0.21 (CH$_3$), 0.15 (H-3' and H-5' of PhSO$_2$), 0.13 (H-4' of PhSO$_2$), 0.10 (CH$_3$), 0.08 (CH$_3$). The similarity in slope (0.21 and 0.15) between the meta protons of the mesityl and phenyl groups indicates that the two sulfonyl groups coordinate the lanthanide ion to a similar extent. Therefore, the fact that one methyl of the parent ring is shifted (0.73) even more than the two o-methyls of the mesityl group (0.49) can be explained by assuming that the former is close to both the sulfonyl groups as in the proposed structure 11b.

Second elution product, 10b: 0.64 g (1.41 mmol); mp 203-204 °C (EtOH); NMR (CDCl$_3$) δ 7.79 (m, 2 H, H-2' and H-6' of PhSO$_2$), 7.47 (m, 3 H, H-3', H-4', and H-5' of PhSO$_2$), 6.78 (br s, 2 H, Me$_3$C$_6$H$_2$), 2.38 (s, 3 H, CH$_3$), 2.23, 2.20, 2.18, and 2.15 (4 overlapping s, 18 H in all, 6 CH$_3$). Anal. Calcd for C$_{25}$H$_{28}$O$_4$S$_2$: C, 65.8; H, 6.1. Found: C, 65.7; H, 6.1.

Photostimulated Reactions of 6a,b and Control Experiments of Tables I and II. In a Pyrex test tube was dissolved the sulfone 6a or 6b (0.15 mmol) in Me$_2$SO (6 mL) or in 6 mL of a 7.5 × 10^{-5} M Me$_2$SO solution of m-dinitrobenzene (expts 5, 10, and 17), and this was deaerated with argon gas by using five freeze-pump-thaw cycles. To this solution either was added 3 mL of a Me$_2$SO solution of sodium arenethiolate at the appropriate concentration (0.25 or 0.05 M) or an additional 3 mL of Me$_2$SO

(expts 11 and 18). The reaction mixture was deaerated again with argon and stoppered with a rubber septum. Reactions carried out in the "dark" were performed with the test tube wrapped in aluminum foil. Reactions performed in "light" were irradiated in a homemade "merry-go-round" apparatus by a 300-W Osram sunlamp placed 10 cm from the reaction vessel. All reactions were worked up as reported in General Methods and chromatographed by first eluting with hexane (except expts 11 and 18), to remove some diaryl disulfide and the corresponding arenethiol, and then with dichloromethane. All successive fractions (eluted with dichloromethane) were collected together and concentrated on a rotary evaporator, and the residue was analyzed by TLC, ^{1}H NMR, and HPLC. The absolute yields reported in Tables I and II were estimated by NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

o-Naphthoquinodimethanes and o-Phenanthroquinodimethanes. Isoindene-Related Species

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Three isoindene-related naphthoquinodimethane and phenanthroquinodimethane species were synthesized and trapped with 4-phenyl-1,2,4-triazoline-3,5-dione. They are 2,2-dimethyl-2H-benz[e]indene (3), 2,2-dimethyl-2H-benz[f]indene (4), and 2,2-dimethyl-9H-cyclopenta[b]phenanthrene (10). Compound 3 could be isolated and characterized by ^{1}H NMR. The effect of solvent on the bisacylation of naphthalene and phenanthrene by dimethylmalonyl chloride is discussed. Also the use of the Vilsmeier reagent generated from PBr$_3$/DMF if highly recommended as a general reagent for conversion of alcohols to alkyl bromides.
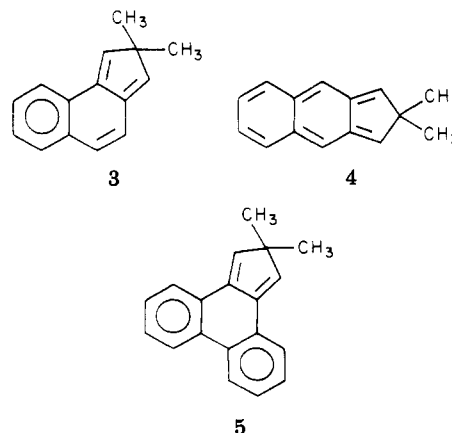
In a recent series of papers we examined the generation and the thermal and photochemical behavior of 2,2-dimethylisoindene (1) and other 2-alkyl-2-methylisoindenes (2).[1-5] 1 was itself able to be isolated either as a gas or
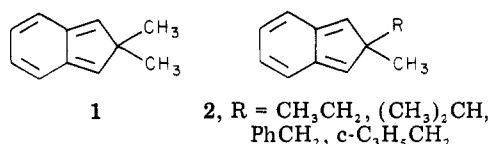
in dilute solution, and it was fully characterized spectroscopically, the first time such an o-benzoquinodimethane species had been able to be so fully characterized.[2,3] Its ^{1}H NMR spectrum showed complex vinylic absorptions at δ 6.08 (4 H) and 6.55 (2 H) in addition to a six-proton

singlet at δ 1.16, all consistent with 1 having nonaromatic character.

We considered it of interest to attempt to prepare and isolate related 1,2- and 2,3-naphtho- and 9,10-phenanthroquinodimethane species 3-5. No such iso-

indene-type species have been previously generated, much less isolated, although related 2,3-naphthoquinodimethane derivatives 6 and 7 have recently been reported and

(1) Dolbier, W. R., Jr.; McCullagh, L.; Rose, D.; Anapolle, K. E. *J. Am. Chem. Soc.* **1975,** *97,* 934.
(2) Dolbier, W. R., Jr.; Matsui, K.; Michl, J.; Horak, D. V. *J. Am. Chem. Soc.* **1977** *99,* 3876.
(3) Dolbier, W. R., Jr.; Matsui, K.; Dewey, H. J.; Horak, D. V.; Michl, J. *J. Am. Chem. Soc.* **1979,** *101,* 2136.
(4) Dolbier, W. R., Jr.; Matsui, K.; McCullagh, L.; Anapolle, K. E. *J. Org. Chem.* **1979,** *44,* 2842.
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characterized from their UV–visible absorption, linear dichroic, and polarized fluorescence and excitation spectra.[6] The parent system (8) has itself been matrix-isolated and similarly characterized.[7] Lastly, a number of heterocyclic


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7

8

9, X = O, S, NH
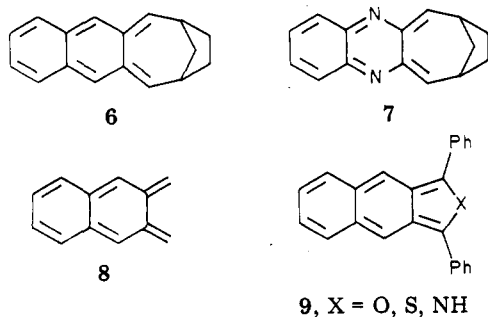
orthoquinoid species, such as naphtho[2,3-*c*]furan and naphtho[2,3-*c*]thiophene (9; X = O, S) have been isolated and characterized,[8] while benz[*f*]isoindoles (9; X = NH) have been generated and trapped.[9] We believed that the isoindene-related species 3–5 could be prepared, much as had 1, and that 5 would be much more stable than 1 with 3 being somewhat more stable, while 4 would be much less stable; these predictions were based on the relative loss of aromaticity of each molecule. There has been considerable theoretical speculation as to the degree of destabilization of *o*-quinodimethane species such as 1–5.[10,11] It is hoped that eventually studies on the thermal and photochemical properties of such a series as 1–5 will provide insight into these questions. In this paper we report the generation and probable NMR characterization of 3 and the generation and trapping of 4 and the related species 10.

10
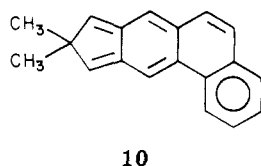
Also presented are details of the use of PBr$_3$/DMF, via the intermediacy of the Vilsmeier reagent, as a method of efficiently converting primary and secondary alcohols to alkyl bromides, a procedure which is superior to the use of Ph$_3$PBr$_2$ with nonvolatile alcohols.

Results and Discussion

The synthetic sequence utilized for the syntheses of 3 and 4 derives from a modification of a very old procedure of Freund and Fleischer for preparing diketones 11 and 12.[12] We found that using CS$_2$ as solvent, as did Freund and Fleischer, led to a difficult-to-separate mixture of 11–13, while if we used nitrobenzene as solvent, a product mixture of 11 and 13 was obtained, which could be readily separated by column chromatography or recrystallization. Little 12 could be detected in the mixture by TLC. On the other hand, the use of CH$_2$Cl$_2$ as solvent led to a product mixture composed largely of 12, which could be purified easily by recrystallization. The course of this

11 (20%)   **13 (17%)**

12 (39%)
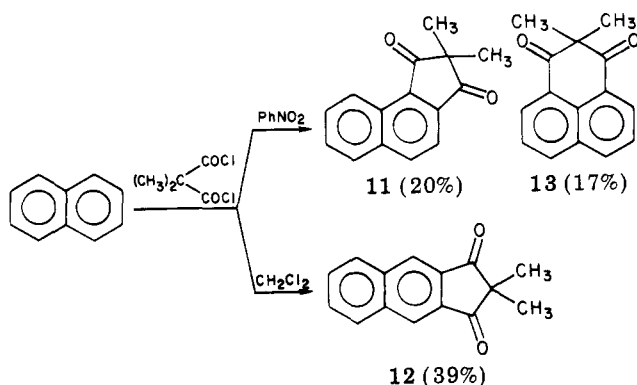
Friedel–Crafts reaction with naphthalene is thus significantly solvent dependent. This is not at all unusual in Friedel–Crafts reactions, and variable steric effects are believed to be largely the cause.[13] In this case use of the two different solvents facilitates the isolation of each of the two desired isomeric diketones. The ^{1}H and ^{13}C NMR spectra of 11–13 are clearly indicative of their structures (see Experimental Section).

Unexpectedly, the Friedel–Crafts acylation of phenanthrene with dimethylmalonyl chloride did not lead to initial acylation at the 9-position (and hence to lead eventually to diketone 14) but led to a good yield (77%) of a single product, 15, which undoubtedly derived from initial

14

15
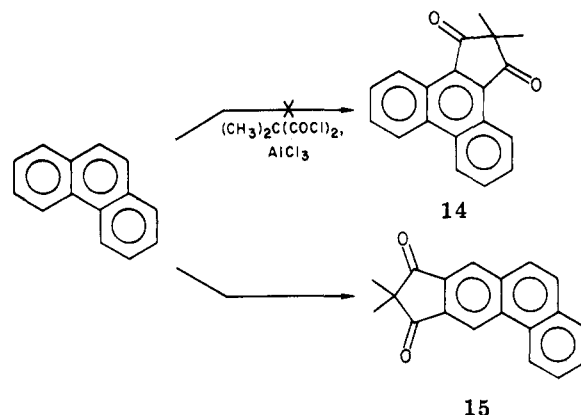
acylation at the 2-position. In retrospect this should not have been surprising since it has been demonstrated clearly by Gore that acylation, and specifically acetylation, of phenanthrene is very much solvent dependent, with a steric effect again being invoked.[14,15] Gore indeed found that under the more congested solvent conditions, acetylation occurred largely at the 2-position. Certainly dimethylmalonyl chloride must be considered in and of itself a bulky acylating agent and hence its avoidance of the 9-position and the 1-position entirely.

The structure determination of 15 is reasonable, with the key observation in the ^{1}H NMR being two broad one-proton singlets at δ 8.48 and 9.30 and a one-proton multiplet at δ 8.83. The two singlets are certainly due to the protons at C-1 and C-4, respectively, since the ^{1}H NMR spectra of 2-acetyl- and 3-acetylphenanthrene show singlets at δ 8.34 and 9.16, respectively.[16] Phenanthrene itself gives rise to a two-proton multiplet in its ^{1}H NMR at δ 8.69, which is assigned to the C$_4$ and C$_5$ protons.[16,17] Hence,

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(15) Gore, P. H.; Thadani, C. K.; Thorburn, S.; Yusuf, M. *J. Chem. Soc. C* **1971**, 2329.

(16) Bartle, K. D.; Smith, J. A. S. *Spectrochim. Acta Part A* **1967**, *23*, 1715.

Table I. Phenanthrene Derivative Proton Chemical Shifts

|	δ values						
compd	H_1	H_2	H_3	H_4	H_5	H_9, H_{10}	ref
15	8.48			9.30	8.83	7.80	this work
phenanthrene (P)	7.88	7.57	7.64	8.69	8.69	7.72	16
2-acetyl-P	8.34		8.09	8.59	8.59	7.72	16
3-acetyl-P	7.86	8.04		9.16	8.68	7.72	16
9,10-bis(carbomethoxy)-P	8.06	7.57	7.65	8.61	8.61		16

the one proton multiplet at δ 8.83 is no doubt due to the proton on C-5. Also notable in the ¹H NMR spectrum of 15 is a sharp two-proton singlet at δ 7.80 due to protons on C-9 and C-10, a signal which is consistent with similar singlets observed in the spectra of 2-acetyl- and 3-acetylphenanthrene, each at δ 7.72.[16]

The transformations of diketones 11, 12, and 15 into diols 16–18 were carried out with relative ease in virtually quantitative yield, using LiAlH₄, while conversions of the diols into dibromides 19–21 led to problems when Ph₃PBr₂ or PBr₃ were utilized. The main problem with the former reagent was the *isolation* of the nonvolatile products from the triphenylphosphine oxide. The problems were completely circumvented by the use of PBr₃/DMF, a reagent which was found to convert primary and secondary alcohols into alkyl bromides in high yield and with great ease of isolation via the in situ generation of the Vilsmeier reagent (vide infra). In both the reduction and the bromination steps, mixtures of diastereomers were obtained. While crude diols 16–18 were used without further purification, the dibromides, obtained in a near-quantitative crude yield, were recrystallized to give about a 70% yield each of isolated pure compound. In the case of 19, this purified dibromide was largely the cis isomer, while 20 and 21 remained mixtures.
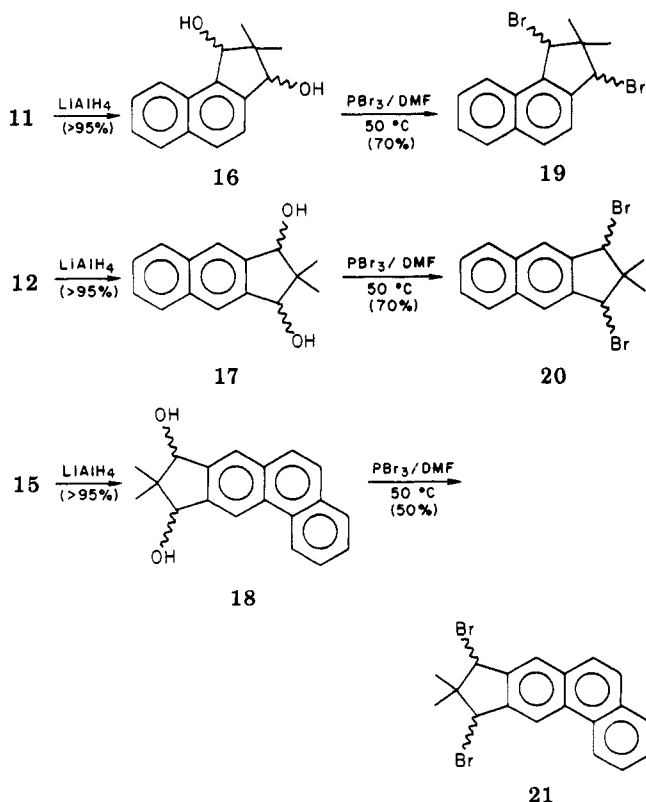
The use of the Vilsmeier reagent 22 to convert the diols into their respective dibromides is a very versatile and

generally effective procedure for the conversion of primary or secondary alcohols into bromides with a minimal chance of rearrangement by a direct displacement mechanism. For nonvolatile compounds, it provides a viable alternative to the use of triphenylphosphine dibromide, largely because of the relative ease of isolation of product. The Vilsmeier reagent 22 can be used in situ, as generated in excess DMF, or it may be isolated by filtration, washed, and used in whatever solvent desired. Most primary and secondary alcohols are conveniently converted in near-quantitative yields to their respective bromides with the in situ reagent at 50 °C. Some elimination competes with substitution for secondary systems. A typical procedure is provided in the Experimental Section. While the chlorine-substituted Vilsmeier has been previously reported to be an excellent reagent for the conversion of alcohols to alkyl chlorides,[18,19] there has been little work with the bromo derivative 22 since its previous source has generally been treatment of the chloro derivative with excess HBr. We have found that careful addition of PBr₃ to an excess of cooled DMF provides an excellent direct source of 22.
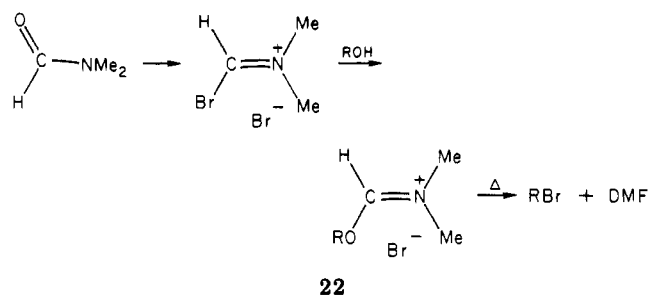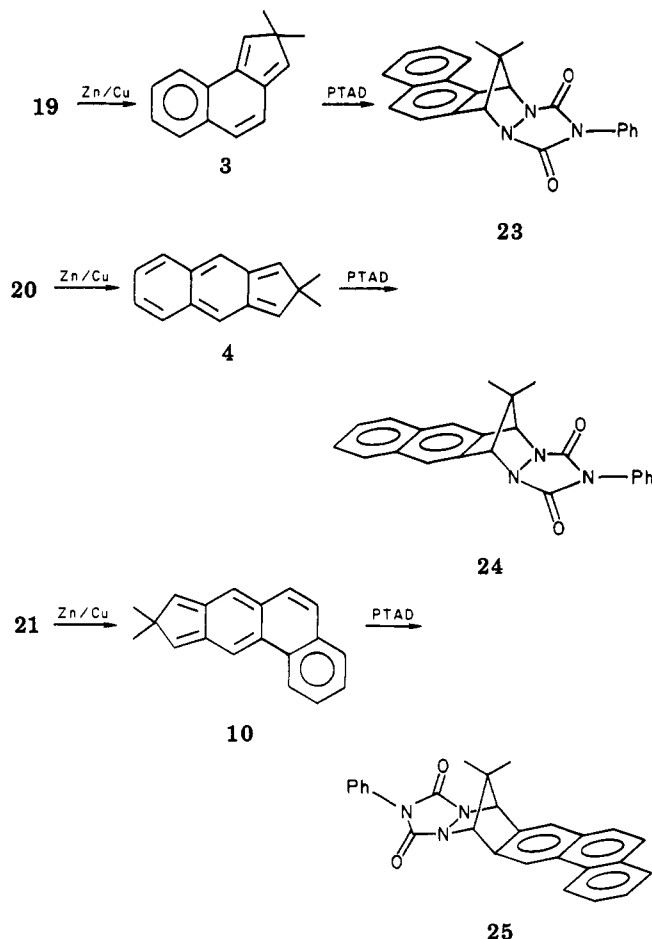

Debromination of dibromides 19–21 using Zn/Cu couple was carried out under conditions where the thus-generated isoindene-type species 3, 4, and 10 could be trapped in a Diels–Alder reaction by the very reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). Concomitant, slow addition of 19–21 and PTAD to the stirred Zn/Cu couple in DMF and CH₂Cl₂ led to a good yield of each of the respective adducts 23–25. Each of the adducts was isolated, purified by column chromatography and/or recrystallization, and characterized fully. Less reactive dienophiles such as dimethyl maleate were unsuccessful in trapping the reactive intermediates. In the absence of PTAD, 3, 4, and 10 apparently oligomerize with such products not having been characterized. No monomeric products, such as methyl shift products,[1] have been observed.

In the case of debromination of 19, an intermediate was able to be detected by ¹H NMR, which we believe to be 3. Its spectrum showed a six-proton singlet at δ 1.24 (which compares with the comparable singlet of 1 at δ 1.16), two one-proton doublets at δ 6.26 (J = 2.5 Hz) and 6.75 (J =

(17) Sadtler Standard Spectra, NMR Spectrum No. 61, Sadtler Research Laboratories Inc., 1976.

(18) Hepburn, D. R.; Hudson, H. R. *Chem. Ind.* 1974, 664; *J. Chem. Soc., Perkin Trans. 1* 1976, 754.

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Conclusion

In conclusion, the work presented above has demonstrated (a) that the regiochemistry of Friedel–Crafts bisacylation of naphthalene by dimethylmalonyl chloride can be influenced significantly by the choice of solvent with 1,2-bisacylation being favored in CH_2Cl_2, while 2,3-bisacylation is favored with $PhNO_2$ as solvent; (b) that Friedel–Crafts bisacylation of phenanthrene by dimethylmalonyl chloride is highly regioselective in favor of the 2,3 product; (c) that 1,2- and 2,3-naphthoquinodimethane species **3** and **4** and 2,3-phenanthroquinodimethane species **10** can be generated by debromination reactions, in each case be trapped by the highly reactive dienophile PTAD, and in the case of **3** be directly detected by ^1H NMR spectroscopy; and (d) that the use of PBr_3/DMF as a reagent for conversion of nonvolatile primary and secondary alcohols to bromides is a procedure which is significantly superior to the use of Ph_3PBr_2 in such reactions.

Experimental Section

Proton NMR spectra were obtained in $CDCl_3$ in one or more of the following spectrometers: Varian EM-360 (at 60 MHz), JEOL FX-100 (at 100 MHz), or Nicolet (at 300 MHz). ^{13}C spectra were obtained on one of the latter two. Me_4Si was the internal standard. Mass spectra were obtained on an AEI MS-30. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, GA.

2,2-Dimethylmalonyl Chloride. In a three-necked, round-bottomed flask were placed 26.4 g of dimethylmalonic acid and 80 mL of dry benzene. The heterogeneous mixture was stirred and an ice bath was used to cool the mixture as 57 g of oxalyl chloride was slowly added. The mixture was warmed to room temperature and then heated for 24 h at 50 °C, after which time the reaction mixture was homogeneous. HCl was continuously evolved. The benzene solvent and excess oxalyl chloride were removed by distillation, and the light-brown residue was distilled at 20–25 mm with product being collected at 75 °C. The yield was 28 g (82%): ^1H NMR δ 1.7 (s).

2,2-Dimethyl-1H-benz[e]indene-1,3(2H)-dione (11) and 2,2-Dimethyl-1H-phenalene-1,3(2H)-dione (13). Into a three-necked flask was placed 28 g (0.165 mol) of dimethylmalonyl chloride in 200 mL of nitrobenzene along with 45 g (0.337 mol) of $AlCl_3$. To the stirred mixture, cooled with an ice bath, was added 21.1 g (0.165 mol) of naphthalene, slowly enough to keep the reaction temperaure below 15 °C. The mixture was then stirred at room temperature for 7 h, after which it was poured into about 800 mL of ice in dilute HCl (5–10%). The organic layer was washed successfully with water, 5% KOH, and water. The aqueous layer was extracted 4 times with 100 mL of $CHCl_3$, and the $CHCl_3$ extracts were combined with the organic layer and dried. The $CHCl_3$ and nitrobenzene were removed by distillation, the latter at 5 mm.

The dark-brown oily residue can be purified by either of two methods.

(a) Distillation at 0.05 mm, bp 150 °C, gave 23 g of a dark-yellow oil which was recrystallized from a 1:6 mixture of $CHCl_3$/pentane to give 6.6 g of product. A second crop could be obtained, giving 2.2 g or a total of 8.8 g (24% yield) of ~95% pure **11**. A further recrystallization gave 3.3 g of very pure product.

(b) The residue was dissolved in MeOH and filtered and the MeOH removed. This oil was dissolved in 1:1 $CHCl_3$/pentane and subjected to column chromatography. Into a 4 cm wide, 50 cm long column was placed 100 g of TLC grade silica gel in pentane. N_2 pressure was applied on top during the chromatography to provide fast elution and the separation was followed by 366-mμ UV light. The *entire* sample was purified at once on this column, giving two eluted products each in a pure state. **11** (7.43 g, 20.1%): mp 119–120 °C; ^1H NMR δ 1.37 (s, 6 H), 7.60–8.40 (m, 5 H), 9.10–9.40 (m, 1 H); ^{13}C NMR δ 20.47 (CH_3), 49.74 (C(CH_3)$_2$), 118.53, 126.82, 128.28, 128.62, 129.74, 130.01, 136.51, 137.15, 137.24, 140.70 (aromatic C), no C=O peaks were observed; IR (CCl$_4$), 842, 1043, 1083, 1167, 1301 (s), 1385, 1447, 1465, 1585

2.5 Hz), and a two-proton multiplet at δ 6.65 (compared to the two vinylic multiplets at δ 6.08 and 6.55 in the spectrum of **1**), and aromatic absorptions at δ 7.24 and 7.7 (three- and one-proton complex multiplets, respectively).
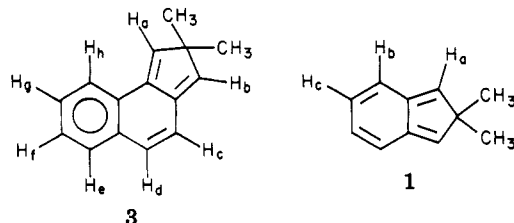
A possible assignment of the proton spectrum of **1** would have protons a and c comprising the four-proton multiplet at δ 6.08. Thus, in the spectrum of **3**, only proton b would remain at such high field (δ 6.26), while proton a would be shifted downfield (δ 6.75) due to its position which is similar to that of the four and five protons of phenanthrene.[17] Assignment of protons a and b is also strongly supported by their common observed 2.5-Hz coupling constant. The coupling constant between protons c and d should be much larger. Protons c and d would fortuitously fall together at δ 6.65 because d will exhibit a downfield shift due to the proximity of the benzene ring. The very low field proton signal should be due to proton h, which also will exhibit a phenanthrene-type deshielding.

The ^1H NMR of the intermediate is thus consistent with its structure being **3**. There is some indication that **3** is significantly more stable than **1** in that in one case it was possible to isolate it almost pure, in concentrated $CDCl_3$ solution, in the presence of air, with only slow buildup of oligomeric materials. **3** did not react with dimethyl maleate but, as with the in situ species **4** and **10**, only could be trapped with the very reactive PTAD.

(w), 1594 (w), 1709 (s), 1746 (s), 2980 (w) cm^{-1}; exact mass calcd for $C_{15}H_{12}O_2$ m/e 224.08373, found m/e 224.08273. (M$^+$, base peak; deviation 4.5 ppm); mass spectrum, m/e 209, 196, 181, 155, 154, 150, 127, 126. **13** (6.0 g, 17%): mp 83–84 °C; ^{1}H NMR δ 1.53 (s, 6 H), 7.72 (H$_\beta$, d of d, J = 8.4, 7.0 Hz, 2 H), 8.26 (H$_\gamma$, d of d, J = 8.4, 1.5 Hz, 2 H), 8.45 (H$_\alpha$, d of d, J = 7.0, 1.5 Hz, 2 H); ^{13}C NMR δ 22.73 (CH$_3$), 59.09 (C(CH$_3$)$_2$), 124.70, 126.63, 127.07, 128.91, 132.71, 134.09 (aromatic C), 199.08 (C=O).

2,3-Dihydro-2,2-dimethyl-1H-benz[e]indene-1,3-diol (16). A standard LiAlH$_4$ reduction and workup led to a virtually quantitative yield of crude diol **16**, which was used directly for conversion to the dibromide. The product was determined from NMR to be a mixture of cis and trans isomers, largely *trans*. *trans*-**16**: ^{1}H NMR δ 1.09 (s, 6 H), 3.0 (br s, 2 H), 4.9 (br s, 1 H), 5.1 (br s, 1 H), 7.4–8.2 (m, 6 H). *cis*-**16**: ^{1}H NMR δ 0.77 (s, 3 H), 1.36 (s, 3 H), 3.0 (br s, 2 H), 4.7 (br s, 1 H), 4.9 (br s, 1 H), 7.4–8.2 (m, 6 H).

1,3-Dibromo-2,3-dihydro-2,2-dimethyl-1H-benz[e]indene (19). Into a 100-mL flask equipped with magnetic stirrer, reflux condenser with CaCl$_2$ tube, and an addition funnel were placed 5 g of PBr$_3$ and 10 mL of Et$_2$O. To this was added with cooling 20 mL of DMF. The reaction was exothermic. Then 1.02 g (0.0045 mol) of diol **16** in 20 mL of DMF was added slowly and the mixture then heated at 50 °C for 7 h. The reaction mixture was cooled and 40 mL of H$_2$O added. The aqueous layer was separated and extracted 4 times with 100 mL of Et$_2$O. The organic layer was combined with the ether extracts and was washed with H$_2$O and dried. Evaporation of Et$_2$O gave a white solid (~2.9 g) which was recrystallized from hexane to yield 1.0 g of (63% yield) dibromide, which proved to be mostly cis isomer. (The trans isomer appeared in increasing amounts in further crops of crystals.) *cis*-**19**: mp 135–137 °C; ^{1}H NMR δ 1.28 (s, 3 H), 1.76 (s, 3 H), 5.28 (s, 1 H), 5.58 (s, 1 H), 7.3–8.3 (m, 6 H). *trans*-**19** (as impurity in cis): ^{1}H NMR δ 1.23 (s, 3 H), 1.60 (s, 3 H), 5.45 (s, 1 H), 5.66 (s, 1 H), 7.3–8.3 (m, 6 H).

2,2-Dimethyl-2H-benz[e]indene (3). a. Isolation and NMR Characterization. Into a dry, one-neck, 5-mL flask were placed 0.25–0.35 g of Zn/Cu couple[20] and 1 mg of hydroquinone. The flask was capped with a rubber septum and flushed (via syringe needles) with N$_2$. To the flask was added, via syringe, 0.3 mL dry DMF-d_7, and then, with cooling, 45 mg of **19** in 0.5 mL of CDCl$_3$ was added slowly. The flask was swirled gently during the addition. After addition was complete the flask was allowed to warm to room temperature and the clear supernatant liquid was syringed from the flask into a NMR tube and sealed: ^{1}H NMR (FX 100) δ 1.24 (s, 6 H), 6.26 (d, 1 H, J = 2.5 Hz), 6.65 (m, 2 H), 6.75 (d, 1 H, J = 2.5 Hz), 7.24 (m, 3 H), 7.7 (m, 1 H).

b. Trapping with 4-Phenyl-1,2,4-triazoline-3,5-dione. Into a 50-mL, three-necked, round-bottomed flask fitted with mechanical stirrer and two addition funnels was placed 1.8 g of Zn/Cu couple in 3 mL of dry DMF. To this, with stirring and cooling with an ice bath, were added slowly and simultaneously 0.5 g of **19** in 10 mL of CH$_2$Cl$_2$ and 15 mL of a CH$_2$Cl$_2$ solution of PTAD (from 0.25 g of urazole and 0.63 g of Pb(OAc)$_4$). The addition took 10 min after which the flask was allowed to warm to room temperature and the contents stirred for 1 h. The mixture was then poured into 100 mL of water and the organic layer separated. The aqueous layer was washed 3 times with 50 mL of CH$_2$Cl$_2$, the organic layers were combined and dried, and the solvents were evaporated under reduced pressure. The residue was subjected to column chromatography as described earlier and the isolated product recrystallized from MeOH/CHCl$_3$ (5:2) to yield 0.265 g (51% yield) of adduct **23**: mp 184–185 °C; ^{1}H NMR δ 0.88 (s, 3 H), 1.63 (s, 3 H), 5.12 (s, 1 H), 5.50 (s, 1 H), 6.7 (m, 2 H), 7.18 (m, 3 H), 7.4–8.4 (m, 6 H); ^{13}C NMR δ 20.11 (CH$_3$), 21.33 (CH$_3$), 60.29 (C(CH$_3$)$_2$), 70.44 (CH), 73.35 (CH), 120.74, 123.91, 125.31, 126.32, 127.40, 128.18, 128.32, 128.43, 128.83, 129.17, 130.74, 133.42, 133.69, 134.15, 138.75, (aromatic C), 158.65 (C=O), 158.98 (C=O). Anal. Calcd for $C_{23}H_{19}O_2N_3$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.68; H, 5.22; N, 11.30.

2,2-Dimethyl-1H-benz[f]indene-1,3(2H)-dione (12). In a manner similar to that for the preparation of diketone **11**, 5.8 g of dimethylmalonyl chloride, 9.7 g AlCl$_3$, and 4.45 g of naphthalene

were allowed to react in a total of 75 mL of CH$_2$Cl$_2$. After the usual workup, the CH$_2$Cl$_2$ solution was dried and evaporaed in vacuo. The green solid residue was recrystallized from hexane to give 2.63 g (39% yield) of pure diketone **12** from the first crop of crystals: mp 132–133 °C; ^{1}H NMR δ 1.36 (s, 6 H), 7.76 (m, 2 H), 8.14 (m, 2 H), 8.55 (s, 2 H); ^{13}C NMR 20.56 (CH$_3$), 51.39 (C(CH$_3$)$_2$), 124.73, 129.52, 130.55, 135.38, 136.75 (aromatic C), 204.67 (C=O); exact mass calcd for $C_{15}H_{12}O_2$ m/e 224.08373, found m/e 224.08345 (M$^+$, 96% of base; deviation 1.2 ppm); mass spectrum, m/e 209 (base), 196, 181, 155, 154, 127, 126.

2,3-Dihydro-2,2-dimethyl-1H-benz[f]indene-1,3-diol (17). Diol **17** was prepared in the same manner as **16**, yielding a mixture of cis and trans isomers, which was used directly in the next step. *cis*-**17**: ^{1}H NMR δ 0.79 (s, 3 H), 1.34 (s, 3 H), 4.52 (d, 2 H, J = 7 Hz), 4.82 (d, 2 H, J = 7 Hz), 7.47 (m, 2 H), 7.83 (m, 4 H); *trans*-**17**: ^{1}H NMR δ 1.08 (s, 6 H), 4.3 (d, 2 H, J = 5.5 Hz), 5.0 (d, 2 H, J = 5.5 Hz), 7.47 (m, 2 H), 7.83 (m, 4 H).

1,3-Dibromo-2,3-dihydro-2,2-dimethyl-1H-benz[f]indene (20). Dibromide **20** was prepared from diol **17** in the same manner as **19**, yielding an oil which was a mixture of cis and trans isomers in 65% yield (from diketone **12**). *cis*-**20**: ^{1}H NMR δ 1.29 (s, 3 H), 1.32 (s, 3 H), 5.25 (s, 2 H), 7.49 (m, 2 H), 7.84 (m, 4 H); ^{13}C NMR δ 23.59 (CH$_3$), 23.79 (CH$_3$), 50.45 (C(CH$_3$)$_2$), 59.99 (CHBr), 124.79, 126.49, 128.11, 133.86, 139.20 (aromatic C). *trans*-**20**: ^{1}H NMR δ 1.30 (s, 6 H), 5.40 (s, 2 H), 7.49 (m, 2 H), 7.84 (m, 4 H); ^{13}C NMR δ 24.32 (CH$_3$), 49.64 (C(CH$_3$)$_2$), 61.23 (CHBr), 124.88, 126.56, 128.17, 133.83, 139.98 (aromatic C).

2,2-Dimethyl-2H-benz[f]indene (4). a. Trapping with 4-Phenyl-1,2,4-triazoline-3,5-dione. A procedure identical with that used in the trapping of **3** was used for the debromination of **20**. A 20% yield of adduct **24** was isolated after column chromatography and recrystallization from MeOH/CH$_2$Cl$_2$. **24**: ^{1}H NMR δ 0.87 (s, 3 H), 1.62 (s, 3 H), 5.00 (s, 2 H), 6.80 (m, 2 H), 7.17 (m, 3 H), 7.52 (m, 2 H), 7.77 (m, 4 H); ^{13}C NMR δ 20.10 (CH$_3$), 20.58 (CH$_3$), 58.43 (C(CH$_3$)$_2$), 71.36 (CH), 122.28, 125.46, 126.59, 128.23, 128.57, 128.89, 130.85, 133.24, 134.91 (aromatic C), 158.02 (C=O). Anal. Calcd for $C_{23}H_{19}O_2N_3$: C, 74.78; H, 5.18, N, 11.37. Found: C, 74.83; H, 5.19; N, 11.30.

9,9-Dimethylcyclopenta[b]phenanthrene-8,10(9H)-dione (15). In a manner similar to that for the preparation of diketone **11**, 21.1 g of phenanthrene, 15.71 g of dimethylmalonyl chloride, 30.1 g of AlCl$_3$ in a total of 250 mL of CH$_2$Cl$_2$ were allowed to react under N$_2$ for 24 h at room temperature. After the usual workup the CH$_2$Cl$_2$ was dried and evaporated in vacuo. Recrystallization from 1:1 CHCl$_3$/hexane yielded 9.6 g (77%) of almost pure diketone **15**, which was unambiguously characterized spectroscopically: mp 203–205 °C; ^{1}H NMR δ 1.40 (s, 6 H), 7.73 (m, H$_6$, H$_7$, H$_8$), 7.80 (s, H$_9$, H$_{10}$), 8.48 (s, H$_4$), 8.83 (m, H$_5$), 9.30 (s, H$_1$); ^{13}C NMR δ 20.58 (CH$_3$), 51.10 (C(CH$_3$)$_2$), 118.75, 123.83, 124.25, 127.40, 127.96, 128.83, 129.02, 130.55, 131.03, 132.94, 135.53, 136.40, 136.45, 136.82 (aromatic C), 204.8 (C=O); exact mass calcd for $C_{19}H_{14}O_2$ m/e 274.09938, found m/e 274.09959 $\pm$ 0.00134 (M$^+$, base peak, 4.9 ppm; deviation 0.00021, 0.8 ppm); mass spectrum, m/e 260, 259, 246, 231, 215, 205, 204, 203, 202, 177, 176, 150, 88, 83, 57.

9,10-Dihydro-9,9-dimethylcyclopenta[b]phenanthrene-8,10-diol (18). Diol **18** was prepared in the same manner as **16**, yielding a mixture of cis and trans isomers in 77% yield (after recrystallization): mp 168–172 °C. *cis*-**18**: ^{1}H NMR δ 0.77 (s, 3 H), 1.36 (s, 3 H), 4.85 (s, 2 H), 3.67 (br s, 2 H), 7.80 (m, 6 H), 8.76 (m, 2 H). *trans*-**18**: ^{1}H NMR δ 1.08 (s, 6 H), 4.81 (s, 2 H), 3.67 (br s, 2 H), 7.80 (m, 6 H), 8.76 (m, 2 H).

8,10-Dibromo-9,10-dihydro-9,9-dimethylcyclopenta[b]phenanthrene (21). Dibromide **21** was prepared from diol in the same manner as **19**, yielding a brownish solid which was recrystallized from hexane/CHCl$_3$ (20:1) to give almost a 50:50 mixture of cis and trans isomers as a light-tan solid in 50% yield: mp 118–120 °C. *cis*-**21**: ^{1}H NMR δ 1.33 (s, 3 H), 1.35 (s, 3 H), 5.25 (s, 1 H), 5.31 (s, 1 H), 7.71 (m, 6 H), 8.67 (m, 2 H). *trans*-**21**: ^{1}H NMR δ 1.33 (s, 6 H), 5.42 (s, 1 H), 5.47 (s, 1 H), 7.71 (m, 6 H), 8.67 (m, 2 H).

2,2-Dimethyl-9H-cyclopenta[b]phenanthrene (10). a. Trapping with 4-Phenyl-1,2,4-triazoline-3,5-dione. A procedure identical with that used in the trapping of **3** was used for the debromination of **21**. A 0.3-g sample of **21** yielded 0.19 g (60% yield) of adduct **25** after recrystallization from CH$_3$OH/CH$_2$Cl$_2$

(20) Le Goff, E. *J. Org. Chem.* **1964**, *29*, 2048.

(5:2): mp 260–261 °C; ^{1}H NMR δ 0.87 (s, 3 H), 1.69 (s, 3 H), 5.09 (s, 1 H), 5.13 (s, 1 H), 6.81 (m, 2 H), 7.17 (m, 3 H), 7.80 (m, 6 H), 8.80 (m, 2 H); ^{13}C NMR δ 20.13 (CH$_3$), 20.72 (CH$_3$), 59.18 (C(CH$_3$)$_2$), 71.48 (CH), 71.93 (CH), 117.36, 123.01, 125.42, 126.78, 126.97, 127.01, 127.64, 128.19, 128.60, 128.86, 130.23, 130.47, 130.77, 132.10, 132.18, 135.50, 135.67 (aromatic C), 158.02 (C=O), 158.13 (C=O). Anal. Calcd for C$_{27}$H$_{21}$N$_3$O$_2$: C, 77.31; H, 5.05; N, 10.02. Found: C, 77.23; H, 5.07; N, 9.99.

A Typical Procedure for PBr$_3$/DMF Reaction with Primary or Secondary Alcohols. Conversion of 1-Octanol to 1-Bromooctane. A 170-mL sample of dry DMF was placed into a dry, 500-mL, round-bottomed flask. To this was added 53.9 g (0.2 mol) of PBr$_3$ dropwise with stirring and cooling. After allowing the mixture to come to room temperature, a solution of 13.0 g (0.10 mol) of 1-octanol in 40 mL of DMF was slowly added. The mixture was warmed at 50 °C for 24 h after which the mixture was poured into 750 mL of H$_2$O and extracted with ether (2 ×

175 mL). After the ether extracts were washed with H$_2$O, and saturated NaHCO$_3$, the solution was dried over MgSO$_4$ and distilled to yield 18.3 g of 1-bromooctane (95% yield).

Kinetics of the Reduction of Isoquinolinium Cations by 1,4-Dihydronicotinamides

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The kinetics of the reduction of a series of 2-methyl-4-X-isoquinolinium cations [**4** (X = H, Br, CONH$_2$, COC$_6$H$_5$, CN)] and 2-methyl-5-X-phthalazinium cations [**6** (X = H, NO$_2$)] by 1-benzyl-1,4-dihydronicotinamide (**5**) have been measured in 20% CH$_3$CN–80% H$_2$O (v/v) at pH 7, 25 °C, and an ionic strength of 1.0. Pseudo-first-order rate constants (k_{obsd}) show kinetic saturation at high concentrations of **4** (X = H and Br), and association constants of 2.1 and 1.5 M^{-1}, respectively, have been evaluated for 1:1 complex formation. Interpretation of these data and earlier data for the reduction of the 2-methyl-5-nitroisoquinolinium cation (**3**) in terms of nonproductive complex formation leads to a linear free-energy relationship between the second-order rate constant (k_2) for reduction and pK_{R^+} for pseudobase formation by these cations: log k_2 = -0.50pK_{R^+} + 4.9. Substituent effects upon k_2 for the reduction of **3** and **4** (X = CONH$_2$, CN) by 1-benzyl-3-W-1,4-dihydropyridines (W = CN, CONH$_2$, CONHCH$_3$, CON(CH$_3$)$_2$) are similar to the substituent effects for cyanide ion dissociation from the corresponding 1-benzyl-4-cyano-3-W-1,4-dihydropyridines. The current study indicates that the relatively strong 1:1 complexes observed in the reduction of 5-nitroisoquinolinium cations by 1,4-dihydronicotinamides are nonproductive and also provides further evidence in support of a one-step hydride-transfer mechanism for these reactions.

We have recently reported[1] upon a detailed kinetic study of the reduction of 5-nitroisoquinolinium cations (**1**) by 1,4-dihydronicotinamides (eq 1). The interpretation of


1
3, R = CH$_3$

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(1)
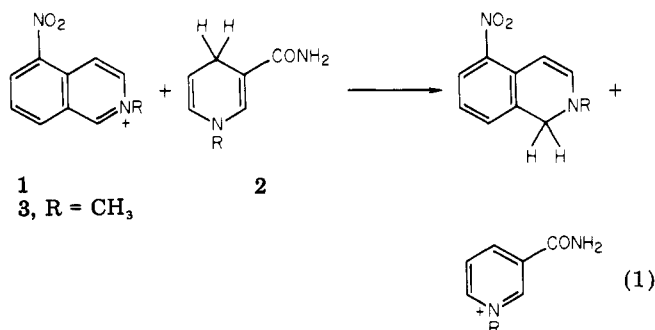
kinetic data for this reaction is complicated by kinetic saturation effects which are consistent with the formation of one or more 1:1 complexes between **1** and **2**. It was established that at least one nonproductive 1:1 complex is formed for **1** (R = CH$_2$C$_6$H$_4$Z); however, the description of the kinetically observed complex for **3** is made difficult by the kinetic equivalence of productive and nonproductive

complexes in such systems. In an effort to gain further insight into the role of complexation in these reactions, we have now studied the rates of reduction of a variety of 4-substituted 2-methylisoquinolinium cations by 1-benzyl-1,4-dihydronicotinamide (eq 2) and have also com-

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5

(2)
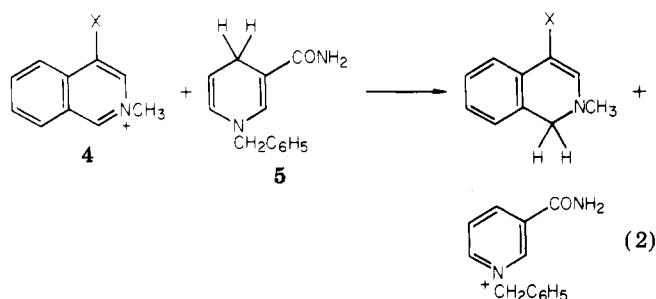
pared the influence of a 5-nitro substituent upon the rates of reduction of phthalazinium (**6** (X = H or NO$_2$)) and isoquinolinium cations.

6
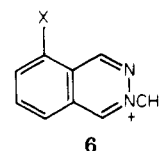
(1) Bunting, J. W.; Sindhuatmadja, S. *J. Org. Chem.* **1981**, *46*, 4211.