9	97
		(95.4 ± 1.1)	
(*E*)-CH_3CH=$CHMgBr$	77.4 ± 2.6	65.0 ± 3.5[f,h]	84
	76.9 ± 2.3	70.1 ± 3.4[f]	92
		(66.4 ± 1.7)	
	79.2 ± 4.7	68.0 ± 1.1	86
	(79.8 ± 2.0)	(70.6 ± 2.9)	
	79.2 ± 4.7	68.1 ± 1.0	86
	(79.8 ± 2.0)	(78.0 ± 0.7)	
	79.2 ± 4.7		87
	(79.8 ± 2.0)	(69.9 ± 1.4)	
(*Z*)-CH_3CH=$CHMgBr$	91.7 ± 1.9	92.6 ± 0.7[f]	101
	95.4 ± 3.7	93.4 ± 1.8	98
	(95.1 ± 0.5)	(95.9 ± 1.7)	
	95.4 ± 3.7	92.7 ± 2.5	97
	(95.1 ± 0.5)		

[a] Error limits are three times standard deviations. [b] For determination of the isomeric purities of the organometallics, see Experimental Section. The values in parentheses for Grignard reagents refer to those obtained by quench with trimethylchlorosilane. [c] Retention as determined by NMR integration. In parentheses are the values for the crude reaction products. Otherwise, the values are for the mixture of sulfides 3 isolated by column chromatography. [d] Although a correlation could be often established between the amount of benzhydryl mercaptan, the time before analysis, and the amount of isomerization, this was not a reproducible effect. For example, the reaction which gave 84% retention had less than 1% benzhydryl mercaptan present. [e] Defined as a ratio of percent of major isomer of 3 to percent of major isomer of the organometallic reagent. Error is ±4%. [f] After work-up the reaction mixture was allowed to stand at room temperature overnight before the solvent was removed in vacuo and the NMR spectra measured; otherwise immediate work-up was used. [g] Isomeric purity of excess organolithium reagent immediately before quench. [h] The reaction mixture was washed with 2 *N* sodium hydroxide to remove possible benzhydryl mercaptan immediately after quench.

tions as shown by analysis of an aliquot of the reaction mixture immediately before aqueous quench. Similar analysis of the Grignard reagents was not conclusive. It was established that the equilibrium ratio of (*Z*)-**3**:(*E*)-**3** is ca. 1.5 in favor of the *Z* isomer at 25° in ether and that some isomerization can be catalyzed by benzhydryl mercaptan, an occasional reaction product. Slightly increased isomerization is noted for experiments which were allowed to stand before analysis and in which benzhydryl mercaptan is a product (Table I) but a control experiment suggests that this can acccount for at most ca. 5% isomerization. Control experiments also establish that isomerization is negligible if (*E*)-**3** is added to reaction mixtures from 1 and phenyllithium or vinylmagnesium bromide after quenching. However, since different catalytic impurities could be present from the reaction of 1 and the 1-propenyl organometallics, that result is possibly ambiguous. Although the source of isomerization is not identified, it is clear that the additions proceed largely with retention.

The similarity of the additions of the vinyl- and 1-propenyllithium and -magnesium bromide reagents to **1** is analogous to the previously reported additions of phenyllithium and phenylmagnesium bromide to the same substrate.[2] In the former case, direct thiophilic addition was established by the fact that reaction of thiobenzophenone-d_{10} with phenyllithium gives benzhydryl-d_{10}-phenyl thioether. In the present work an analogous reaction between 1-d_{10} and phenylmagnesium bromide was shown to give the same product with the same labeling. Accordingly greater than 95% of the addition is directly to sulfur for the Grignard reagent and less than 5% rearrangement occurs after initial addition to sulfur occurs under these conditions.

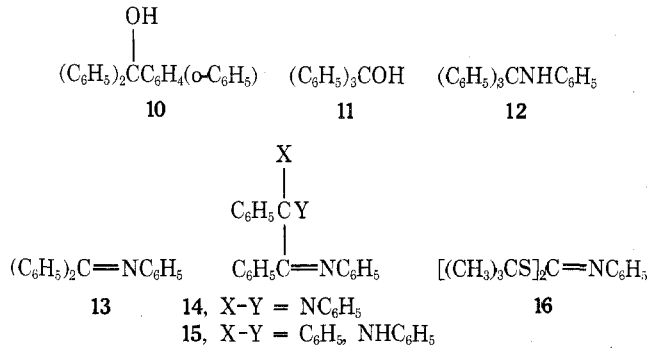
Additions of Phenyllithium to Derivatives of Dithiocarbonates. Our previous study showed that phenyl trithiocarbonate (**4**) reacts with phenyllithium to give tris-



(phenylthiomethane) in 66% yield at −78° although the reaction is complicated by the formation of a carbene from the initial thiophilic adduct at room temperature.[2b,7,26] To test the possibility that sulfur substitution, which would be expected to stabilize the carbanion resulting from hetero-

philic addition,[27] could promote that reaction pathway for carbonyl or imine functions, the products from the reactions of phenyllithium and the dithiocarbonates **5–8** have been investigated.

The reaction of **5** with 2 equiv of phenyllithium affords *o*-biphenyldiphenylcarbinol (**10**), triphenylcarbinol (**11**), thiophenol, and recovered **5** in 5, 51, 66, and 17.5% yields, respectively. The formation of **10** is attributed to 2-biphenyllithium, formed in the preparation of the organometallic from bromobenzene and phenyllithium via benzyne.[28] Hydrolysis of the phenyllithium used in this study, followed by GLC analyses, did show the presence of biphenyl along with bromobenzene, and benzene. When the imine **6** was treated with 3 equiv of phenyllithium, triphenylmethylaniline (**12**), benzophenone anil (**13**), benzophenone, and thiophenol were obtained in 66, 25, 5, and 83% yields, respectively. Presumably benzophenone arises by hydrolysis of **13** during work-up.



10 **11** **12**

13 **14**, X-Y = NC_6H_5 **15**, X-Y = C_6H_5, NHC_6H_5 **16**

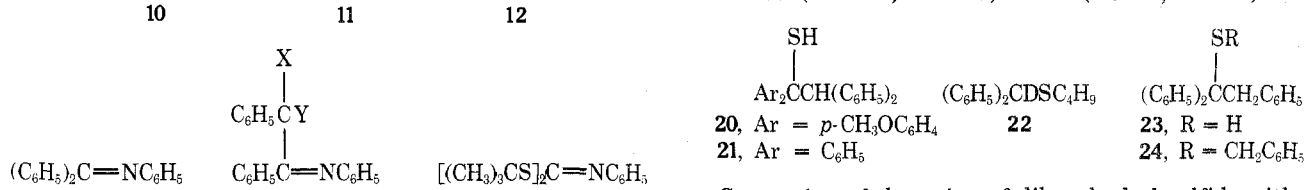
The cyclic dithiocarbonate **7** reacts with 3.3 equiv of phenyllithium to give triphenylcarbinol (**11**) and ethanedithiol in 78 and 83% yields. The reaction of the corresponding imine, however, is more complex. With 4 equiv of phenyllithium, the products from **8** include **12** and ethanedithiol in 11 and 10% yields. However, benzil dianil (**14**) and β-thiophenylethanethiol and its disulfide are also found in 47, 37, and 39% yields.

Although the reactions of **5–7** can be rationalized in a straightforward way by carbophilic addition of phenyllithium, the reaction path for **8**, while clearly not azophilic, is less apparent. To provide a model for heterophilic addition in this system, we have investigated the reaction of **9** with 2.2 equiv of phenyllithium. Treatment of the aqueous basic extract from that reaction with dimethyl sulfate gives 62% methyl dithiobenzoate and 70% thioanisole along with 21% starting material. In an attempt to determine whether the products from the reaction of **8** could arise from phenyl isocyanide the reaction of that compound with 4 equiv of phenyllithium was carried out at −23° in ether. The products are **14** (68%), a material tentatively identified as 2-anilino-*N*,1,2,2-tetraphenyl-1-imine (**15**, 2%), and benzanilide (7%). The formation of **14** finds analogy in the formation of benzilbis(cyclohexyl)imide from the reaction of cyclohexyl isocyanide with phenylmagnesium bromide[29] and may involve air oxidation of the corresponding bisenamine.[30] The reaction of 4 equiv of phenyllithium with di-*tert*-butyl phenylimidodithiocarbonate (**16**) was also examined and found to proceed normally yielding 92.5% of **12**.

These reactions of **5–8** and **18** suggest that sulfur substitution on a carbonyl or imine is not sufficient to promote heterophilic additions.

Addition of Phenyllithium to a Thio Amide. Since sulfur substitution on carbon does not promote heterophilic addition to oxygen and nitrogen, a question of interest is whether substitution on the carbon of a thiocarbonyl can inhibit the thiophilic path. Thio amides are reported to react with Grignard reagents at carbon by reduction,[14,31] and we have found that reaction of *N,N*-dimethylthiobenzamide (**17**) with 2.3 equiv of phenyllithium gives *N,N*-dimethyltriphenylmethylamine (**18**) in 50% yield, as well as 33% triphenylcarbinol and 4% benzophenone. The latter two products presumably arise by hydrolysis on work-up. Apparently, substitution of nitrogen on the thiocarbonyl carbon, like substitution of oxygen,[11,13,15] is sufficient to repress thiophilic addition.

Addition of Benzyl Sodiums and Lithiums to Aromatic Thioketone. In contrast to the thiophilic additions of other organometallics to aryl thioketones,[2,7] benzhydrylsodium is reported to add to such thiocarbonyl groups at carbon.[16] In order to determine the effect of such a structural change and of metal variation on the course of the addition, the reactions of 4,4′-dimethoxythiobenzophenone (**19**) with benzhydrylsodium and benzhydryllithium and of thiobenzophenone with benzhydryllithium have been examined. In each case products of thiophilic addition could not be isolated and the major products are the thiols **20** and **21** resulting from carbophilic additions in yields ranging from 55% (from **19**, M = Na) to 68% (from **1**, M = Li).



20, Ar = *p*-$CH_3OC_6H_4$ **21**, Ar = C_6H_5 **22** **23**, R = H **24**, R = $CH_2C_6H_5$

Generation of the anion of dibenzhydryl sulfide with *n*-butyllithium in tetrahydrofuran followed by deuterium oxide quench gave diphenylmethane-d_1 and benzhydryl *n*-butyl sulfide-d_1 in ca. 20% yield, along with recovered undeuterated starting material. A trace of **21** was detected by NMR. This attempt to form the first intermediate in the possible heterophilic addition shows that if thiophilic addition occurs, intramolecular rearrangement to the carbophilic product would probably occur much more slowly than fragmentation to thioketone.

Since it was observed that thiobenzophenone reacts with benzhydryllithium to give **21**, the effect of benzyl structure of the organometallics was further investigated by the reaction of **1** with benzylmagnesium chloride and with benzyllithium. In the former case the reduction product benzhydryl mercaptan (8%), the carbophilic product benzyldiphenyl mercaptan (**23**, 20.5%), and the double addition product[3d,e,4c,10] benzyldiphenyl benzyl sulfide (**24**) are formed. The products with benzyllithium are benzhydryl mercaptan (12.5%) and **23** (44%) along with benzyl mercaptan.[32] Apparently benzylic structures in the organometallic repress thiophilic addition.

Additions of Vinyl- and Propenyllithium and -magnesium Bromide to Phenanthraquinone. It has been reported by Wege[17b] and Blomberg et al.[17c] that phenanthraquinone (**25**) reacts with vinyl- and phenylmagnesium bromide to give 9-vinyloxy- and 9-phenyloxy-10-hydroxyphenanthrenes. In order to determine the stereochemistry and effect of the metal ion on an oxophilic reaction, we have investigated the reaction of vinyllithium, (*E*)-1-propenyllithium, and (*Z*)- and (*E*)-1-propenylmagnesium bromide with **25**.

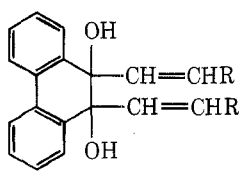
Reaction of **25** with 3.8 equiv of vinyllithium in tetrahydrofuran gives a crude product which has NMR absorptions attributable to the vinyl group of the carbophilic addition product **26** in 73% yield and no detectable absorptions (<5%) of the vinyl group of the possible oxophilic product **27**. Comparison of the physical properties of the product, isolated in 14% yield, with those reported for the trans isomer[17b] confirms the identity of **26**. The carbophilic

Table II
Retention of Stereochemistry of the 1-Propenyl Groups in 9,10-Di(1-Propenyloxy)-9,10-dihydroxy-9,10-dihydrophenanthrene (28) and 9-(1-Propenyloxy)-10-hydroxyphenanthrene (29) from Reactions of (Z)- and (E)-1-Propenylmagnesium Bromide with Phenanthraquinone (25) at 25°

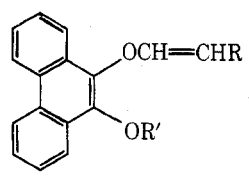
Grignard reagent	Isomeric purity[a] Grignard	28	29	Retention of stereochemistry, %[f] 28	29
(Z)-CH_3CH=$CHMgBr$	88.3 ± 0.8	79.0 ± 0.8 (43)[d]	73.2 ± 1.3 (17)[d]	89	82
	90.3 ± 1.6[b]				
	89.4 ± 2.4[c]				
(E)-CH_3CH=$CHMgBr$	72.2 ± 0.7	75.6 ± 1.2 (43)[d]	89.2 ± 0.4 (29.4)[d]	103	122
	73.5 ± 1.3[b]				
	73.9 ± 0.8[c]				
(E)-CH_3CH=$CHMgBr$[e]	72.2 ± 0.7	75.0 ± 0.9 (27.8)[d]	88.3 ± 1.5 (15.2)[d]	102	118
	73.5 ± 1.3[e]				
	74.7 ± 0.3[c]				

[a] Determined by NMR unless otherwise noted; errors are three times standard deviations. [b] Determined by GLC of trimethylsilyl ethers. [c] Determined after reaction of 25 with the 1-propenylmagnesium bromides from the stereochemistry of the 1-(1-propenyl)-1,1-diphenylcarbinol obtained on reaction with benzophenone. [d] Values in parentheses are percent yields. [e] Inverse addition of reagents; ca. 25% 25 was recovered in this case and ca. 10% 25 was recovered for the cases shown as the first two entries. [f] Defined as ratio of percent major isomer of product to percent major isomer in organometallic. A result greater than 100% reflects an increase in the product having the same geometry as that of the major isomer of the organometallic. Errors are estimated as ±4%.

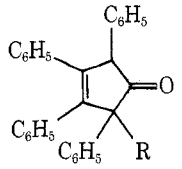
pathway is also observed on reaction of **25** with 1-propenyllithium which is 94% *E* and 6% *Z* isomers, to give a 63% yield of **28**, presumably with trans hydroxyl groups and containing 93% *E* and 7% *Z* propenyl groups. The *EE*-trans isomer of **28** was isolated in 28% yield.



26, R = H
28, R = CH_3



27, R = R′ = H
29, R = CH_3; R′ = H
30, R = CH_3; R′ = $COCH_3$



32, R = $CH{=}CH_2$
33, R = CH_2CH_3

As reported,[17b] reaction of **25** with 3.8 equiv of vinylmagnesium bromide in tetrahydrofuran gave 22% **26** and 43% **27**, along with ca. 1% of 2-methylphenanthro[9,10-*d*][1,3]-dioxole, also noted previously as a product of cyclization of **27**. Reactions of **25** with 4 equiv of (*Z*)- and (*E*)-1-propenylmagnesium bromide gives **28** and **29**. Although **28** was obtained in analytically pure form as a mixture of stereoisomers, **29** had to be converted to a urethane for analytical characterization. The acetate, **30**, was also prepared, and separate samples of **30** containing 86% (*Z*)- and 15% (*E*)-1-propenyl groups and 4% (*Z*)- and 96% (*E*)-1-propenyl groups were subjected to reaction with 4 equiv of 1-propenylmagnesium bromide to establish that the anions of **29** retain geometry under the reaction and isolation conditions.

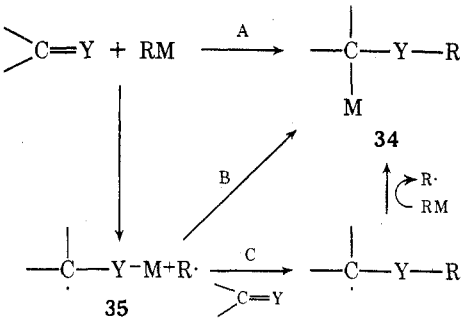
The relationship of the stereochemistries of the 1-propenyl groups of the organometallic reactants and the oxophilic and carbophilic products based on NMR analyses is presented in Table II. Those results show that there is predominant retention of geometry of the organometallic on oxophilic addition to phenanthraquinone. However, in every case there is also significantly more *E* isomer in the product than in the reactant. The fact that essentially the same stereochemistry is observed for **28** and **29** in normal and inverse addition establishes that these comparisons are free from complications due to microscopic diffusion.

Addition of Vinyllithium to Tetraphenylcyclopentadienone (31). It has been reported by Dimroth and Laufenberg that **31** undergoes oxophilic addition with *tert*-butylmagnesium chloride.[18] We have investigated the reaction of **31** with 2.2 equiv of vinyllithium and found that the product is 2-vinyl-2,3,4,5-tetraphenyl-3-cyclopenten-1-one (**32**). The structure of **32** is assigned on the basis of spectroscopic and analytical data. In particular, the nonconjugated carbonyl absorption at 1745 cm^{-1},[33] the ultraviolet absorption at λ_{max} 263 nm,[18,34] and the retention of essentially these values in **33**, the compound produced by hydrogenation of **32**, rule out the alternative structures which have a vinyl group at position 3. While oxophilic addition is not observed, it is not clear whether **32** results from 1,6 addition of vinyllithium to **31** or by rearrangement of the initial carbophilic product.[34]

Discussion

It does not seem to us that, at present, a unifying mechanism which rationalizes all the observations which have been made about heterophilic additions[1-7,10-12,17-19] can be proposed, although a rational choice between three possible pathways can be made. As outlined in Scheme I, the simplest processes would be a direct two-electron addition of the organometallic to the heteroatom to produce carbanion **34**, as shown in path A. Another route could involve initial one-electron transfer to form the caged radical **35**, which

Scheme I



could subsequently collapse to **34** as suggested in path B. A third possibility, outlined as path C, would be initiated by escape of the radical from the cage, followed sequentially by attack of the radical on the heteroatom of another substrate and attack of the resulting radical on the organometallic to produce a chain-carrying radical. Similar mechanisms and intermediate species, often involving bonding to the metal, have been suggested for these and related reactions.[2-4,7,35-38]

Analysis of the stereochemical course of additions of 1-propenyl organometallics as used by Whitesides and Casey[36] has already become a classic test for the intermediacy of free radicals in such reactions. Under the assumptions[36,37] that the rate of achievement of a 1:1 *Z:E* equilibrium ratio for the free propenyl radical is 10^9 sec^{-1} and that the radical would attack the ca. 0.1 *M* substrates at a diffusion controlled rate of 10^{10} l. mol^{-1} sec^{-1} it is predicted that if path C is followed the stereoisomers of **3** and **29** would be formed in ratios which would show a maximum of 67% retention in the products. If the assumption of an equilibrium constant of 1 for the equilibrating 1-propenyl radical is not correct, the calculated maximum retention would be decreased for the products from one isomer and increased, but not greater than 100%, for the products from the other isomer. In either case the predicted extent of isomerization is inconsistent with the results in Tables I and II. Accordingly the heterophilic reactions of **3** and **25** with the 1-propenyl organometallics do not appear to involve a free-radical path to a major extent.

Distinction between paths A and B is more problematical. Indeed, one possibility is that the transition state for addition has characteristics of both one- and two-electron transfers such that the usual dichotomy becomes meaningless.[39] Although quantitative product compositions are not usually known, it is interesting that the yields of thioethers from the reactions of thiobenzophenone with organolithiums are in an order benzhydryl $\simeq$ benzyl < *n*-butyl < phenyl $\simeq$ vinyl, which is the reverse of that for electron transfer from organolithiums to olefins.[40] While this result can be taken as evidence against rate-determining formation of a species analogous to **35** for these cases, it should be noted that with Grignard reagents and other thioketones, the extent of thiophilic addition does not always follow a regular order and a pronounced solvent effect on the order can be observed.[3d,8g,41] The observation of ESR signals[2,3] and the formation of benzhydryl mercaptan from the reaction of **1** and the 1-propenylmagnesium bromides also raises the possibility that radicals may be involved, although CIDNP effects were not observed. The solvent effect and the apparent lack of a pronounced metal ion effect in thiophilic additions also provide difficulties for a general HSAB interpretation.[3d]

In the case of oxophilic addition to phenanthraquinone, the facts that phenyl- and vinylmagnesium bromide add in this mode while methyl- and ethylmagnesium bromide[17b] and vinyllithium do not, in opposition to the ability of these reagents to transfer one electron to benzophenone,[40-42] might also be taken to rule out rate-determining formation of the ketyl ion pair represented by **35.** Interestingly, this order appears to be opposite to the correlation of organometallic structure and oxophilic addition observed with 2,4,5-trimethyl-2-acetoxycyclohexadien-1-one, a reaction which is believed to involve an initial one-electron transfer.[19b]

Overall, the present inference is that heterophilic additions to thiobenzophenone and phenanthraquinone probably proceed by a two-electron formation of the carbon–heteroatom bond to give the anion **34** directly. While the relative stability of the resulting anions would make this course of addition more general for the thiocarbonyl bond than for a carbonyl or imine bond, anion stability does not appear to be a singularly dominant factor in determining the reaction pathway. Thus the relative stabilities of the anions do not appear to provide a rationale for the failure of benzyl and benzhydryl organometallics to add to the sulfur of aromatic thioketones. An interesting speculation is that carbophillic additions generally proceed via initial *n* complexation with the metal ion[35] and that complexation is more favorable for the anionically stable benzyl organometallics. The preceding results do show an apparent lack of a metal ion effect in thiophilic addition. Clearly, more information is needed for formulation of detailed mechanisms.

Rearrangement after an initial heterophilic addition[5,12] has been ruled out for the addition of phenylmagnesium bromide to thiobenzophenone by the labeling studies (vide supra). The possibility of rearrangement in the reaction of benzhydryllithium with thiobenzophenone[43] is ruled out by the fact that treatment of dibenzhydryl sulfide with *n*-butyllithium followed by deuterium oxide quench gives overwhelmingly benzhydryl-*n*-butyl sulfide-d_1. Clearly fragmentation to thiobenzophenone followed by thiophilic addition of *n*-butyllithium occurs under the reaction conditions. The possibility of direct displacement followed by formation of a carbanion which is subsequently deuterated may be discounted because the starting thioether is recovered undeuterated. Nonetheless, rearrangement of an initial adduct is conceivable for some other cases.

None of the above rationalizations account for the isomerizations observed on addition of 1-propenylmagnesium bromides to **1** and **25.** Although controls show that up to 5% of the isomerizations observed could occur after product formation, the ca. 14% isomerization in heterophilic additions of (*E*)-1-propenylmagnesium bromide to thiobenzophenone and the ca. 20% isomerizations in the additions of (*Z*)- and (*E*)-1-propenylmagnesium bromide to phenanthraquinone are outside that limit. The fact that a ca. 14% isomerization was not observed for reaction of **1** with (*Z*)-1-propenylmagnesium bromide may be due to difficulty of detecting such a change when the *E* isomer makes up only ca. 8% of the Grignard reagent. For the reaction of **1** the degree of isomerization is consistent with a *Z:E* reactivity ratio for the organometallic reagents of 1.7 ± 0.3. A *E:Z* reactivity ratio of 2.9 ± 0.5[44] would similarly rationalize the isomerization observed on addition to **25.** The possibility that isomerization represents reaction of a free radical which escapes from the cage is discounted because that mechanism does not explain the greater than 100% retention enrichment of *E* isomer observed in the reaction of **25** with 1-propenylmagnesium bromides.

The reaction of **9** with phenyllithium to give phenylthiolate and dithiobenzoate further illustrates the point that in some cases secondary reactions may obscure the initial thiophilic addition.[2-5] The precedented[2b,26,45,46] mechanistic rationale involves initial thiophilic addition followed by formation of a carbene which could add phenyllithium and undergo fragmentation to lithium dithiobenzoate and ethylene. Another case in which reactions subsequent to heterophilic addition determine the structure of the product is the formation of novel double addition compound **24** from thiobenzophenone and benzylmagnesium bromide. Presumably this arises via radical formation after initial addition, as postulated by Dagonneau.[3b,47]

Experimental Section

General. Melting points were determined on a Buchi or Nalge melting point apparatus and are uncorrected; boiling points are

uncorrected. The proton chemical shifts are reported in δ (parts per million) relative to Me_4Si as internal standard. The ir spectra were measured as a Nujol mull or a KBr pellet, and the frequencies were calibrated against polystyrene. Mass spectra were obtained on a Varian MAT CH-5 spectrometer. Gas–liquid partition chromatography (GLC) was carried out on a Varian Aerograph A-90-P gas chromatograph with a 15 ft × 0.25 in. 20% XF-1150 on acid-washed Chromosorb P column unless otherwise noted. Microanalyses were performed by Mr. J. Nemeth and associates.

Compounds which are sensitive to air and moisture were handled in a dry bag under a dry nitrogen atmosphere and reactions were carried out under nitrogen. Dry ether obtained from Mallinckrodt Chemical Works was used as received. Tetrahydrofuran (THF) was dried by distillation from sodium napthalide or sodium benzophenone ketyl. The lithium metal (Lithium Corp. of America) contained 1% sodium. The magnesium turnings (Mallinckrodt analytical reagent) contained a maximum of 0.01% of heavy metal (as lead), 0.03% of iron, and 0.15% of manganese as impurities.

Extractive work-up refers to addition of the reaction mixture to excess water followed by extraction with diethyl ether, and washes of aqueous hydrochloric acid and water prior to drying ($MgSO_4$) and evaporation of the solvent. Preparative column chromatographies were carried out in silica gel or alumina.

Diphenyl dithiocarbonate (4),[48] ethylene trithiocarbonate (**9**),[49] ethylene dithiocarbonate (**7**),[50] ethylene phenylimidodithiocarbonate (**8**),[51] methyl dithiobenzoate,[52,53] and benzidianil[30,54] were prepared by literature procedures and shown to have physical and spectral properties as expected.

Diphenyl phenylimidodithiocarbonate (6) was prepared according to the procedure of Harley-Mason:[55] mp 123.5–124.5°; ir (Nujol) 1580 s (C=N), 1475 sh, 1430 sh, 1370 m, 1205 m, 1155 w, 1065 m, 1020 m, 1000 w, 985 s, 910 m, 887 m, 845 w, 765 m, 748 s, 740 m, 703 sh, and 690 cm^{-1} s; NMR (CCl_4) δ 6.6–7.5 (m, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 321 (2.4, M^+), 213 (17.1), 212 (100.0), 109 (54.9), 77 (24.8).

Anal. Calcd for $C_{19}H_{15}NS_2$: C, 70.99; H, 4.70; N, 4.36; S, 19.95. Found: C, 70.85; H, 4.65; N, 4.43; S, 20.08.

Ethylene trithiocarbonate (9) was synthesized according to the procedure of Husemann:[50] mp 35–36° (lit.[50] mp 36.5°); ir, NMR, and mass spectra are consistent with the assigned structure.

Di-*tert*-butyl phenylimidodithiocarbonate (16) was synthesized in a manner analogous to the preparation of **6** from phenyl isocyanide dichloride and *tert*-butyl mercaptan. The crude product was purified by recrystallization from ethanol to give **16** in 65% yield as slightly yellow-brown crystals: mp 62–64.5°; ir (Nujol) 1575 s, 1200 w, 918 s, 880 m, 805 vw, 753 m, and 690 cm^{-1} m; NMR (CCl_4) δ 1.47 (s, 18, *t*-C_4H_9), 6.93 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 281 (3.8, M^+), 192 (15.3), 136 (21.4), 135 (12.2), 77 (12.2), 57 (100.0), 41 (15.0)

Anal. Calcd for $C_{15}H_{23}NS_2$: C, 64.00; H, 8.24; N, 4.98; S, 22.78. Found: C, 64.23; H, 8.22; N, 5.14; S, 22.84.

β-Phenylthioethanethiol (39) and Its Disulfide (40). To a solution of 2.6 g (0.044 mol) of ethylene sulfide and 4.4 g (0.04 mol) of thiophenol in 20 ml of hexane was added 10 drops of triethylamine.[56] After 7 hr of heating at reflux, distillation gave 5.0 g (73%) of **39** as a colorless liquid: bp 113–115° (1.5 mm); ir (neat) 3050 w, 2900 w, 2800 vw, 2550 w (SH), 1580 s, 1475 s, 1430 s, 1420 sh, 1265 m, 1210 m, 1135 w, 1090 m, 1070 w, 1015 m, 740 vs, 700 sh, and 690 cm^{-1} s; NMR (CCl_4) δ 1.18 (t, 1, SH, J = 7.7 Hz), 2.83 (A_2B_2X, 4, $-CH_2CH_2SH$), 7.17 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 170 (32.1, M^+), 123 (34.4), 110 (100.0), 61 (56.4), 45 (51.6).

Oxidation of **39** with bromine provided **40** as a colorless liquid in 75% yield: ir (neat) 3030 w, 2900 w, 1580 s, 1475 m, 1250 m br, 1110 m, 1085 m, 1065 m, 1024 s, 738 vs, 700 w sh, and 688 cm^{-1} vs; NMR (CCl_4) δ 3.93 (A_2B_2, 8, $-CH_2CH_2-$), 7.18 (m, 10, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 338 (1.8, M^+), 141 (16.6), 138 (10.4), 137 (100.0), 135 (12.9), 110 (11.3), 109 (51.5), 77 (15.6), 65 (15.7), 59 (11.5), 45 (16.5), 39 (10.1).

Anal. Calcd for $C_{16}H_{18}S_4$: C, 56.76; H, 5.36; S, 37.88. Found: C, 56.61; H, 5.31; S, 37.77.

Phenyllithium was prepared in ethereal solutions by the reaction of lithium metal with bromobenzene[57] or by metal–halogen exchange between *n*-butyllithium and bromobenzene.[58] Phenyllithium prepared by the first method was used for the reactions with **4** and **6** and its concentration was determined by hydrolysis. Phenyllithium prepared by the second method was used for other reactions and its concentration was determined by titration with *sec*-butyl alcohol with 1,10-phenanthroline as an indicator.[59]

Vinyllithium was prepared in 93% yield from tetravinyltin (Alfa Inorganics) and *n*-butyllithium in hexane.[60] The concentration was determined by the *sec*-butyl alcohol method.[59]

Vinylmagnesium bromide was prepared by the method of Normant[61] from magnesium and vinyl bromide in THF.

(*Z*)- and (*E*)-1-Propenyllithium were prepared from ca. 97–98% isomerically pure (*Z*)- and (*E*)-1-bromo-1-propene (Chemical Samples Co.) and lithium wire at 0°.[36] The concentrations were determined by titration with *sec*-butyl alcohol.[59]

The NMR spectra of the 1-propenyllithiums were generally in good agreement with those reported[62] except that the coupling constant between the methyl protons and the geminal olefinic proton of (*E*)-1-propenyllithium was ca. 1 Hz. The NMR spectra showed no peaks which might be ascribed to the presence of unreacted 1-bromo-1-propenes. Hydrolysis of (*E*)-1-propenyllithium gave a solution which had <1% bromopropenes.[36] The isomeric purities of the latter were chemically determined by quenching three 0.5-ml aliquots of the organolithium solution with 0.5 ml of 1,2-dibromoethane, followed by GLC analysis of the resulting mixtures for isomeric 1-bromo-1-propenes.[36] The 1-propenyllithiums were shown to be geometrically stable in solution at room temperature for several days.

(*Z*)- and (*E*)-1-Propenylmagnesium bromides were prepared in THF from the isomeric 1-bromo-1-propenes and magnesium in a manner similar to that for vinylmagnesium bromide.[61] The concentration was determined by the back-titration method.[63]

The isomeric purities of 1-propenylmagnesium bromides were determined by NMR integration of the olefinic protons[64] and, in some instances, also by quench of aliquots with trimethylchlorosilane.[65] The isomer ratios obtained by GLC analysis of the (*Z*)- and (*E*)-1-propenyltrimethylsilane were in good agreement with those obtained from the NMR spectra. Unreacted 1-bromo-1-propenes were not detected in the GLC analysis of the 1-propenyltrimethylsilanes and are estimated as less than 1%.

Reaction of Thiobenzophenone (1) with Vinyllithium. To 7 ml (5.2 mmol) of 0.74 *M* vinyllithium in ether was added at room temperature 0.58 g (2.9 mmol) of **1** in 35 ml of ether over an 18-min period. After 1 hr, extractive work-up provided 649 mg of an oil, which was purified by chromatography to give 264 mg (40%) of vinyl benzhydryl sulfide (**2**) obtained as an oil: ir (neat) 3077 sh, 3038 w, 1510 sh, 1584 s, 1490 s, 1449 s, 1381 w, 1339 vw, 1321 vw, 1280 w br, 1079 m, 1032 m, 956 m, 870 w br, 777 w, 747 s, 720 w, and 694 cm^{-1} s; NMR (CCl_4) δ 7.22 (m, 10, C_6H_5), 6.4–4.85 (ABX, 3, $-CH{=}CH_2$), 5.30 (s, 1, Ph_2CH-); mass spectrum (70 eV) *m/e* (rel intensity) 226 (2.2, M^+), 182 (10.6), 168 (16.4), 167 (100.0), 166 (12.1), 165 (29.7), 152 (16.3), 105 (27.5), 77 (17.8).

Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.17. Found: C, 79.79; H, 6.24; S, 14.08.

Reaction of 1 with Vinylmagnesium Bromide. To 5.4 ml (7.4 mmol) of 1.37 *M* vinylmagnesium bromide in THF was added at 0° 727 mg (3.7 mmol) of **1** in 30 ml of THF over a 10-min period. After 2 hr at 0°, the dark brown reaction mixture was quenched with saturated aqueous ammonium chloride, filtered, and worked up extractively to give 840 mg of an oil which afforded 297 mg (36%) of **2** on chromatography.

Reaction of 1 with 1-Propenyl Organometallics. (*E*)-1-Propenyllithium. To 7.4 ml (6.2 mmol) of 0.84 *M* (*E*)-1-propenyllithium (isomeric purity 94.7 ± 1.5%) in ether was added 0.62 g (3.1 mmol) of **1** in 30 ml of ether at 0° over a 15-min period. After 1 hr of stirring, 1.5 ml of the reaction mixture was quenched with 0.5 ml of 1,2-dibromoethane. GLC analysis showed that the excess lithium reagent was 95.8 ± 1.9% *E* isomer. The remainder of the reaction mixture was quenched with 25 ml of water and after being allowed to stand overnight and worked up extractively gave 741 mg of a green-yellow oil. The NMR spectrum of this material showed it to contain (*Z*)-**3** and (*E*)-**3** in a ratio of 14.1:85.9 (±1.8%). Chromatography of a portion of this material gave 256 mg (45% overall yield for purification of all material) of **3** as an oil. The isomer ratio was found to be 13.1% (*Z*)-**3** and 86.9% (*E*)-**3** (±2.1%) by NMR.

(*Z*)-1-Propenyllithium. To 9.3 ml (6.0 mmol) of 0.65 *M* (*Z*)-1-propenyllithium (isomeric purity 98.3 ± 0.9%) in ether was added 0.60 g (3 mmol) of **1** in 25 ml of ether at 0° over a 15-min period. Work-up as for the *E* case revealed less than 1% isomerization of the lithium reagent and gave after chromatography of a portion of the crude product, 241 mg (overall yield 38%) of **3**. NMR integration of the methyl peaks showed that the isomer ratio was 94.6% (*Z*)-**3** and 5.4% (*E*)-**3** (±2.0%).

(*E*)-1-Propenylmagnesium Bromide. To 5.4 ml (5.13 mmol) of 0.95 *M* (*E*)-1-propenylmagnesium bromide (isomeric purity 79.2

± 4.7% from NMR and 79.8 ± 2.0% from GLC analysis (vide supra) in THF was added at 0° to 502 mg (2.53 mmol) of 1 in 25 ml of THF. After 1 hr, saturated ammonium chloride was added and filtration followed by extractive work-up gave 605 mg of product. The NMR spectrum of this material showed that the isomeric purity of (*E*)-3 was 70.6 ± 2.9%. Benzhydryl mercaptan was also detected by NMR in ca. 14% yield. Chromatography of 448 mg of this oil afforded 261 mg (overall yield 58%) of 3 as an oil which was 28.1% (*Z*)-3 and 71.9% (*E*)-3 (±2.8).

(*Z*)-1-Propenylmagnesium Bromide. To 5.7 ml (5.4 mmol) of 0.95 *M* (*Z*)-1-propenylmagnesium bromide (isomeric purity 95.4 ± 3.7% from NMR and 95.1 ± 0.5 from GLC) was added at 0° to 540 mg (2.7 mmol) of 1 in 26 ml of THF over a 13-min period. The same work-up as for the *E* case provided 184 mg (overall yield 29%) of 3 after chromatography. The NMR analyses showed that this contained 92.7% (*Z*)-3 and 7.3% (*E*)-3 (±2.5%). The NMR spectrum of the crude product showed presence of benzhydryl mercaptan in 14% yield.

Characterization of the Isomeric 1-Propenyl Benzhydryl Sulfides (3). (*E*)-1-Propenyl Benzhydryl Sulfide [(*E*)-3]. To 20 ml (9.2 mmol) of 0.46 *M* (*E*)-1-propenyllithium (88% isomeric purity) was added at 0° 0.96 g (4.9 mmol) of 1 in 35 ml of ether over a 16-min period. Extractive work-up after 1 hr provided 1.153 g of a dark green oil. Chromatography of 1.054 g of this material gave 439 mg (overall yield 41%) of (*E*)-3: ir (neat) 3058 w, 3021 m, 2890 w, 2849 vw, 1603 m, 1587 vw sh, 1493 s, 1449 s, 1359 vw, 1326 vw br, 1295 vw, 1244 w, 1076 m, 1031 m, 937 s, 745 s, and 696 cm^{-1} s; NMR (CCl_4) δ 1.65 (m, 3, CH_3), 5.18 (s, 1, Ph_2CH–), 5.68 (nonfirst-order ABX_3, 2, –CH=CH–) (irradiation at δ 1.65 ppm led to collapse of this signal and appearance of the olefinic protons as an AB pattern with J = 15 Hz consistent with the trans assignment),[37e,66] 7.23 (m, 10, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 240 (8.3), 168 (17.3), 167 (100.0), 165 (26.4), 152 (14.0).

Anal. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71; S, 13.34. Found: C, 79.78; H, 6.68; S, 13.11.

Pure (*E*)-3 was stable at room temperature for at least 3 days but after a week, the NMR spectrum showed small peaks due to the *Z* isomer.

(*Z*)-1-Propenyl Benzhydryl Sulfide [(*Z*)-3]. To 12 ml (7.4 mmol) of 0.62 *M* (*Z*)-1-propenyllithium (94% isomeric purity) was added 0.73 g (3.7 mmol) of 1 in 30 ml of ether at 0° over a 14-min period. After 1 hr work-up similar to that for (*E*)-3 afforded 0.858 g of an oil which contained (*E*)-3:(*Z*)-3 in a 10:90 ratio according to the NMR spectrum. Chromatography of a portion of this oil, 0.779 g, provided 254 mg (overall yield 32%) of 3: ir (neat) 3090 vw, 3075 vw, 3050 w, 3020 m, 2900 w, 2830 vw, 1600 m, 1500 s, 1450 s, 1380 w, 1330 m, 1165 m br, 1075 m, 1030 m, 1000 vw, 930 m br, 750 s, and 700 cm^{-1} s; NMR (CCl_4) δ 1.70 (X_3 part of ABX_3, 3, CH_3, J = 1.2 and 6.4 Hz), 5.21 (s, 1, Ph_2CH–), 5.62 (AB part of ABX_3, 2, –CH=CH–, J = 1.2, 6.4, and 9.4 Hz), irradiation of the methyl signal resulted in collapse of the multiplet into a simple AB pattern with J_{AB} = 9.4 Hz,[37e,66] 7.23 (m, 10, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 240 (4.2), 168 (16.2), 167 (100.0), 166 (10.4), 165 (26.9), 152 (14.5), 58 (7.0), 43 (12.2), 32 (7.9), 31 (9.3).

Anal. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71, S, 13.34. Found: C, 79.84; H, 6.66; 13.19.

Equilibration of 1-Propenyl Benzhydryl Sulfides in Ether. A mixture of 109 mg of 3 containing ca. 30% *Z* and 70% *E* isomers and 10 mg of thiophenol in 5 ml of ether was gently refluxed under nitrogen. The change in the isomer ratio was periodically determined by NMR spectroscopy. After 10, 29, and 50 hr of heating, the amount of (*Z*)-3 was found to be 49 ± 2.7, 60.3 ± 3.9, and 61.4 ± 4.5%, respectively. In another experiment, a mixture of 106 mg of 3 consisting of ca. 94% *Z* and ca. 6% *E* isomer and 16 mg of thiophenol in 3 ml of ether was stirred at room temperature under nitrogen. After 24 and 48 hr of stirring, the amount of (*Z*)-3 decreased to 62.3 ± 1.3 and 61.6 ± 1.1%, respectively. The equilibrium constant for (*Z*)-3:(*E*)-3 is ca. 1.5 at 25–35° in ether in favor of the *Z* isomer.

Stability of 1-Propenyl Benzhydryl Sulfides toward Work-up Procedures. Typical control experiments involved addition of (*E*)-3 of known isomeric purity to a quenched reaction mixture of thiobenzophenone and phenyllithium or vinylmagnesium bromide, followed by reisolation of 3 and determination of its isomeric purity by NMR. It was shown that (*E*)-3 was stable to that procedure and aqueous base but that 7–8% isomerization can occur in tetrahydrofuran in the presence of 1 equiv of benzhydryl mercaptan on standing 12 hr at room temperature. Accordingly, it is estimated that up to 5% isomerization could occur by a similar process in the work-up of some reactions reported in Table I. It was also shown, however, that extraction with aqueous base, immediately after quenching, did not eliminate the isomerization observed with (*E*)-1-propenylmagnesium bromide (Table I).

Reaction of thiobenzophenone-d_{10} and phenylmagnesium bromide was carried out as previously reported[2b] to give benzhydryl phenyl-d_{10} sulfide. The mass spectrum of the product shows a ratio of *m/e* 172:177 ($C_{13}H_6D_5$:$C_{13}HD_{10}$) of 2.4:100 and a ratio of *m/e* 109:114 (C_6H_5S:C_6D_5S) of 100:5.6. This fragmentation is consistent with a composition of at least 95% $C_6H_5SCH(C_6D_5)_2$.

Reaction of 5 with Phenyllithium. A solution of 0.858 g (3.5 mmol) of 5 in 50 ml of ether was added dropwise to 6.5 ml (7 mmol) of 1.08 *M* phenyllithium over a 10-min period. After 1 hr, the reaction mixture was quenched with water and worked up extractively to give 0.508 g (66%) of thiophenol and 1.317 g of pale yellow crystals. Chromatography and recrystallization (pentane) afforded (1) 0.151 g (17.5%) of 5, mp 41–43°, mmp 41.5–43°, ir identical with that of authentic 5; (2) 57.5 mg (4.9%) of white crystals identified as 2-biphenyldiphenylcarbinol 10, mp 89.5–90.5° (lit.[67] mp 86–88°), ir, NMR, analysis, and mass spectrum were consistent with the assigned structure; (3) 0.468 g (51.5%) of triphenylcarbinol (11), mp 161.5–163° (mmp 162–164.5°). The ir, NMR, and mass spectra were identical with those of an authentic sample (Aldrich Chemical Co.).

Reaction of 6 with Phenyllithium. A solution of 0.800 g (2.5 mmol) of 6 in 50 ml of ether was added to 5.5 ml (7.5 mmol) of 1.36 *M* phenyllithium in ether over a 3-min period. After 1 hr the reaction mixture was quenched with water and worked up extractively to give 0.456 g (83%) of thiophenol and 1.181 g of an oil. Chromatography provided (1) 0.555 g (66%) of triphenylmethylaniline (12) obtained as a partly crystalline, light-brown glass which on two recrystallizations (hexane) afforded 203 mg of 12, mp 144–145° (lit.[68] mp 148–149°), ir, NMR, mass spectrum, and analysis were consistent with the assigned structure; (2) 161 mg (25%) of a yellow oil which slowly crystallized and was identified as benzophenone anil 13 from comparison of its ir and NMR spectra with those of authentic material (mp 113–114°),[69] mp (from hexane) 111–113° (mmp 112–114°); (3) 24 mg (5.3%) of impure benzophenone.

Reaction of 7 with Phenyllithium. To 26 ml (13.1 mmol) of 0.507 *M* phenyllithium in ether was added at −78° 0.483 g (4 mmol) of 7 in 30 ml of ether over a 20-min period, whereupon a white precipitate appeared. After 1 hr of stirring, followed by warming to room temperature, the reaction was quenched to give 0.996 g of faintly yellow crystals, mp 147–153°. Recrystallization from cyclohexane afforded 0.814 g (78%) of 11 as white crystals: mp 160–162° (mmp 160–162°), ir and NMR spectra were identical with those of an authentic sample.

The aqueous layer provided 0.311 g (83%) of 1,2-ethanedithiol.

Reaction of 8 with Phenyllithium. To 25 ml (10 mmol) of 0.40 *M* phenyllithium was added 0.487 g (2.5 mmol) of 8 in 25 ml of ether at −23° over a 12-min period. After being allowed to stir for 1 hr at −23° and for 3 hr at room temperature, the reaction mixture was quenched with water and extractive work-up provided 869 mg of an oil.

Column chromatography provided (1) 193 mg of a yellow, viscous mixture of the disulfide of β-thiophenylethanethiol (24% overall yield) and triphenylmethyl aniline 12 (11% overall yield), identified by TLC, ir, and NMR spectra. This mixture was purified by crystallization from ether–hexane to give (1) 28 mg of 12 as brown crystals, mp 145.5–147.5° (mmp 146–149°), ir and NMR spectra as previously assigned (vide supra); (2) 82 mg of yellow, viscous 40 (15% overall yield as determined by NMR integration with methylene dichloride as standard) contaminated with small amounts of 12 and benzildianil 14; (3) 289 mg of an oily solid, which was mainly 14 (47% overall yield as determined by NMR integration with methylene dichloride as standard) according to TLC, ir, and NMR spectra. Recrystallization from ethanol gave 137 mg of 14 as yellow crystals, mp 138–142° (mmp 141–143°), ir and NMR spectra were identical with those of authentic material.

From the aqueous layer, a liquid mixture of 39 and 40 (by NMR) was obtained in yields of 37 and 10%, respectively.

Reaction of 9 with Phenyllithium. To 9 ml (6.6 mmol) of 0.73 *M* phenyllithium in ether was added, at −78°, 0.412 g (3 mmol) of 9 in 30 ml of ether over a 30-min period. After an additional 30 min, the reaction mixture was quenched with methanol and allowed to warm to room temperature. Extractive work-up with ether after the addition of water provided a mixture of biphenyl and 9 according to the ir, NMR, and GLC (10 ft × 0.25 in. SE-30 on firebrick 188°) analyses. Integration of the NMR spectrum with 1,2-dibromoethane as reference indicated recovery of 0.63 mmol (21%) of 9.

The brown aqueous layer from extraction was collected in an ice bath, and to it was added 0.57 ml (6 mmol) of dimethyl sulfate. After being heated to reflux for 30 min, a red oil separated and the aqueous layer became colorless. Extractive work-up gave 0.573 g of a red oil, which was a mixture of thioanisole (70% overall yield) and methyl dithiobenzoate (62% overall yield) according to the NMR spectrum. The identities were confirmed by preparative GLC (10 ft × 0.25 in. SE-30 on firebrick, 187°) and comparisons of ir, NMR, and mass spectra with those of authentic materials.

Reaction of Phenyl Isocyanide with Phenyllithium. To 35 ml (13.2 mmol) of 0.38 *M* phenyllithium was added at −23° 454 mg (4.4 mmol) of phenyl isocyanide[70] in 10 ml of ether over a 10-min period. A dark brown color developed immediately. Work-up was similar to that (vide supra) for the reaction of 8 with phenyllithium.

Chromatography provided (1) 14 mg of biphenyl; (2) 12 mg (1.2%) of yellow, weakly fluorescent material, mp 206–211°, with ir and mass spectra identical with those of material assigned as 2-anilino-*N*,1,2,2-tetraphenylethan-1-imine (**15**, vide infra); (3) 538 mg (crude yield 68%) of impure benzildianil according to its ir and NMR spectra, mp 113–121° [two recrystallizations gave material with mp 139–141, mmp 140–142°. The ethanol-insoluble portion of the residue obtained by evaporation of the mother liquors was 16 mg (1.7%) of a pale yellow solid tentatively identified as **15**: mp 213–216°; ir (Nujol) 3310 m, 1640 s, 1600 vs, 1500 s, 1480 s, 1420 m, 1375 m, 1320 s, 1280 vw, 1255 m br, 1170 m br, 1085 m, 1070 m, 1045 m, 1030 m, 1000 w, 940 w, 910 w br, 898 vw, 873 w, 846 w, 810 w br, 773 m, 750 s, 736 m, 708 s, and 692 cm^{-1} s; mass spectrum (70 eV) *m/e* (rel intensity) 438 (1.2, M^+), 345 (11.3), 259 (23.5), 258 (100.0), 257 (10.7), 181 (13.7), 180 (85.0), 77 (56.2). Further concentration of the mother liquor gave 128 mg of yellow crystals, mp 136–139°, which showed the same ir spectrum as **14**.]; (4) 61 mg (7%) of benzanilide, mp 159–161° (mmp 158–160°). The ir and NMR spectra of this compound were identical with those of authentic material (Aldrich Chemical Co.).

Reaction of 16 with Phenyllithium. To 26 ml (8 mmol) of 0.31 *M* phenyllithium in ether was added 563 mg (2 mmol) of **16** in 25 ml of ether over a 12-min period. The reaction mixture was heated at reflux for 3 hr followed by extractive work-up which afforded 732 mg of a yellow oily solid. Chromatography gave 622 mg (92.5%) of solid, which was identified as *N*-triphenylmethylaniline (**12**) containing a trace impurity by its NMR spectrum; recrystallization (hexane) gave 434 mg of light brown crystals, mp 149–151° (mmp 149–151°). The ir NMR, and mass spectra of this material were identical with those of authentic **12**.

Reaction of 17 with Phenyllithium. To 19 ml of 0.35 *M* phenyllithium in ether was added 491 mg (3 mmol) of **17** in 20 ml of ether over a 16-min period. After 2 hr at room temperature, extractive work-up provided 848 mg of an oil. Chromatography provided (1) 428 mg (50%) of *N*,*N*-dimethyltriphenylmethylamine (**18**), mp 90–92° [The ir and NMR spectra of this material were identical with those of an authentic sample prepared by the method of Hemilian and Silverstein.[71] Rechromatography on alumina with hexane as an eluent raised the melting point to 93–94.5° (mmp 93.5–94.5°).]; (2) 279 mg of a solid which was a mixture of benzophenone and triphenylcarbinol according to its ir and NMR spectra. The yields of these materials would be 4 and 33%, respectively. Recrystallization from cyclohexane afforded 99 mg of triphenylcarbinol, mp 156–158° (mmp 157–159°)

Reaction of Benzhydrylsodium with 19. Reaction of benzhydrylsodium[72] with **19** (Aldrich Chemical Co., mp 115–117.5°) in ether in a manner analogous to the procedure of Bergman and Wagenberg[72] gave 0.469 g (55%) of 2,2-diphenyl-1,1-di(4-methoxyphenyl)ethanethiol (**20**) as white needles: mp 149–152° (lit.[16] 155°); ir, NMR, spectrum, and analysis are consistent with the established structure.

Reaction of Benhydryllithium with 19. To 6 ml of 0.60 *M* benzhydryllithium[73] in THF was added 0.517 g (2 mmol) of **19** in 50 ml of ether over a 25 min period. After 1 hr, extractive work-up gave 1.515 g of an oil. Chromatography provided (1) 178 mg of 1,1,2,2-tetraphenylethane; (2) 711 mg of a yellow solid [Recrystallization from ethanol afforded 511 mg (60%) of pure **20**: mp 150–153° (mmp 149–152°); ir, NMR, and mass spectra were identical with authentic material. A second crop, 51 mg (6%), of impure **20**, mp 145–150° was also obtained.]; (3) 144 mg of white powder which could be recrystallized from ethanol to give 67 mg (8%) of white needles, identified as 2,2-diphenyl-1,1-di(4-methoxyphenyl)ethanol, mp 173–175° (lit.[16] 183°). The ir, NMR, mass spectrum, and analysis were consistent with the assigned structure.

Reaction of Benzhydryllithium with 1. To 10 ml (5.7 mmol) of 0.57 M benzhydryllithium[73] in THF was added 0.681 g (3.43 mmol) of 1 in 30 ml of ether over a 20-min period. After 1 hr of stirring at room temperature, extractive work-up provided 2.022 g of oily crystals which was shown by its NMR spectrum to be a mixture of diphenylmethane, 1,1,2,2-tetraphenylethanethiol (**21**), and 1,1,2,2-tetraphenylethane. Integration of the NMR spectrum with toluene as reference indicated that the yield of **21** was 84%. Recrystallization from 2-propanol gave 1.273 g of pale yellow needles, mp 155–165°. Chromatography of a 504-mg portion gave 318 mg (64% overall yield) of **21**, mp 165–167.5° (lit.[16] mp 167–168°). Recrystallization from 2-propanol raised the melting point to 166–169°; the ir, NMR, mass spectrum, and analysis were consistent with the assigned structure and different from those of independently prepared dibenzhydryl sulfide.

Dibenzhydryl sulfide was prepared in 35% yield from benzhydryl mercaptan and benzhydryl chloride, mp 63–64.5 (lit.[74] mp 65–66.5°). The ir, NMR, mass spectrum, and analysis were consistent with the assigned structure.

Reaction of Dibenzhydryl Sulfide with *n*-Butyllithium. To 0.584 g (1.6 mmol) of dibenzhydryl sulfide in 15 ml of THF was added at −23° (Dry Ice–carbon tetrachloride) 1 ml (1.6 mmol) of 1.6 M *n*-butyllithium, whereupon a brown color developed immediately. After 2 hr of stirring at −23°, the reaction mixture was quenched with 4 ml of deuterium oxide. Extractive work-up gave 634 mg of an oil. A 496-mg portion of this material was separated by chromatography into three fractions: (1) 66 mg of a colorless oil identified as diphenylmethane-d_1 (ca. 83% deuterium from NMR integration); (2) 90.7 mg (22% overall yield) of an oil identified as benzhydryl *n*-butyl sulfide-d_1 (**22**, ca. 100% deuterium) from the NMR spectrum, which was identical with that of benzhydryl *n*-butyl sulfide except that the former did not show the benzhydryl methine peak; (3) 315 mg (54% overall yield) of an oil identified as the starting sulfide without any significant deuterium incorporation according to its NMR spectrum.

Reaction of Benzylmagnesium Chloride with 1. To 4 ml (4.2 mmol) of 1.06 *M* benzylmagnesium chloride[63] was added at room temperature over a 16-min period 0.44 g (2.2 mmol) of 1 in 25 ml of ether. The reaction mixture was allowed to stir for 3 hr and worked up extractively to give 722 mg of a green oil. Chromatography provided the following.

(1) A blue oil (51 mg) was obtained, the main component of which was benzhydryl mercaptan (overall yield 8% as determined by integration of the NMR spectrum with 1,1,2,2-tetraphenylethane as a reference).

(2) A solid (189 mg) was obtained which recrystallized from 2-propanol to give 131 mg (20.5%) of benzyldiphenylmethyl mercaptan **23** as pale yellow crystals: mp 105–106.5°; ir (Nujol) 2551 vw (SH), 1600 w, 1585 sh, 1575 w, 1585 s, 1230 w, 1180 w, 1080 w, 1030 m, 1000 vw, 980 w, 955 vw, 910 w, 847 w, 785 w, 755 s, 748 sh, 703 vs, and 697 cm^{-1} s; NMR (CCl_4) δ 2.17 (s, 1, SH, exchanges with deuterium oxide in the presence of pyridine), 3.67 (s, 2, $PhCH_2$–), 6.4–7.4 (m, 15, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 257 (13.2), 256 (20.2), 200 (16.3), 199 (100.0), 198 (12.7), 180 (35.3), 178 (42.1), 167 (21.4), 165 (33.3), 121 (59.2), 91 (15.0), 77 (14.4), 45 (16.1), 28 (22.1).

Anal. Calcd for $C_{20}H_{18}S$: C, 82.71; H, 6.25; S, 11.04. Found: C, 82.62; H, 6.20; S, 11.10.

(3) Benzyldiphenyl(benzylthio)methane [**24**, 177 mg (21%)] was obtained. Recrystallization from hexane afforded 131 mg of slightly yellow crystals of **24**, mp 121.5–123.5° (lit.[75] mp 126–127°). The ir, NMR, and mass spectrum are consistent with the assigned structure.

(4) A brown oil (205 mg) was obtained which by ir and TLC analysis contained benzophenone as the major component.

Reaction of Benzyllithium with 1. To 12.5 ml (6.6 mmol) of 0.53 *M* benzyllithium[76] cooled in an ice bath was added 0.587 g (3 mmol) of 1 in 25 ml of ether over a 15-min period. After 2 hr of stirring, extractive work-up provided 1.071 g of an oil, which on chromatography gave (1) 55 mg (9%) of benzhydryl mercaptan; (2) 142 mg of a pale yellow, oily solid, which was a mixture of benzhydryl mercaptan (2%) and **23** (10%) according to the NMR spectrum (the yields are based on the NMR integration with dibenzhydryl sulfide used as internal standard); (3) 295 mg (34%) of somewhat impure **23**, mp 97–103°, which was recrystallized from ethanol to give an analytical sample, mp 107–110°. Its ir, NMR, and mass spectrum were identical with those of authentic material (vide supra). The aqueous layer was acidified and extracted with ether to give 12% benzyl mercaptan identical in TLC, ir, and NMR properties with authentic material (Aldrich Chemical Co.).

Reaction of 25 with Vinyllithium. To 18 ml (11.3 mmol) of

0.63 *M* vinyllithium in THF was added 0.626 g (3 mmol) of **25** partially suspended in 30 ml of THF over a 12-min period. After 2 hr of stirring at room temperature, the reaction mixture was gently refluxed for 45 min. Extractive work-up, after an ammonium chloride quench, provided 0.956 g of a green oil. The NMR spectrum (CCl_4) of this material showed no peaks in the regions of 6.5–7.0 and 4.0–4.9 ppm, indicating the absence of 9-hydroxy-10-vinyloxyphenanthrene.[17b] The major component was *trans*-9,10-dihydroxy-9,10-divinyl-9,10-dihydrophenanthrene (*trans*-**26**), which was present in 73% yield by NMR. Two chromatographic purifications afforded 181 mg (23%) of a light yellow solid, which was recrystallized from hexane to give 109 mg (14%) of *trans*-**26**, mp 87–88° (lit.[17b] mp 85–86°). The ir, NMR, mass spectral, and analytical data were consistent with the assigned structure.

Reaction of 25 with Vinylmagnesium Bromide. Reaction according to the procedure of Wege[17b] provided 856 mg of an oily mixture of 9-hydroxy-10-vinyloxyphenathrene (**27**) and *trans*-9,10-dihydroxy-9,10-divinyl-9,10-dihydrophenanthrene (*trans*-**26**) in ca. 56 and 32% yields, respectively, by NMR. Chromatography provided a small amount (0.8%) of 2-methylphenanthro[9,10-*d*][1,3]dioxole according to the previously assigned spectrum,[17b] mixed with **27** followed by 275 mg (39%) of **27**, mp 69–73° (lit.[17b] mp 71–73°). The ir, NMR, mass spectrum, and analysis were consistent with the assigned structure.

Reaction of 25 with (*E*)-1-Propenyllithium. To 12.5 ml (12 mmol) of 0.95 *M* (*E*)-1-propenyllithium (isomeric purity 93.5 ± 0.6%) in ether was added at room temperature 626 mg (3 mmol) of **25** in 35 ml of THF over a 20-min period. After 2 hr of stirring, the reaction mixture was quenched with saturated aqueous ammonium chloride and worked up extractively. Chromatography gave 511 mg (63%) of crude *trans*-9,10-dihydroxy-9,10-di(1-propenyl)-9,10-dihydrophenanthrene (*trans*-**28**) which contained by NMR 93 ± 1% (*E*)-1-propenyl and 7 ± 1% (*Z*)-1-propenyl groups as an oily, yellow-brown solid. The distinction between *Z* and *E* propenyl groups is made on the basis of the observed olefinic coupling constants of J_E = 15 and J_Z = 10 Hz. A portion of this material, 483 mg, was recrystallized from 20% benzene–hexane to give 278 mg of light orange crystals, mp 138–146°. Treatment of this material with decolorizing charcoal in a 25% benzene–hexane solution, followed by recrystallization from the same solvent, gave 137 mg (16%) of (*E,E*)-*trans*-**28**: mp 148–150°; ir (Nujol) 3450 s, 3365 sh, 1675 vw, 1285 vw, 1200 m, 1190 sh, 1170 vw, 1150 vw, 1070 vw, 1050 w, 1010 vw, 1000 vw, 968 s, 950 vw, 938 vw, 920 vw, 893 w, 883 vw, 856 vw, 970 vw, 770 vw, 752 s, 740 s, 740 m, 763 s, and 697 cm^{-1} br w; NMR ($CDCl_3$) δ 1.54 (d of d, 3, CH_3, J = 1.3 and 6.3 Hz), 2.21 (br s, 2, OH), 5.37–6.04 [ABX_3, 4, (*E*)-CH_A=CH_BCH_3, J_{AB} = 15.4, $J_{CH_3\text{-}H_A}$ = 1.3, and $J_{CH_3\text{-}H_B}$ = 6.3 Hz], 7.22–7.72 (m, 8, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 292 (17.8), 244 (18.4), 223 (100.0), 221 (15.4), 205 (12.7), 195 (17.2), 194 (12.1), 181 (15.8), 69 (42.7), 41 (14.2).

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.45; H, 6.92.

Reactions of 25 with Propenylmagnesium Bromides. A solution of **25** (625 mg, 3.0 mmol) in THF (35 ml) was added dropwise over 15 min under N_2 at 25° to 12.75 mmol of the 1-propenylmagnesium bromide in 25 ml of THF. After completion of the addition, the solution was stirred for an additional 2 hr before a 10-ml aliquot of the reaction mixture was withdrawn by syringe and the stereochemistry of the unreacted Grignard determined by GLC and ^1H NMR methods (vide infra).

The remainder of the reaction mixture was quenched with 25 ml of saturated ammonium chloride and worked up extractively to provide an oil that was purified by chromatography to give 9-hydroxy-10-(1-propenyloxy)phenanthrene (**29**) and 9,10-dihydroxy-9,10-di(1-propenyloxy)-9,10 dihydrophenanthrene (**28**).

The NMR spectra of crude **28** and **29** indicated each to be 80–85% pure with 8–10% **25** and 5–10% of other unidentified impurities, a result which was consistent with TLC analyses. The stereochemistries of the propenyl group of **28** and **29** shown in Table II were determined by integration of the methyl signals.

Analysis of Unreacted Grignard. Eight milliliters of the aliquot was added to benzophenone in THF at room temperature over 15 min. The stereochemistry of the product, 1-(1-propenyl)-1,1-diphenylcarbinol,[77] obtained as a pale yellow oil, was determined by NMR integration of the methyl doublets at δ 1.48 and 1.68 ppm for the *Z* and *E* isomers, respectively. The *Z* isomer had J_{AB} of 11 Hz and the *E* isomer showed a value of 15 Hz. Several control experiments established that the addition of propenyl Grignards to benzophenone occurs stereospecifically either in the presence or absence of added magnesium alkoxide.

Product Identification. The enol 9-(1-propenyloxy)-10-hydroxyphenanthrene (**29**) is air sensitive and could not be isolated in analytically pure form. The stereochemistries of the 1-propenyl groups were assigned from the NMR spectrum: (*Z*)-**29**, NMR (CCl_4) δ 1.90 (d of d, 3, CH_3, J_{AX} = 7, J_{BX} = 1.5 Hz), 4.67 (d of q, 1, CH_A, J_{AB} = 6 Hz), 6.0 (s, 1, OH), 6.06 (d of q, CH_B), 7.00–8.58 (m, 8, ArH); (*E*)-**29**, NMR (CCl_4) δ 1.58 (d of d, 3, CH_3, J_{AX} = 7, J_{BX} = 1.5 Hz), 4.00, (d of q, 1, J_{AB} = 12 Hz), 6.0 (s, br, 1, OH), 6.43 (d of q, 1), 6.93–8.50 (m, 8, ArH).

The phenylurethane of (*E*)-**29** was prepared with phenyl isocyanate.[78] Chromatography on silica gel gave a pale yellow solid which could be recrystallized from carbon tetrachloride–hexane and twice from 10% benzene–hexane to give white crystals: mp 155–160°; NMR δ 1.53 (d of d, 3, J_{AX} = 7, J_{BX} = 1.5 Hz), 5.12 (d of q, 1, J_{AB} = 12.0 Hz), 6.52 (d of q, 1), and 7.00–8.58 ppm (m, 13); ir (KBr) 3315 (NH), 1755 (sh), 1725, 1603, 1540, 1447, 1240, 1225, 1165, 1131, 1089, 759, and 740 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 369 (P^+, 0.35), 299 (25.0), 251 (20.2), 250 (100.0), 221 (39.8), 210 (36.0), 181 (13.1), 180 (51.7), 119 (45.7), 91 (11.6).

Anal. Calcd for C, 78.02; H, 5.18; N, 3.79. Found: C, 77.75, H, 5.12; N, 3.90.

An acetate of **29** was also prepared by reaction with pyridine and acetic anhydride. Extractive work-up and chromatography gave the acetate **30** as a pale yellow oil. Numerous attempts to crystallize or obtain an analytical sample were unsuccessful: (*Z*)-**30**, NMR (CCl_4) δ 1.86 (d of d, 3, J_{AX} = 7, J_{BX} = 1.5 Hz), 2.39 (s, 3, CH_3), 4.70 (d of q, 1, J_{AB} = 6 Hz), 6.23 (d of q, 1,), 7.44–8.66 (m, 8, ArH); (*E*)-**30**, NMR (CCl_4) δ 1.47 (d of d, 3, J_{AX} = 7, J_{BX} = 1.5 Hz), 2.28 (s, 3, CH_3), 5.06 (d of q, 1, J_{AB} = 12 Hz), 6.35 (d of q, 1), 7.21–8.55 (m, 8, ArH).

The diol 9,10-di(1-propenyl)-9,10-dihydrophenanthrene (**28**), purified by recrystallization from 10% benzene–hexane, was a mixture of stereoisomers. The NMR of (*E*)-**28** is very similar to that reported for (*E*)-**26** (vide supra). The assignments to (*Z*)-**28** are δ 1.86 (m, 6, CH_3), 2.60 (br s, 2, OH), 5.1–5.8 (AB part of a non-first-order ABX_3, 4, –CH=CHCH_3), 7.33–7.83 (m, 8, ArH).

Control Experiments. In order to examine the stereochemical stability of the anion of **29** to the reaction conditions, and the product **29** to work-up, the anion was generated in the presence of excess Grignard by reaction of **30** with 4 equiv of (*E*)-1-propenylmagnesium bromide. Isolation of **29** showed retention of the initial geometry of **30** for both the *Z* and *E* isomer.

Reaction of Tetraphenylcyclopentadienone (31) with Vinyllithium. To 60 ml (4.4 mmol) of 0.74 *M* vinyllithium in ether was added over a 17-min period 0.771 g (2 mmol) of **31** partially suspended in 50 ml of ether. After 1 hr of stirring at room temperature, extractive work-up provided 0.859 g of a yellow-brown, oily solid. The NMR spectrum of this material showed an absence of peaks between 4.2 and 4.6 ppm expected for *O*-vinyl groups. This material was triturated with a mixture of hexane and ether to give 0.354 g (43%) of crude 2-vinyl-2,3,4,5-tetraphenylcyclopent-3-en-1-one (**32**), mp 157–161°. Recrystallization from a mixture of benzene and hexane afforded **32** as pale yellow crystals: mp 162–165°; ir (Nujol) 1748 cm^{-1} (nonconjugated C=O);[32] uv max (CH_2Cl_2) 263 nm (ϵ 11,600) and 235 (15,100);[33] NMR ($CDCl_3$) δ 7.30–7.00 (m, 20, C_6H_5), 6.17 (m, 1, –CH=CH_2), 5.42 (m, 2, –CH=CH_2), 4.98 (s, 1, PhCH); mass spectrum (70 eV) *m/e* (rel intensity) 413 (32.6), 412 (93.0), 385 (35.9), 384 (98.2), 307 (18.8), 294 (33.3), 293 (100.0), 292 (19.8), 291 (24.9), 289 (11.8), 279 (10.3), 278 (11.2), 267 (19.1), 265 (12.3), 229 (12.4), 228 (11.3), 216 (12.3), 215 (42.6), 205 (12.8), 204 (11.5), 203 (12.2), 202 (15.9), 191 (18.6), 179 (12.3), 178 (26.5), 168 (11.2), 167 (45.5), 165 (21.0), 153 (15.8), 152 (15.5), 151 (11.7), 128 (13.6), 115 (27.6), 105 (18.0), 91 (68.9), 50 (10.5), 44 13.7), 28 (62.9).

Anal. Calcd for $C_{31}H_{24}O$: C, 90.26; H, 5.86. Found: C, 90.54; H, 5.92.

Hydrogenation of 32. A solution of 165 mg (0.40 mmol) of **32** in 20 ml of ethyl acetate was hydrogenated in the presence of 15.5 mg of platinum oxide at room temperature under atmospheric pressure. The reduction appears to be complete within 10 min but was allowed to proceed for 3 hr. After the catalyst was removed by filtration, the filtrate was concentrated to give 168 mg of a grayish, oily solid. The NMR spectrum of this crude product indicated that the vinyl group was absent. Recrystallization of this material from a mixture of benzene and hexane afforded 91 mg (55%) of 2-ethyl-2,3,4,5-tetraphenylcyclopent-3-en-1-one (**33**) as colorless crystals: mp 149–153°; ir (Nujol) 1744 s, 1595 w, 1485 m, 1340 vvw, 1305 vw, 1275 vw, 1220 vw, 1180 w, 1165 vvw, 1150 vw, 1070 w, 1050 w, 1030 w, 1000 vw, 970 vvw, 955 vvw, 922 vvw, 915 vw, 822 vw, 800 w, 777 w, 770 m, 765 sh, 737 m, 720 m, 710 m, 698 m, and 694 cm^{-1} sh; uv

max (CH_2Cl_2) 235 nm (ϵ 15,600) and 267 (11,600); NMR ($CDCl_3$) δ 6.77–7.45 (m, 20, C_6H_5), 4.82 (s, 1, –CHPh–), 1.58–2.77 (m, 2, $-CH_AH_BMe$, J_{AB} = 13.3, $J_{CH_2CH_3}$ = 7.3 Hz), 0.95 (t, 3, CH_3, J = 7.3 Hz); mass spectrum (70 eV) m/e (rel intensity) 415 (23.1), 414 (60.7, M^+), 386 (26.0), 385 (83.3), 358 (34.4), 357 (100.0), 280 (21.8), 279 (58.6), 278 (12.3), 265 (14.4), 203 (12.1), 202 (12.4), 191 (12.6), 179 (14.4), 178 (24.0), 119 (10.1), 115 (20.6), 105 (24.8), 103 (12.2), 91 (39.7), 78 (23.0), 77 (22.8), 32 (19.9), 28 (78.9).

Anal. Calcd for $C_{31}H_{26}O$: C, 89.82; H, 6.32. Found: C, 89.59; H, 6.31.

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Registry No.—**1,** 1450-31-3; **2,** 54663-82-0; (*E*)-**3,** 56195-65-4; (*Z*)-**3,** 56195-66-5; **5,** 13509-36-9; **6,** 50375-41-2; **7,** 2080-58-2; **8,** 705-65-7; **9,** 822-38-8; **15,** 56195-80-3; **16,** 56247-12-2; **17,** 15482-60-7; **19,** 958-80-5; **23,** 56195-67-6; **25,** 84-11-7; (*E,E*)-*trans*-**28,** 56195-68-7; (*Z,Z*)-*trans*-**28,** 56195-69-8; (*Z*)-**29,** 56195-70-1; (*E*)-**29,** 56195-71-2; (*Z*)-**30,** 56195-72-3; **31,** 479-33-4; **32,** 56195-74-5; **33,** 56195-75-6; **39,** 17109-66-9; **40,** 56195-76-7; phenyl isocyanide dichloride, 622-44-6; *tert*-butyl mercaptan, 75-66-1; ethylene sulfide, 540-63-6; thiophenol, 108-98-5; vinyllithium, 917-57-7; vinyl bromide, 593-60-2; (*E*)-1-propenyllithium, 6386-72-7; (*Z*)-1-propenyllithium, 6524-17-0; (*E*)-1-propenyl bromide, 590-15-8; (*Z*)-1-propenyl bromide, 590-13-6; phenyllithium, 591-51-5; phenyl isocyanide, 931-54-4; benzhydrylsodium, 5152-68-1; benzhydryllithium, 881-42-5; dibenzhydryl sulfide, 1726-03-0; *n*-butyllithium, 109-72-8; benzyl chloride, 100-44-7; benzyllithium, 766-04-1

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The Peripheral Synthesis of Medium-Ring Diaza Heterocycles via β-Elimination Reactions

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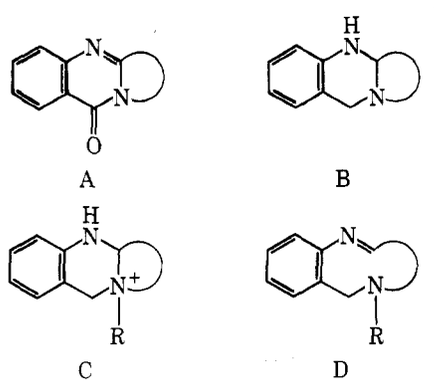
Compounds **4** and **7**, respectively, obtained from the corresponding quinazolinones, were methylated to give **5** and **8** respectively. Treatment with base led to the medium-ring diaza compounds **6b** and **9**, respectively.

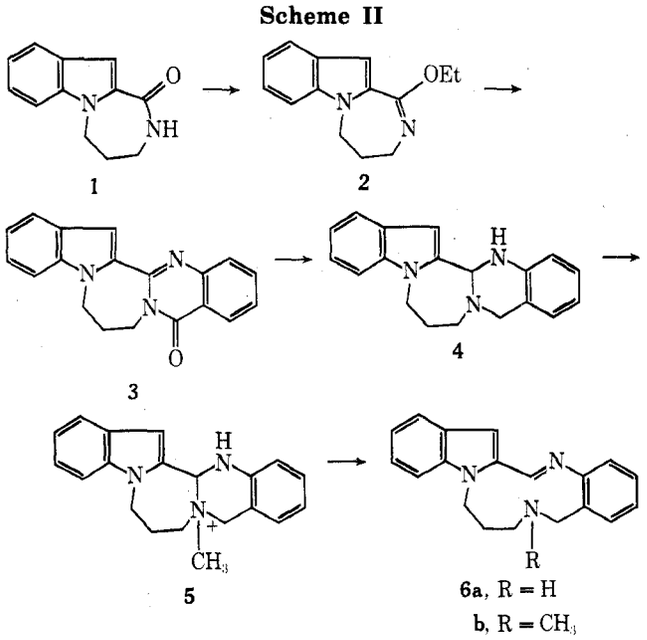
The peripheral synthesis of medium-ring azacycles as disclosed in the literature[1] involves the selective cleavage of the central bond of a fused 1-azabicycloalkanone. This was achieved via quaternization of the nitrogen in the proximity of an activating substituent leading to the selective cleavage of one nitrogen–carbon bond.

We have applied this concept to the formation of medium-ring diazacycles under nonreductive conditions. Similar to a Hofmann degradation,[2] the nitrogen–carbon bond cleavage is induced by a tetraalkylammonium salt. An aniline was placed in a 1,3 position to the ammonium salt as depicted in structure C of Scheme I. The more basic tertiary nitrogen should guarantee the selective alkylation of B by an alkyl halide to give C. We expected ring enlargement to D to occur in the presence of a suitable base via β-elimination with abstraction of a proton from the secondary amine. The precursors for B are well documented in the literature[3] and are readily prepared from *o*-anthranilic acid and an activated lactam, e.g., an imino ester, to give the fused quinazolinones of the general structure A. These can be reduced to the compounds of the general structure B in the presence of lithium aluminum hydride.[4]

Scheme I



Scheme II



As our starting material we selected the known[5] [1,4]diazepino[1,2-*a*]indol-1-one (**1**) (Scheme II). The imino ester **2** was prepared with the aid of Meerwein's salt following standard literature procedures.[3a,b] This activated lactam formed the novel pentacyclic quinazolinone **3** when heated with anthranilic acid in analogy to similar reactions described in the literature.[3a] Spectral and analytical data were found in agreement with the assigned structure **3**. Treatment of this compound with lithium aluminum hydride in refluxing tetrahydrofuran resulted in the reduction of both functional groups[4] of **3** to give **4**.

With dry hydrochloric acid, the base **4** was transformed into a bishydrochloride according to analytical data.

While two of the three nitrogens present in **4** are basic