in one of the reservoir syringes of a Durrum-Gibson Model D-110 stopped-flow spectrophotometer, and a solution of the nucleophile (and, where appropriate, its conjugate acid) in 60% dioxane was placed in the other reservoir syringe. After the reactants were mixed, the course of the reaction was then monitored on the storage oscilloscope at an appropriate wavelength. These wavelengths were the same as those used for runs employing conventional spectrophotometry. For those α-disulfones whose kinetics were followed only by stopped-flow spectrophotometry the wavelengths were as follows: *p*-chlorobenzyl α-disulfone, 246 nm; *m*-chlorobenzyl α-disulfone, 250 nm.

Pseudo-first-order rate constants for each run were determined from the slope of a plot of log $(A_t - A_\infty)$ vs. time. All plots showed excellent linearity, and duplicate runs showed excellent reproducibility.

Deuterium-Exchange Reactions of Trifluoromethyl Sulfones. The alkyl trifluoromethyl sulfone $RCH_2SO_2CF_3$ (R = *n*-Pr or Ph; 10–20 mg) was dissolved in 1 mL of 70% CD_3CN–30% D_2O containing the desired concentrations of sodium acetate and acetic acid, and the solution was placed in an NMR tube and kept at constant temperature. At appropriate time intervals the integrated NMR spectrum of the solution was measured, and from this the extent to which the protons on the methylene group adjacent to the sulfonyl function had undergone exchange with the deuterium of the solvent was determined. For the *n*-butyl sulfone the ratio of the integrated intensity of the signal for the methyl group to that for the hydrogens on the carbon α to the sulfonyl group was used to measure the degree of exchange. In the case of the benzyl sulfone the ratio of the integral for the aromatic protons of the phenyl group to the integral for the methylene group protons was employed.

That exchange in the presence of $[OD^-] = 0.002$ M was too fast to be able to be followed by the NMR procedure was shown by the fact that when *n*-butyl trifluoromethyl sulfone (60 mg), dissolved in 1 mL of 70% CD_3CN–30% D_2O, was placed in an NMR tube and 20 μL of a 0.1 N stock solution of sodium deuterioxide in D_2O was added, exchange of the protons on the carbon adjacent to the sulfone group was complete by the time (45 s) the NMR spectrum could be determined.

Acknowledgment. The support of this research by the Robert A. Welch Foundation (Grant D-650) is gratefully acknowledged.

Supplementary Material Available: Tabulation of results of individual kinetic runs with α-disulfones (Table II) and sulfonyl chlorides (Table V) (3 pages). Ordering information is given on any current masthead page.

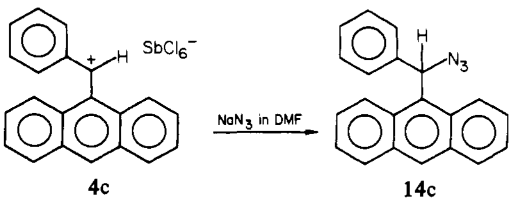
Reactions of (9-Anthryl)arylmethyl Chloride and Its Homologues with Nucleophiles under Solvolytic Conditions. Notable Effects of Reaction Conditions and Substituents on the Reaction Sites

Fujimaro Ogata, Masato Takagi, Masatomo Nojima,* and Shigekazu Kusabayashi

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan. *Received August 7, 1980*

Abstract: The reactions of (9-anthryl)arylmethyl chlorides **2a–e** (the substituents are *p*-MeO, *p*-Me, H, *p*-Cl, and *m*-Cl), the corresponding bromides **3b–d** (the substituents are *p*-Me, H, and *p*-Cl), and the antimonate salts **4b-e** (the substituents are *p*-Me, H, *p*-Cl, and *m*-Cl) with several nucleophiles have been examined. When **2** was allowed to react with sodium ethoxide, ethanol in the presence of triethylamine, sodium azide in aqueous DMF, and sodium borohydride in aqueous diglyme, a mixture of anthracene derivatives and compounds with a quinoidal structure was obtained. The yield of the quinoidal product increased as the substituent became increasingly electron withdrawing. The reaction of the bromide **3** gave also a mixture of an anthracene derivative and the quinoidal compound; the product composition was almost the same as that obtained by the reaction of **2**. By contrast, the preferential formation of the anthracene derivatives was observed in the reactions of the antimonate salt **4** with the same nucleophiles. When **2** was treated with sodium borohydride in trifluoroacetic acid, only the anthracene hydrocarbon was isolated. The reaction of 9-(diphenylmethylene)-10-chloro-9,10-dihydroanthracene (**6a**) under the same conditions, however, yielded predominantly the thermodynamically less stable quinoidal compound **28a**. When (10-methylanthracen-9-yl)benzyl chloride (**9a**) was allowed to react with several nucleophiles, the corresponding quinoidal compounds were obtained in good yields. However, the reactions of (10-phenylanthracen-9-yl)benzyl chloride (**9b**) and the corresponding antimonate salt **11b** gave mainly the anthracene derivatives. In the case of 9-benzylidene-10-isopropyl-10-chloro-9,10-dihydroanthracene (**9c**), the product composition remarkably depends on the nucleophilicity of reagent; sodium ethoxide, a powerful nucleophile, attacks predominantly the benzylic site. In contrast, the quinoidal compound **30c** was the main product when ethanol was the nucleophile. A mechanism which emphasizes the role of a tight ion pair for attack by a nucleophile on the ring site and that of a free ion (and a solvent-separated ion pair) for attack on the benzylic site has been proposed to explain the effects of reaction conditions and the substituents on the reaction sites.

Recently we reported[1,2] that the reaction of (9-anthryl)benzyl hexachloroantimonate (**4c**) with the nucleophiles H_2O, ^-OH, MeOH, ^-OMe, EtOH, ^-OEt, ^-Oi-Pr, and $^-N_3$ gave exclusively products with the anthracene structure by attack of a nucleophile on the benzylic site (eq 1). By contrast, the reaction of (9-anthryl)benzyl chloride (**2c**) with the same nucleophiles in protic solvents yielded a mixture of anthracene derivatives and com-

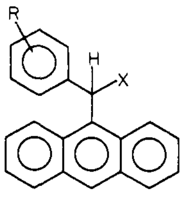


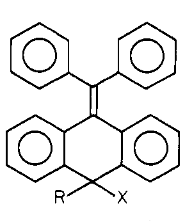
4c 14c (1)

---

[1] Takagi, M.; Ogata, F.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2948.

[2] Takagi, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2941.

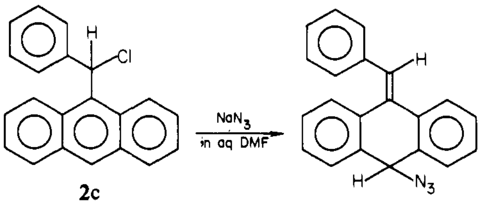




1a, R = *p*-OMe, X = OH
1b, R = *p*-Me, X = OH
1c, R = H, X = OH
1d, R = *p*-Cl, X = OH
1e, R = *m*-Cl, X = OH
2a, R = *p*-OMe, X = Cl
2b, R = *p*-Me, X = Cl
2c, R = H, X = Cl
2d, R = *p*-Cl, X = Cl
2e, R = *m*-Cl, X = Cl
3b, R = *p*-Me, X = Br
3c, R = H, X = Br
3d, R = *p*-Cl, X = Br

5a, R = H, X = OH
5b, R = Me, X = OH
5c, R = Ph, X = OH
6a, R = H, X = Cl
6b, R = Me, X = Cl
6c, R = Ph, X = Cl

pounds with a quinoidal structure (eq 2).[1] The reactions of

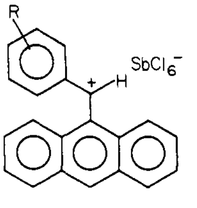


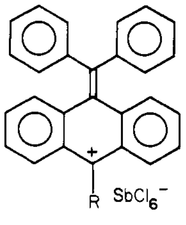
2c

15c

+ 14c (2)

9-(diphenylmethylene)-9,10-dihydro-10-anthracenium hexachloroantimonate (**7a**) with the same nucleophiles gave mainly

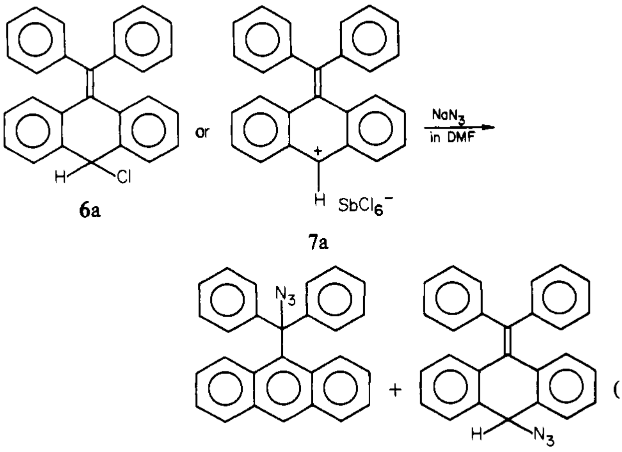




4b, R = *p*-Me
4c, R = H
4d, R = *p*-Cl
4e, R = *m*-Cl

7a, R = H
7c, R = Ph

the quinoidal products by attack on the 10-position of the anthracene ring (eq 3).[2] For the reactions of 9-(diphenyl-



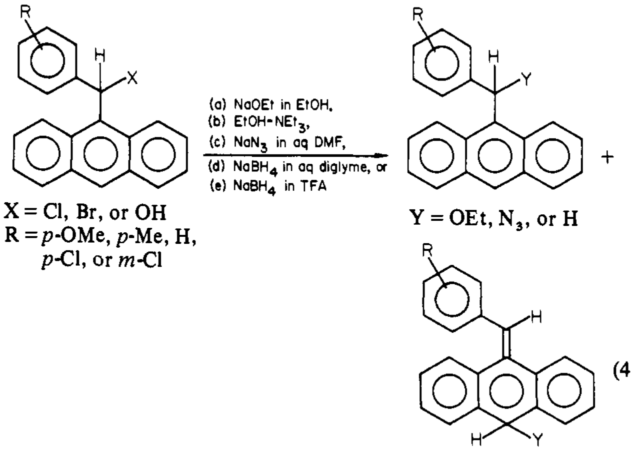
6a

7a

(3)

from 6a, 50:50
from 7a, 30:70

methylene)-10-chloro-9,10-dihydroanthracene (**6a**), however, data were obtained which suggest that approach of nucleophile to the 10-position is more hindered than in the case of **7a** (eq 3).[2] It is important, we believe, to elucidate the factors which give rise to these unprecedented differences in the behavior between the chloride and the antimonate salt, not only because the elucidation may lead to some useful information for the sake of syntheses of thermodynamically less stable quinoidal compounds and understanding of their properties[3] but also because it may serve to obtain further insight into the well-investigated solvolysis mechanism.[4] In the light of these results, we have examined the reactions of (9-anthryl)arylmethyl chlorides **2a–e**, the bromides **3b–d**, and the antimonate salts **4b–e** with several nucleophiles under solvolytic conditions (eq 4 and 5). The reactions of (10-methylanthracen-9-yl)benzyl chloride (**9a**) and its homologues were also investigated, with the expectation of clarifying the effect of the substituent at the 10-position of anthracene on the reaction sites.

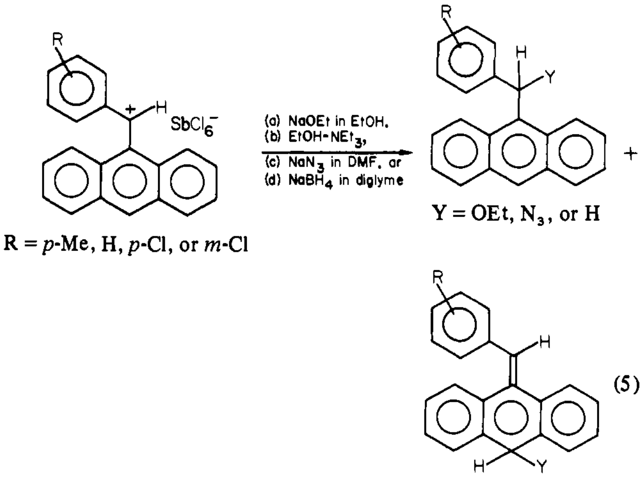


X = Cl, Br, or OH
R = *p*-OMe, *p*-Me, H,
p-Cl, or *m*-Cl

Y = OEt, N_3, or H

(4)

Y = OEt, N_3 or H



R = *p*-Me, H, *p*-Cl, or *m*-Cl

Y = OEt, N_3, or H

(5)

Y = H

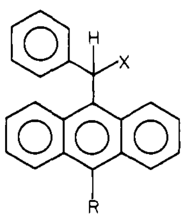
Results and Discussions

Reaction of (9-Anthryl)arylmethyl Chloride and Its Homologues. The reaction of the chloride **2** with sodium ethoxide in ethanol (Table I) or with ethanol in the presence of triethylamine[5] (Table

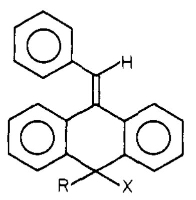
---

(3) (a) Jaeger, C. W.; Kornblum, N. *J. Am. Chem. Soc.* **1972**, *94*, 2545. (b) Rappoport, Z.; Greenblatt, J.; Apeloig, Y. *J. Org. Chem.* **1979**, *44*, 3687 and references cited therein. (c) Cho, H.; Harvey, R. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1140. (d) Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141. (e) Hart, H.; Ruge, B. *Tetrahedron Lett.* **1977**, 3143. (f) Bowden, B. F.; Cameron, D. W. *J. Chem. Soc., Chem. Commun.* **1977**, 78. (g) Bowden, B. F.; Cameron, D. W. *Tetrahedron Lett.* **1977**, 383.

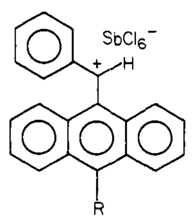
(4) (a) Bentley, T. W.; Schleyer, P von R. *Adva. Phys. Org. Chem.* **1977**, *14*, 1-67. (b) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348. (c) Ritchie, C. D.; Gandler, J. *J. Am. Chem. Soc.* **1979**, *101*, 7318 and references cited therein. (d) Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; Cornell University Press: New York, 1969. (e) Bunton, C. A. "Nucleophilic Substitution at a Saturated Carbon Atom"; Elsevier: New York, 1963. (f) Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962. (g) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89-173. (h) Winstein, S.; Appel, B.; Baker, R.; Diaz, A. *Spec. Publ.—Chem. Soc.* **1965**, *No. 19*, 109.



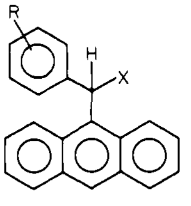
8a, R = Me, X = OH
8b, R = Ph, X = OH
8c, R = *i*-Pr, X = OH
9a, R = Me, X = Cl
9b, R = Ph, X = Cl



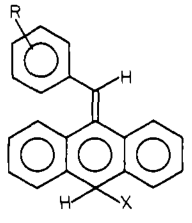
10a, R = Me, X = OH
10b, R = Ph, X = OH
10c, R = *i*-Pr, X = OH
9c, R = *i*-Pr, X = Cl



11b, R = Ph
11c, R = *i*-Pr



12a, R = *p*-OMe, X = OEt
12b, R = *p*-Me, X = OEt
12c, R = H, X = OEt
12d, R = *p*-Cl, X = OEt
12e, R = *m*-Cl, X = OEt,
14a, R = *p*-OMe, $X = N_3$
14b, R = *p*-Me, $X = N_3$
14c, R = H, $X = N_3$
14d, R = *p*-Cl, $X = N_3$
14e, R = *m*-Cl, $X = N_3$
16a, R = *p*-OMe, $X = N = PPh_3$
16e, R = *m*-Cl, $X = N = PPh_3$
18a, R = *p*-OMe, X = H
18b, R = *p*-Me, X = H
18c, R = X = H
18d, R = *p*-Cl, X = H
18e, R = *m*-Cl, X = H
20c, R = H, X = O-*t*-Bu
22c, R = H, X = OMe



13b, R = *p*-Me, X = OEt
13c, R = H, X = OEt
13d, R = *p*-Cl, X = OEt
13e, R = *m*-Cl, X = OEt
15a, R = *p*-OMe, $X = N_3$
15b, R = *p*-Me, $X = N_3$
15c, R = H, $X = N_3$
15d, R = *p*-Cl, $X = N_3$
15e, R = *m*-Cl, $X = N_3$
17a, R = *p*-OMe, $X = N{=}PPh_3$
17b, R = *p*-Me, $X = N{=}PPh_3$
17e, R = *m*-Cl, $X = N{=}PPh_3$
19b, R = *p*-Me, X = H
19c, R = X = H
19d, R = *p*-Cl, X = H
19e, R = *m*-Cl, X = H
21c, R = H, X = O-*t*-Bu
23c, R = H, X = OMe

II) gave a mixture of the compound with the anthracene derivative **12** and the quinoidal compound **13**. From the *p*-methoxy derivative **2a**, however, the anthracene derivative **12a** was obtained exclusively. The **13**:**12** ratio increased as the substituent became increasingly electron withdrawing. When the antimonate salt **4** was treated with sodium ethoxide, however, **12** was obtained exclusively (Table I). Under the reaction conditions we examined for ethanolysis, the quinoidal compound **13** was found not to rearrange to the thermodynamically more stable anthracene derivative **12**. Thus, it may be concluded that products were formed under kinetically controlled conditions. The similar difference for the sites of capture between the chloride **2** and the antimonate salt **4** was also observed in the reaction with sodium azide; a mixture of **14** and **15** was obtained in the reaction of **2** in aqueous DMF, and the ratio again depended on the substituent (Table III). In addition, the **14d**:**15d** ratio did not change when the proportion of NaN_3 to the chloride **2d** was varied from 1.5 to 12. The same behavior was observed in the reaction of **3b**, too. By contrast, the reaction of the antimonate salt **4** in DMF yielded only the anthracene derivative **14**. When the chloride **2** was treated with sodium borohydride in aqueous diglyme, a mixture of **18** and **19** was obtained (Table IV). The reaction of **2** with the same nucleophile in trifluoroacetic acid (TFA),[6,7] however, gave exclusively the anthracene hydrocarbon **18** (**2e** was the exception) (Table V). Under the same conditions the alcohols **1** and **5** were easily reduced to give the corresponding hydrocarbons (Table V).

Table I. Reaction with Sodium Ethoxide[a]

substrate	react. time, min	product (% yield)[b]
2a	10	12a (80)
2b	10	12b:13b = 54:46 (82)
2c	15	12c:13c = 26:74 (86)
2d	10	12d:13d = 24:76 (96)
2e	30	12e:13e = 14:86 (91)
3b	15	12b:13b = 40:60 (91)
3c	10	12c:13c = 22:78 (91)
3d	30	12d:13d = 22:78 (94)
4b	5	12b (83)
4c	5	12c (95)
4d	5	12d (85)
4e	5	12e (69)
9a	5	29a:30a = 21:79 (88)
9b	5	29b (90)
9c	5	29c:30c = 68:32 (87)
11b	5	29b (74)
11c	5	29c:30c = 27:73 (73)

[a] The reaction with 3 molar equiv of sodium ethoxide in ethanol at 20 °C. [b] The isolated yield; the ratio of the products was calculated from the comparison of the peak areas of the NMR spectra of the crude products.

Table II. Reaction with Ethanol[a]

substrate	react. time, min	product (% yield)[b]
2a	10	12a (91)
2b	10	12b:13b = 49:51 (95)
2c	10	12c:13c = 33:67 (84)
2d	10	12d:13d = 21:79 (92)
2e	30	12e:13e = 13:87 (91)
3b	30	12b:13b = 50:50 (93)
4b	5	12b (69)
4c	5	12c (60)
4d	5	12d (76)
4e	5	12e (69)
9a	5	29a:30a = 10:90 (91)
9b	5	29b (93)
9c	5	29c:30c = 29:71 (95)
11b	5	29b (70)
11c	5	29c:30c = 31:69 (70)

[a] The reaction was performed in the presence of 3 molar equiv of triethylamine. [b] The isolated yield; the ratio of the products was calculated from the comparison of the peak areas of the NMR spectra of the crude products.

Table III. Reaction with Sodium Azide[a]

substrate	react. time, min	solvent	product (% yield)[b]
2a	10	aq DMF[c]	14a:15a = 75:25 (85)
2a	10	DMF	14a:15a = 68:32 (85)
2b	30	aq DMF	14b:15b = 37:63 (75)
2c	30	aq DMF	14c:15c = 33:67 (90)
2d	30	aq DMF	14d:15d = 28:72 (94)
2e	30	aq DMF	14e:15e = 24:76 (96)
3b	15	aq DMF	14b:15b = 36:64 (93)
3b	15	DMF	14b:15b = 32:68 (94)
3c	15	aq DMF	14c:15c = 26:74 (89)
3d	20	aq DMF	14d:15d = 26:74 (91)
4b	5	DMF	14b (61)
4c	5	DMF	14c (60)
4d	5	DMF	14d (65)
4e	5	DMF	14e (59)
9a	5	aq DMF	31a:32a = 27:73 (80)
9b	5	aq DMF	31b:32b = 45:55 (95)
11c	5	DMF	31c:32c = 52:48 (86)

[a] The reaction with 3 molar equiv of sodium azide. [b] The isolated yield; the ratio of the products was calculated from comparison of the peak areas of the NMR spectra of the crude products. [c] aq, aqueous.

---

(5) In the absence of triethylamine, the same mixture of products was obtained, but the quinoidal compound **13** rearranges slowly to **12** during the prolonged reaction in this condition.

(6) Gribble, G. W.; Kelly, W. J.; Bmery, S. E. *Synthesis* **1978**, 763.

(7) In trifluoroacetic acid **2**, **3**, **6**, and **9** generate the corresponding carbonium ions; the UV maxima (nm) are as follows: **2a**, 734 and 460; **2b**, 701 and 472; **2c**, 672 and 473; **2d**, 684 and 472; **2e**, 659 and 473; **3b**, 702 and 470; **3c**, 672 and 472; **3d**, 682 and 473; **6a**, 803 and 454; **6b**, 802 an d 460; **6c**, 825 and 412; **9a**, 663 and 450; **9b**, 680 and 463; **9c**, 667 and 460.

Table IV. Reaction with Sodium Borohydride in Aqueous Diglyme[a]

substrate	react. time, min	product (% yield)[b]
2a	30	18a (81)
2b	30	18b:19b = 45:55 (81)
2c	30	18c:19c = 42:58 (86)
2d	30	18d:19d = 33:67 (96)
2e	30	18e:19e = 33:67 (86)
3b	30	18b:19b = 46:54 (88)
3c	30	18c:19c = 37:63 (95)
3d	30	18d:19d = 32:68 (94)
4b[c]	5	18b:19b = 89:11 (59)
4c[c]	5	18c:19c = 80:20 (73)
4d[c]	5	18d:19d = 65:35 (80)
4e[c]	5	18e:19e = 73:27 (82)
6a	60	27a:28a = 40:60[d] (95)
6b	10	27b:28b = 65:35 (72)
6c	10	27c (85)[d]
9a	5	33a:34a = 45:55 (80)
9b	5	33b (90)
9c	5	33c:34c = 56:44 (95)
11b[c]	5	33b (90)
11c[c]	5	33c:34c = 40:60 (74)

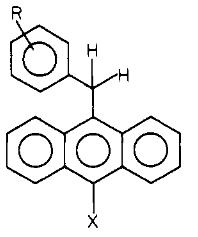
[a] The reaction was performed in 80% diglyme unless otherwise noticed. [b] The isolated yield; the ratio of the products was calculated from the comparison of the peak areas of the NMR spectra of the crude products. [c] The reaction was performed in diglyme. [d] The data are taken from ref 2.

Table V. Reaction with Sodium Borohydride in TFA[a]

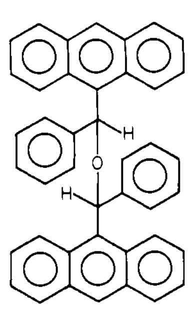
substrate	product (% yield)	substrate	product (% yield)
2a	18a (70)	6b	27b:28b = 40:60 (75)
2b	18b (95)	5b	27b:28b = 38:62 (70)
2c	18c (91)	6c	27c (85)
2d	18d (91)	5c	27c (67)
2e	18e:19e = 78:22 (91)	7c	27c (65)
1a	18a (74)	9a	33a (77)
1b	18b (78)	9b	33b (95)
1c	18c (95)	9c	33c (93)
1d	18d:19d = 68:32 (90)	8a	33a (95)
1e	18e:19e = 57:43 (91)	8b	33b (75)
6a	27a:28a = 20:80 (68)	10a	33a (90)
5a	27a:28a = 10:90 (60)	10b	33b (84)
7a	27a:28a = 25:75 (60)	10c	33c (85)

[a] The reaction was performed in trifluoroacetic acid (TFA) at 0 °C for 5 min. [b] The isolated yield; the ratio of the products was calculated from the comparison of the peak areas of the NMR spectra of the crude products.

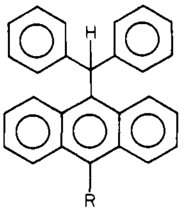
Although 15% of **19d** rearranges to the isomeric anthracene derivative **18d** under the reaction conditions, the exclusive formation of **18d** suggests that the hydride ion donor attacks only the benzylic site of the carbocation generated from **1d** under these conditions. The lower nucleophilicity of sodium borohydride in TFA would enable the latter reaction to proceed by the later and high-lying transition state to give the thermodynamically more stable hydrocarbon **18**.[8] However, the following facts suggest that there may be also another reason for the above results: in the same conditions the reaction of **6a** gave the less stable isomer **28a** with a quinoidal structure in higher yield compared with that in aqueous diglyme (Table IV and V). Similarly, the higher **27b**:**28b** ratio was observed in the reaction of **6b** in aqueous diglyme compared with that in TFA. Different from the case of other substrates, the reactions of both 9-(diphenylmethylene)-10-phenyl-10-chloro-9,10-dihydroanthracene (**6c**) and the antimonate salt **7c** with some hydride ion donors afforded only the anthracene derivative **27c**, suggesting that the phenyl ring attached to the 10-position is not on the same plane as the anthracene ring, and approach of nucleophile to this site is difficult. Treatment of salt **4c** with sodium borohydride in diglyme[9] afforded a mixture of **18c** and **19c**. However, the **18c**:**19c** ratio in this reaction (80:20) was remarkably higher than that obtained in the reaction of **2c** in aqueous diglyme (42:58) (Table IV).



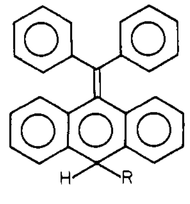
25b, R = *p*-Me, X = OEt
25d, R = *p*-Cl, X = OEt
25e, R = *m*-Cl, X = OEt
26c, R = H, X = O-*t*-Bu



24c



27a, R = H
27b, R = Me
27c, R = Ph



28a, R = H
28b, R = Me
28c, R = Ph

It is remarkable that the product compositions obtained by the reactions of the bromide **3** were very similar to those obtained by the reactions of the chloride **2**. Of course, the bromide **3** reacts faster than **2**;[10] the reaction of **3c** with potassium *tert*-butoxide in *tert*-butyl alcohol gave a mixture of the anthracene derivative **20c** and the quinoidal compound **21c**, in contrast to the quantitative recovery of **2c** under the same conditions. All the quinoidal compounds we prepared rearranged to the anthracene derivatives under the thermodynamically controlled conditions (Experimental Section).

In summary, the reactions of chloride **2** and bromide **3** with sodium ethoxide in ethanol, ethanol in the presence of triethylamine, sodium azide in aqueous DMF, and sodium borohydride in aqueous diglyme gave a mixture of the compounds with a quinoidal structure and the anthracene derivatives, and the electron-withdrawing group promoted the formation of the quinoidal compound in higher yield. In contrast, the same nucleophiles except sodium borohydride attack exclusively the benzylic site of **4** to give the anthracene derivatives. The reaction of **2** with sodium borohydride in TFA also occurs at the benzylic site.

The following facts suggest that the reactions of **2** and **3** proceed via the formation of cationic species. (1) The reaction of **2c** with sodium azide in anhydrous DMF was complete only after 24 h.[1] By contrast, **2c** disappeared in 30 min when the reaction was performed in aqueous DMF. Considering the low nucleophilicity of sodium azide in protic solvent,[11] ionization of **2c** should be rate determining at least for the reaction in aqueous DMF. Consistently, the preliminary kinetic run (the reaction of **2e** with 2 molar equiv of sodium azide in 95% DMF at 20 °C, which was followed by the conventional conductometric technique) obeyed the first-order rate law (rate constant, 1.6×10^{-4} s^{-1}). As is expected from the stability of the carbonium ions generated, the reactions of **2a**, **3b**, and **6a** in anhydrous DMF, however, were complete in 15 min. (2) For attack of a weak nucleophile such as ethanol on the ring position to occur, considerable charge distribution at this position is necessary. This can only be accomplished by ionization of **2**. (3) Lithium aluminum hydride reduction in ether, in which ionization of **2c** does not seem to be important, gave **18c** predominantly.[1] By contrast, sodium boro-

---

(8) (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. (b) Pross, A. *Adv. Org. Chem.* **1977**, *14*, 69–132.

(9) The reaction in aqueous diglyme gave only the corresponding alcohol 1.

(10) Church, M. G.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1940**, 966.

(11) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.

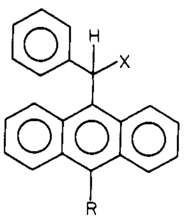
Table VI. Reaction with Sodium Methoxide[a] or Methanol[b]

substrate	nucleophile	product (% yield)[c]
3c	NaOMe	22c:23c = 30:70 (89)
9a	NaOMe	35a:36a = 57:43 (85)
9b	NaOMe	35b (95)
9c	NaOMe	35c:36c = 57:43 (93)
11b	NaOMe	35b (95)
11c	NaOMe	35c:36c = 22:78 (73)
9a	MeOH	35a:36a = 11:89 (94)
9b	MeOH	35b (95)
9c	MeOH	35c:36c = 20:80 (92)

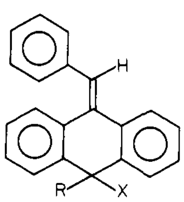
[a] The reaction with 10 molar equiv of sodium methoxide in methanol. [b] The reaction was performed in the presence of 3 molar equiv of triethylamine. [c] The isolated yield; the ratio of products was calculated from the comparison of the peak areas of the NMR spectra of the crude products.

hydride reduction in aqueous diglyme, in which ionization of **2** is well established to be rate determining,[12] gave **19** in good yield. Thus, it seems reasonable to conclude that the cationic species from **2** and **3**, compared with the antimonate salt **4**, are prone to be attacked by nucleophiles at the 10-position of the anthracene ring.

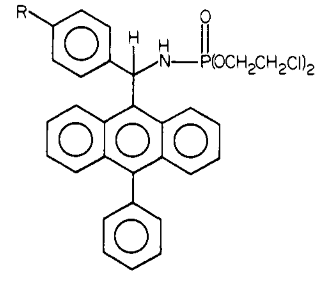
Reaction of (10-Methylanthracen-9-yl)benzyl Chloride and Its Homologues. When (10-methylanthracen-9-yl)benzyl chloride (**9a**) was allowed to react with sodium ethoxide in ethanol, a mixture of the anthracene derivative **29a** and the quinoidal compound **30a** was obtained (Table I). It is noteworthy that the **29a**:**30a** ratio (21:79) is lower than the **12c**:**13c** ratio (26:74) obtained by the reaction of **2c** with the same nucleophile. The same relation for the product compositions is found to hold for the reactions with ethanol (Table II) and with sodium azide (Table III). These results may be explained in terms of the advantageous increase of positive charge at the 10-position by substituting the C-10 hydrogen of **2c** with a methyl group; in this case the effect of crowding at C-10 on the product composition seems to be minor. The quinoidal compounds **30a**, **32a**, **34a**, and **36a** rearranged completely to the isomeric anthracene derivatives **29a**, **31a**, **33a**, and **35a**, respectively, under the thermodynamically controlled conditions (Experimental Section). After a phenyl group was substituted, however, a remarkable retardation of attack by a nucleophile on the anthracene ring was observed: the nucleophiles H^-, ^-OMe, MeOH, ^-OEt, and EtOH attacked selectively the benzylic sites of (10-phenylanthracen-9-yl)benzyl chloride (**9b**) and the antimonate salt **11b**. In a high population of the conformer of **11b**, the dihedral angle between the phenyl ring and the anthracene ring is expected to be ~67°.[13] This must prevent the approach of a nucleophile on the ring position of **11b**, whereas nucleophile attack at this position might be favored due to the advantageous charge density. However, sodium azide, a small nucleophile, attacked both the ring and the benzylic site of **9b** in aqueous DMF (eq 6 and Table VII). The labile quinoidal compound **32b** was characterized by converting it to the corresponding amidophosphate **47** (eq 7). This behavior of **9b** is in marked contrast to that of 9-(diphenylmethylene)-10-phenyl-10-chloro-9,10-dihydroanthracene (**6c**); the reaction of **6c** gives



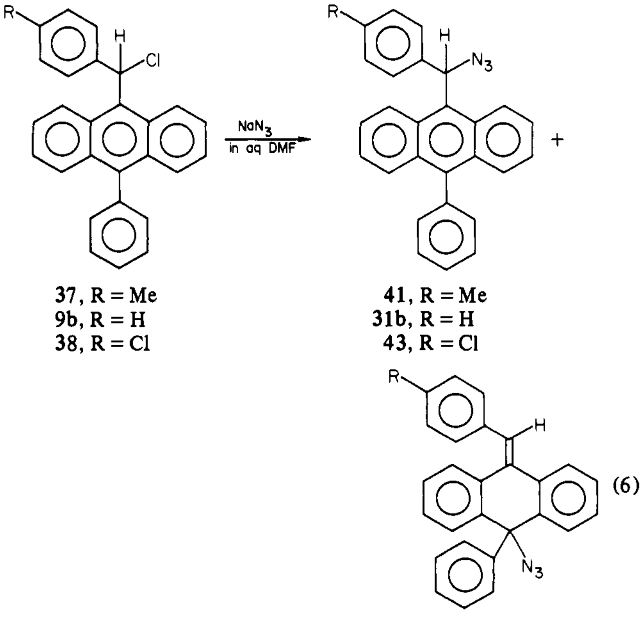
29a, R = Me, X = OEt
29b, R = Ph, X = OEt
29c, R = *i*-Pr, X = OEt
31a, R = Me, X = N_3
31c, R = *i*-Pr, X = N_3
33a, R = Me, X = H
33b, R = Ph, X = H
33c, R = *i*-Pr, X = H
35a, R = Me, X = OMe
35b, R = Ph, X = OMe
35c, R = *i*-Pr, X = OMe



30a, R = Me, X = OEt
30c, R = *i*-Pr, X = OEt
32a, R = Me, X = N_3
32c, R = *i*-Pr, X = N_3
34a, R = Me, X = H
34b, R = Ph, X = H
34c, R = *i*-Pr, X = H
36a, R = Me, X = OMe
36c, R = *i*-Pr, X = OMe



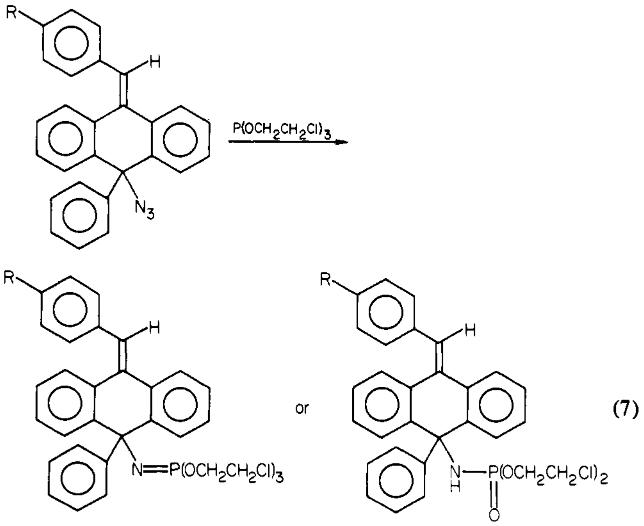
48, R = Me
49, R = Cl



37, R = Me
9b, R = H
38, R = Cl

41, R = Me
31b, R = H
43, R = Cl

42, R = Me
32b, R = H
44, R = Cl



45, R = Me
46, R = Cl

47, R = H

---

(12) Bell, H. M.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 1473.

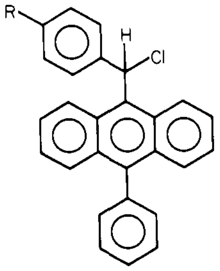
(13) Bergmann, E. D.; Robinovitz, A.; Aroney, M. J.; Le Fèvre, R. J. W.; Radom, L.; Ritchie, G. L. D. *J. Chem. Soc. B* **1968**, 1551.

Table VII. Reaction of (10-Phenylanthracen-9-yl)benzyl Chloride with Sodium Azide[a]

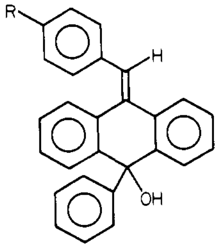
chloride	proportion of NaN_3	solvent	react. time, min	product (% yield)[b]
37	1.5	aq DMF	20	41:42 = 76:24 (85)
37	3	aq DMF	20	41:42 = 76:24 (83)
37	9	aq DMF	20	41:42 = 72:28 (90)
37	15	aq DMF	20	41:42 = 71:29 (85)
9b	1.5	aq DMF	20	31b:32b = 75:25 (87)
9b	3	aq DMF	20	31b:32b = 65:35 (85)
9b	6	aq DMF	20	31b:32b = 63:37 (83)
9b	15	aq DMF	20	31b:32b = 60:40 (85)
38	1.5	aq DMF	20	43:44 = 65:35 (88)
38	3	aq DMF	20	43:44 = 64:36 (85)
38	9	aq DMF	20	43:44 = 64:36 (85)
38	15	aq DMF	20	43:44 = 58:42 (83)
37	3	DMF	10	41 (30)[c,d]
37	3	DMF	120	41 (75)[c,d]
9b	3	DMF	120	31b (52), 29b (40)[c]
9b	3	DMF	1440	31b (90)[c]
11b	3	DMF	5	31b (65)

[a] The reaction was performed at 20 °C. [b] The yield of the anthracene derivative isolated by column chromatography on silica gel (Experimental Section). [c] The ratio of the products was estimated from comparison of the absorbance of the UV spectrum of the crude products at 310 (the quinoidal compound) and 376 nm (the anthracene derivative). When the substrate was 37, the ratio was calculated from the comparison of the peak areas of the NMR spectra of the crude products; the ratio obtained by this method was identical with that obtained by the UV spectroscopy. [c] After workup the reaction mixture was treated with ethanol to convert the unreacted chloride to the corresponding ethyl ether. [d] (10-Phenylanthracen-9-yl)-*p*-methylbenzyl ethyl ether was also obtained as a product; 20% for 2 h of reaction and 60% for 10 min of reaction.

exclusively (10-phenylanthracen-9-yl)diphenylmethyl azide.[2] In the latter case the benzylic site, in spite of the existence of large steric hindrance, must be exclusively attacked by N_3^- because of the advantageous charge density on this position. In the reactions of **37**, **9b**, and **38**, the yield of the quinoidal compound increased as the substituent became increasingly electron withdrawing. In addition, the increase of the proportion of sodium azide resulted in the increase of the yield of the quinoidal compound. The reaction of the antimonate salt **11b**, however, afforded only the anthracene derivative **31b**. When the reaction was performed in DMF, the rate of disappearance of the chloride was quite slow (40% recovery of the starting material **9b** after reacting for 2 h).



37, R = *p*-Me
38, R = *p*-Cl



39, R = *p*-Me
40, R = *p*-Cl

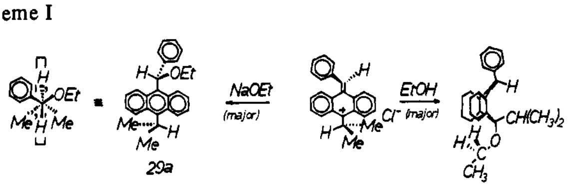
The effect of an isopropyl group at the 10-position on the relative thermodynamic stabilities of the compounds with anthracene and quinoidal structures are remarkable. Treatment of (10-isopropylanthracen-9-yl)benzyl alcohol (**8c**) with a trace amount of sulfuric acid in aqueous dioxane gave **10c** quantitatively. Under the thermodynamically controlled conditions, equilibrium mixtures of **29c** and **30c** (27:73) and **35c** and **36c** (21:79) were obtained. The following may be the reasons for these results. The molecular models and the NMR data suggest that the α-methine proton of isopropylanthracene exists on the same plane as the anthracene ring (see the discussion in ref 2). As a result, there are two hydrogens which eclipse the hydrogens of the anthracene ring at the 1-, 4-, 5-, and 8-positions in the case of (9-α-substituted-benzyl)-10-isopropylanthracene (in the case of **33c**, however, there exists only one hydrogen). In contrast, the quinoidal compound, which is known to have a boat conformation with the bulkier substituent in the pseudoaxial position,[3d] is not subject to such peri interactions (Scheme I). In connection with this, Cho, Harvey, and Rabideau have found that 9-isopropylidene-10-isopropyl-9,10-dihydroanthracene is more stable than the isomeric hydrocarbon 9,10-diisopropylanthracene.[3c] When the substituent of a quinoidal compound at the 10-position becomes larger, however, the interaction of this substituent (which occupies the pseudoequatorial position, when it is less bulkier than isopropyl group) with two phenyl rings increases, compelling this compound to be unstable as the isomeric anthracene derivative (Scheme I). There seems to be a high kinetic barrier between **33c** and **34c**; the appropriate conditions could not be found in which the hydrocarbon rearranges to another isomer (Experimental Section). Not consistent with the behavior of **2a–e**, **3b–d**, and **9a**,**b**, the reaction sites of **9c** depend on the nucleophilicity of reagent. When NaN_3, NaOEt, and NaOMe were the nucleophiles, the anthracene derivatives were obtained predominantly. However, the less powerful nucleophiles EtOH and MeOH (Table VI) attacked mainly the ring position (Scheme I). From the view of electrostatic interaction between the cationic species from **9c** and a nucleophile, the ring site may be an advantageous position. Thus, for a weak nucleophile attack on the ring site may be favorable. Because of the existence of large steric hindrance for approach of nucleophile to this position, however, powerful nucleophile is prone to attack the less charge-developed and less crowded benzylic site. The similar dependency of the reaction sites of nucleophiles has been observed in the reactions of **6a** and **6c**.[2] When **6c**, for example, was allowed to react with sodium ethoxide, 9-(*p*-ethoxydiphenylmethyl)-10-phenylanthracene was obtained quantitatively, while ethanol attacked both the 10-position of the anthracene ring and the benzylic site to yield 9-(diphenylmethylene)-10-phenyl-10-ethoxy-9,10-dihydroanthracene and 9-(α-ethoxydiphenylmethyl)-10-phenylanthracene, respectively. The reactions of the antimonate salt **11c** yielded predominantly quinoidal derivatives; consistent with the behavior of the other salts **4b–e**, **6a**, and **11b**, nucleophile is prone to attack the salt **11c** at the position where the leaving group was originally bonded. In summary, the smaller hindrance for approach of nucleophile to the ring position and the greater instability of the anthracene derivative in the case of the 10-isopropyl derivative compared with the 10-phenyl derivative must be the reason for the appearance of the notable effect of the isopropyl group on the reaction sites of **9c** and **11c**.

Mechanism. The behavior of the chlorides **2a–e**, **6a**, and **9a–c** and also the bromides **3b–d** as ambident electrophiles is remarkably different from that of the corresponding antimonate salts. The small difference in stability between an anthracene derivative and a quinoidal compound[3b] must be responsible for our unprecedented results.[14] Thus, the positions attacked will be affected by a small perturbation in our reactions. It may be needless to say that the charge density of the benzylic site and that of the ringe site, along with the steric crowding at the 10-position of the anthracene ring (as are shown in the cases of **6c**, **9b**, and **9c**), must be important factors to decide the sites to be attacked: the decrease of reactivity at C-10 in the chloride **2** with an electron-donating group is interpreted in terms of the decrease of effective charge of a cationic species from **2** at this position as the result of the increased charge density on the aryl ring. In the reactions of **9a–c** also, the variation of charge distribution by substituting the C-10 hydrogen of **2c** with a substituent seems to be reflected on the data. To explain the difference in the behavior between the cationic species from the chloride and the antimonate salt, however, it seems to be

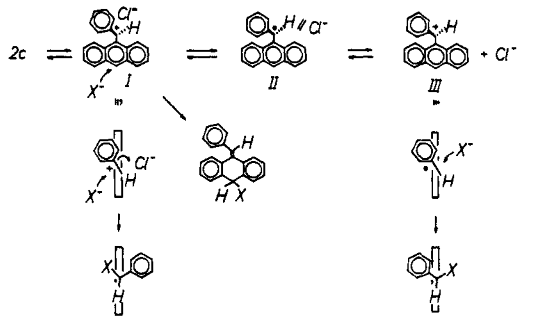
---

[14] (a) Zaugg, H. E.; Michaels, R. J.; Baker, E. J. *J. Am. Chem. Soc.* **1968**, *90*, 3800. (b) Lorand, J. P.; Bartlett, P. D. *Ibid.* **1966**, *88*, 3294. (c) Schoepfle, C. S.; Trepp, S. G. *Ibid.* **1936**, *58*, 791. (d) Brook, A. G.; Gilman, H.; Miller, L. S. *Ibid.* **1953**, *75*, 4759 (e) Hoffmann, H.; Schellenbeck, P. *Chem. Ber.* **1966**, *99*, 1134. (f) Heck, R.; Magee, P. S.; Winstein, S. *Tetrahedron Lett.* **1964**, 2033.

Scheme I



Scheme II



necessary to consider the additional factors.

The chloride **2** under solvolytic conditions is reasonably expected to generate a series of progressively more dissociated intermediates, i. e., the tight ion pair I, the solvent-separated ion pair II, and the free ion III (Scheme II).[15] The ground state of the carbonium ion is considered to be represented by the conformation in which the plane containing the benzylic carbon and three atoms bonded with it is not on the same plane as the anthracene ring because of the large interaction between the bulky phenyl group and the hydrogens at the 1- and 8-positions.[2,3b] The closer association of Cl^- in the tight ion pair I is expected to block nucleophile attack from that side.[16,17] However, approach from the opposite side also seems to be difficult because the phenyl ring and the approaching nucleophile are crowded together.[18,19] Furthermore, the phenyl ring (or the bonded nucleophile) has to pass over the anthracene ring by rotation of the single bond containing C-9 of the anthracene ring so the product can adopt a more favorable conformation; in the most favorable conformation of α,α-disubstituted (9-anthryl)methane, hydrogen, the smallest substituent, exists on the same plane as the anthracene ring (Scheme II).[2] Thus, it may be concluded that the reaction at the benzylic site of the tight ion pair I is highly retarded from steric reasons. Electronic repulsion between a nucleophile and a gegenanion in I, however, may be a part of the reason; retardation of the reaction of the cationic species from **6a** at the 10-position (where the leaving group was bonded) has been observed,[2] in spite of the lack of steric hindrance for nucleophilic attack at this position from the backside. Alternatively, the tight ion pair may retain, to a degree, the configuration of the starting material, preventing nucleophilic attack from the backside.[20] The attack of a nucleophile on the 10-position of I, however, does not seem to be prevented by any reason discussed above and becomes to be advantageous if sufficient charge is developed on this position.[21,22] These proposals seem to be consistent with the important conclusions obtained by the reactions of ^{18}O-labeled para-substituted benzhydryl *p*-nitrobenzoate[23] and ^{18}O-labeled triphenylmethyl benzoate[24] in aqueous acetone (these substrates are highly relevant with **2** and the related substrates for the carbocation stability[25] and steric crowding at the benzylic site): in the former substrate, not a tight ion pair but a solvent-separated ion pair is trapped by azide ion to yield an inversed product in excess, while in the latter substrate capture of azide ion proceeds predominantly by way of triphenylmethyl species which have become dissociated and no longer contain the OBz portion of the original ROBz molecule.[26] Approach of the nucleophile to the benzylic site of a fully dissociated carbonium ion III (and a solvent-separated ion pair II) must be easy because of the lack of steric interactions and/or electronic interactions with the remote anion. As a result, the formation of a thermodynamically more stable anthracene derivative should become a favorable process in the case of III (and II). In summary, we would like to propose the following hypotheses: (a) a tight ion pair generated from **2** is prone to be attacked by a nucleophile at the ring position while (b) attack on a free ion (and a solvent-separated ion pair) occurs exclusively at the benzylic site.

With consideration of the low nucleophilicity of the gegenanions ($SbCl_6^-$ and Cl^- strongly solvated by TFA) and the stability of the carbonium ion, the antimonate salt **4** in a solvent with high ionizing power and the cationic species generated from **2** by dissolving in TFA are expected to exist mainly as a free carbonium ion III (and a solvent-separated ion pair II), giving the anthracene derivative exclusively.[27] By contrast, the reaction of **4c** with sodium borohydride in ether, in which the salt **4c** seems to be present in the form of ion aggregate or tight ion pair making benzylic site blocked by the bulky gegenanion(s), however, affords a mixture of **18c** and **19c** in the molar ratio of 43:57.[1,28] The notable dependency of the product composition on solvent found in the reactions of **2a** with sodium azide (the **14a**:**15a** ratios were 75:25 in aqueous DMF and 68:32 in DMF) may be interpreted in terms of the higher proportion of a free ion and a solvent-separated ion pair in aqueous DMF with higher ionizing power than in DMF.[4g] The same dependency of the product composition on solvent was also observed in the reactions of **3b** (Table III). The notable substituent effect on the reaction sites observed in the reactions of (9-anthryl)arylmethyl chlorides **2a–e** and (10-phenylanthracen-9-yl)arylmethyl chlorides **37**, **9b**, and **38** may be explained in terms of the proposed hypotheses: it has been well documented that an increase in stability of the cation fragment generally results in an increase in degree of dissociation,[29] i.e.,

---

(15) Raber, D. J.; Harris, J. M.; Schleyer, P. von R. *Ions Ion Pairs Org. React.* **1974**, *2*, 247–374.

(16) Product formation by nucleophilic attack on a tight ion pair occurs, in most cases, with inversion of configuration.

(17) (a) Lambert, J. B.; Putz, G. J.; Mixan, C. E. *J. Am. Chem. Soc.* **1972**, *94*, 5132. (b) Nordlander, J. E.; McCrary, T. J. *Ibid.* **1972**, *94*, 5133.

(18) When the solvolysis of optically active cyclooct-2-enyl 3,5-dinitrobenzoate labeled with deuterium at C-1 was examined, more than 90% of the product was obtained with retention of configuration and with no deuterium scrambling. Wiberg and Nakahira[19] interpreted this result as being consistent with minimal allyl participation in the solvolysis mechanism and with steric interactions restricting the attack at the backside of the carbon bearing the leaving group.

(19) Wiberg, K. B.; Nakahira, T. *Tetrahedron Lett.* **1974**, 1773.

(20) (a) Merritt, M. V.; Bronson, G. E.; Baczynskj, L.; Boal, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 346. (b) Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. von R. *Ibid.* **1970**, *92*, 2538. (c) Grunwald, E.; Heller, A.; Klein, F. S. *J. Chem. Soc.* **1957**, 2604.

(21) The LCAO–MO calculation of (9-anthyrl)methyl cation suggests that the charge density on the 10-position is the same as that of the methyl carbon.[22]

(22) Streitwieser, A., Jr.; Brauman, J. I. "Supplemental Tables of Molecular Orbital Calculations"; Pergamann Press: London, 1965; Vol. 1, p 377.

(23) (a) Goering, H. L.; Levy, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 120. (b) Goering, H. L.; Hopf, H. *Ibid.* **1971**, *93*, 1224.

(24) (a) Winstein, S.; Appel, B. R. *J. Am. Chem. Soc.* **1964**, *86*, 2718, (b) *Ibid.* **1964**, *86*, 2720.

(25) The relative stability between (9-anthryl)-*p*-methoxybenzyl cation and triphenylmethyl cation seems to be comparable, while the (9-anthryl)diphenylmethyl cation is more stable than triphenylmethyl cation; **2a** dissociates in CH_2Cl_2 with the development of a dark green color, while the reaction of triphenylmethyl hexachloroantimonate with **6a** gave exclusively **7a**.

(26) These results must lead to the expectation that the benzylic site of I is not attacked by a nucleophile. The same results, however, do not necessarily deny the possibility that the reactive C-10 of I is attacked by a nucleophile. Of course, the degree of dissociation of the cationic species depends on the ionizing power of solvent,[4g] and thus the proportion of a free ion III and a solvent-separated ion pair II is expected to be considerably high in a solvent such as 80% DMF, considering the stability of the cationic species generated from **2**.

(27) Freedman, H. H. "Carbonium Ions"; Olah, G. A., Schleyer, P. von R., Ed.; Wiley-Interscience: New York, 1973; Vol. 4, pp 1501–1578.

(28) Olah, G. A.; Svoboda, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 3794.

(29) Gradual changes in stability for *para*-substituted benzhydryl *p*-nitrobenzoates appear to have little effect on the total amount of ion pair return, while external return (as measured by the common-ion rate depression) increases with stability.[23] This result has been interpreted as the increase in stability results in a greater amount of dissociation to the solvent-separated ion pair and more return from the solvent-separated ion pair.[4g]

as the substituent becomes increasingly electron withdrawing, the proportion of a tight ion pair to a free ion plus a solvent-separated ion pair increases, which results in the formation of a quinoidal compound in higher yield. As pointed out previously, however, the variation of the charge density at the ring position may be an alternative reason for the substituent effect. It is more likely that the concurrent operation of these factors reflects on the data.

In connection with our proposals, it is important to notice that there exists a remarkable difference between an ion pair and a free ion in an ambident nucleophile for the sites of attack by an electrophile, originally noticed by Kornblum,[30] has now been well recognized;[31] a free anion has a tendency to react at the most electronegative site, while the attack of an electrophile is prone to occur at the site not complexed by the countercation in the case of an ion pair. As a reasonable extrapolation, the similar difference for the reaction sites between an ion pair and a free ion is expected to appear in the reaction of cationic species with ambident character, if some circumstances are satisfied: (a) the counteranion is complexed tightly at the most electropositive site, preventing nucleophile attack from the front side, (b) attack by a nucleophile from the backside is also restricted because of steric interactions and/or some other reasons, and (c) the site not complexed by a counteranion is sufficiently reactive, and the product obtained by attack on this position has a reasonable stability. Incidentally the substrates **2a–e**, **3b–d**, **6a–c**, and **9a–c** used in this work may be the compounds which satisfy the above conditions.[32,33]

Summary

The reactions of (9-anthryl)arylmethyl chloride **2** with several nucleophiles under solvolytic conditions have been examined to give, along with the anthracene derivatives, the thermodynamically less stable quinoidal compounds in good yields. In contrast, the corresponding antimonate salt **4** afforded exclusively the anthracene derivatives. So that these results could be explained, a hypothesis has been proposed: a tight ion pair generated from **2** by ionization is prone to be attacked by a nucleophile on the position not bearing the leaving group. It is true this hypothesis is somewhat intuitive, but all the data reported in this work and also in the previous papers[1,2] do not seem to be inconsistent with the proposal. More important is that this proposal is necessary to predict the reaction conditions for the syntheses of new and thermodynamically unfavorable quinoidal compounds (or in some cases anthracene derivatives) from **2** and its homologues in good yields. This idea is currently being subjected to experimental test.

Experimental Section

General. ^{1}H NMR spectra were obtained with a JNM-PS-100 spectrometer in $CDCl_3$. MS data were obtained with a Hitachi RMU-6H spectrometer, infrared spectra with a Hitachi 215 spectrometer, and UV spectra with a Varian Techron 635 spectrometer in dioxane unless otherwise noted.

9-Anthrylbenzyl alcohol (**1c**),[1] 9-(diphenylmethylene)-10-hydroxy-9,10-dihydroanthracene (**5a**),[34] 9-(diphenylmethylene)-10-phenyl-10-hydroxy-9,10-dihydroanthracene (**5c**), (10-methylanthracen-9-yl)benzyl alcohol (**8a**),[35] (10-phenylanthracen-9-yl)benzyl alcohol (**8b**),[36] 9-benzylidene-10-methyl-10-hydroxy-9,10-dihydroanthracene (**10a**),[37] 9-benzylidene-10-phenyl-10-hydroxy-9,10-dihydroanthracene (**10b**),[36] 9-anthrylbenzyl chloride (**2c**),[1] 9-(diphenylmethylene)-10-chloro-9,10-dihydroanthracene (**6a**),[38] 9-(diphenylmethylene)-10-chloro-10-phenyl-9,10-dihydroanthracene (**6c**)[38] (10-methylanthracen-9-yl)benzyl chloride (**9a**),[35] 9-anthrylbenzyl hexachloroantimonate (**4c**),[1] 9-(diphenylmethylene)-9,10-dihydro-10-anthracenium hexachloroantimonate (**7a**),[2] and 9-(diphenylmethylene)-10-phenyl-9,10-dihydro-10-anthracenium hexachloroantimonate (**7c**)[2] were prepared by the reported methods. The alcohols **1ab** and **1de** were prepared by reduction of the corresponding para and meta substituted 9-benzoylanthracene.[38] In a similar manner (10-isopropylanthracen-9-yl)benzyl alcohol (**8c**) was prepared from 9-benzoyl-10-isopropylanthracene. 9-(Diphenylmethylene)-10-methyl-10-hydroxy-9,10-dihydroanthracene (**5b**) was obtained by the reaction of 9-(diphenylmethylene)-10-anthrone with methylmagnesium iodide. Treatment of 9-benzylidene-10-anthrone with isopropylmagnesium bromide afforded 9-benzylidene-10-isopropyl-10-hydroxy-9,10-dihydroanthracene (**10c**). Similarly 9-(*p*-methylbenzylidene)-10-phenyl-10-hydroxy-9,10-dihydroanthracene (**39**) and 9-(*p*-chlorobenzylidene)-10-phenyl-10-hydroxy-9,10-dihydroanthracene (**40**) were prepared from the corresponding anthrones.

Preparation of Chlorides and Bromides. Dry HCl gas was bubbled through a solution of an alcohol (15 mmol) and anhydrous $CaCl_2$ (15 mmol) in CH_2Cl_2 (50 mL) at 20 °C for 20 min. After removal of $CaCl_2$ by filtration, the solvent was evaporated in vacuo. Then, the crude products were titurated with petroleum ether. The solid was collected and purified by recrystallization from an appropriate solvent (Table VI). The chlorides **1ab**, **1de**, **9a**, and **9c** were prepared by this method. Treatment of alcohols **1b–d** with 10 molar equiv of acetyl bromide at 40 °C for 20 min gave the corresponding bromides **3b–d**, respectively.

Preparation of Hexachloroantimonate Salt. The salts were prepared following the method of Holmes and Pettit,[39] by which they prepared diphenylmethyl hexachloroantimonate in a stable form. To a solution of a chloride (10 mmol) in CCl_4 (20 mL) was added a solution of $SbCl_5$ (10 mmol) in CCl_4 (20 mL) at 20 °C over 10 min. The solid was filtered, washed with CCl_4, and dried over $CaCl_2$ in vacuo.[1,2] All the operations were performed under nitrogen to avoid moisture. The salts **7a** and **7c** were stable in solutions and were purified by recrystallizations,[2] while salts **4b–e** and **11b–c** were unstable in solutions to afford gradually unidentified polymeric products with slow fading of the characteristic colors (the salts were fairly stable when kept in an inert atmosphere).[1] However, the sharp melting points and the characteristic UV absorptions (Table VI) suggested that these salts were almost pure (the UV spectra of these salts were identical with those of solutions of the corresponding chlorides in TFA).[7]

Reaction with Sodium Azide. A solution of (9-anthryl)-*p*-methylbenzyl chloride (**2b**) (1.0 g, 3.2 mmol) and sodium azide (0.62 g, 10 mmol) in 80% aqueous DMF (50 mL) was kept at 20 °C for 30 min. The NMR and UV spectra of the crude products suggested the existence of (9-anthryl)-*p*-methylbenzyl azide (**14b**) and 9-(*p*-methylbenzylidene)-10-azido-9,10-dihydroanthracene (**15b**) [NMR δ 2.32 (s, 3 H) and 5.40 (s, 1 H); UV 310 nm]. The anthracene derivative **14b** was isolated by triturating the crude products with benzene–petroleum ether. The mother liquor contained a large amount of the quinoidal azide, **15b**, but this compound could not be isolated in pure state because of lability for column chromatography on silica gel or alumina (**15b** rearranged to **14b** quantitatively during column chromatography). So that **15b** could be characterized, the mother liquor was treated with 1 molar equiv of triphenylphosphine in refluxing benzene for 2 h.[40] Trituration of the crude products with benzene–petroleum ether gave the quinoidal phosphazene **17b** in a pure state. The reactions of **2a** and **2e** afforded the quinoidal azides **15a** [NMR δ 3.80 (s, 3 H) and 5.42 (s, 1 H)] and **15e** [NMR δ 5.27 (s, 1 H); UV 309 nm], respectively, which were also characterized by converting them to the corresponding phosphazenes **17a** and **17e**, respectively. However, the quinoidal azides **15c** and **15d** were isolated in pure states by repeated fractional recrystallizations.

When **9a** was treated with sodium azide, a mixture of 9-benzylidene-10-methyl-10-azido-9,10-dihydroanthracene (**32a**) [NMR δ 1.73 (s, 3 H); UV 309 nm] and (10-methylanthracen-9-yl)benzyl azide (**31a**) was obtained in a molar ratio of 73:27. All the efforts to isolate **32a** (or to a form of phosphazene derivative) in a pure state failed. The following facts, however, suggested that the quinoidal compound **32a** really formed. The column chromatography of the crude products af-

---

(30) Kornblum, N.; Lurie, A. P. *J. Am. Chem. Soc.* **1959**, *81*, 2705.

(31) Le Noble, W. J. "Highlights of Organic Chemistry"; Marcel Dekker: New York, 1974; pp 821–840.

(32) In the simple allylic system, however, the dependency of the reaction sites on the reaction conditions due to the difference in the state of cationic species is difficult to determine because of the participation of a symmetrical intermediate as the predominant contributor for the formation of product in solvolysis.[33]

(33) (a) Goering, H. L.; Anderson, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 6469 and references cited therein. (b) Sneen, R. A. *Acc. Chem. Res.* **1973**, *6*, 46. In this article the author stresses the possibility of the participation of an asymmetric tight ion pair (along with a symmetric intermediate), in which the counter ion is closely associated in space with the allylic carbon atom to which it was covalently bonded; thus, a balance between charge density and steric factors determined the proportion of S_N2 and S_N2' product.

(34) Cognacq, J. -C.; Chodkiewicz. W. *Bull. Soc. Chim. Fr.* **1966**, 1995.

(35) Gibson, S.; Mosnaim, A. D.; Nonhebel, D. C.; Russell, J. A. *Tetrahedron*, **1969**, *25*, 5047.

(36) Julian, P. L.; Cole, W.; Diemer, G.; Schafer, J. G. *J. Am. Chem. Soc.* **1949**, *71*, 2058.

(37) Flynn, K. G.; Bergson, G. *Ark. Kemi.* **1967**, *27*, 393.

(38) Nojima, M.; Takagi, M.; Morinaga, M.; Nagao, G.; Tokura, N. *J. Chem. Soc., Perkin Trans. 1* **1978**, 488.

(39) Holmes, J.; Pettit, R. *J. Org. Chem.* **1963**, *28*, 1695.

(40) Leffler, J. E.; Honsberg, U.; Tsuno, Y.; Forsblad, I. *J. Org. Chem.* **1961**, *26*, 4810.

forded, along with resinous substances, the anthracene azide **31a** in a yield of 78%. (10-Isopropylanthracen-9-yl)benzyl azide (**31c**) and 9-benzylidene-10-isopropyl-10-azido-9,10-dihydroanthracene (**32c**) were isolated by column chromatography on silica gel.

The reaction of **9b** gave a mixture of **31b** and **32b**. From the crude products the anthracene derivative **31b** was isolated by recrystallization. The mother liquor was treated with 1 molar equiv of tris(2-chloroethyl) phosphite in benzene under reflux for 12 h to yield the corresponding amidophosphate **47**, which was isolated by column chromatography on silica gel.

The reaction of **9b** in DMF was performed as follows. To a solution of sodium azide (24 mmol) in DMF (15 mL) was added **9b** (8 mmol) in DMF (15 mL) during 5 min at 20 °C while a current of nitrogen was bubbled through. Then, the bubbling was continued with stirring for a further 2 h. The reaction mixture was poured into ice-cold potassium hydroxide, and the products were extracted with ether. After evaporation of ether, the reaction mixture was treated with ethanol for 30 min. The column chromatography of the crude products on silica gel afforded first **31b** (52%) and then **29b** (40%).

Reaction with Sodium Ethoxide. To a solution of sodium ethoxide (10 mmol) in ethanol (50 mL) was added **2b** (1.0 g, 3.2 mmol) in one portion, and the mixture was stirred at 20 °C for 10 min. Analyses by UV and NMR spectroscopies indicated that the products consisted of α-(9-anthryl)-*p*-methylbenzyl ethyl ether (**12b**) [NMR δ 2.19 (s, 3 H); UV 388 nm] and 9-(*p*-methylbenzylidene)-10-ethoxy-9,10-dihydroanthracene (**13b**) [NMR δ 2.32 (s, 3 H) and 5.25 (s, 1 H); UV 313 nm] in a molar ratio of 49:51. So that the quinoidal compound **13b** could be characterized, the mixture was treated with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol for 2 h (this treatment converted **13b** to **25b**). The column chromatography on silica gel using 1:10 benzene–petroleum ether gave first **12b** (0.48 g, 46%) and then 9-(*p*-methylbenzyl)-10-ethoxyanthracene (**25b**) (0.50 g, 49 %). The reaction of (10-methylanthracen-9-yl)benzyl chloride (**9a**) (1.0 g, 3.2 mmol) afforded a mixture of (10-methylanthracen-9-yl)benzyl ethyl ether (**29a**) and 9-benzylidene-10-methyl-10-ethoxy-9,10-dihydroanthracene (**30a**), which were isolated by column chromatography on silica gel using 1:10 benzene–petroleum ether. The first fraction contained **30a** (0.18 g, 18%), and the second fraction contained **29a** (0.70 g, 70%).

Reaction of 9c with Ethanol in the Presence of triethylamine. The chloride **9c** (1.0 g, 2.9 mmol) was added to ethanol (50 mL) containing triethylamine (1 mL) in one portion, and the mixture was allowed to react at 20 °C for 5 min. After workup the crude products were triturated with benzene–petroleum ether to afford **30c** (0.5 g, 50%). The column chromatography of the mother liquor on silica gel gave **29c** (0.25 g, 25%) and **30c** (0.2 g, 20%).

Reaction with Sodium Borohydride in Aqueous Diglyme. To a solution of sodium borohydride (0.5 g, 13.2 mmol) in aqueous 70% (v/v) diglyme (30 mL) was added **2b** (0.5 g, 1.6 mmol) at 20 °C for 10 min. The reaction was continued for a further 20 min under nitrogen. Column chromatography on silica gel (elution with 1:10 benzene–petroleum ether) afforded first 9-(*p*-methylbenzylidene)-9,10-dihydroanthracene (**19b**) (0.18 g, 40%). From the second fraction 9-(*p*-methylbenzyl)anthracene (**18b**) (0.19, 41%) was isolated.

Reaction of 9-(Diphenylmethylene)-10-methyl-10-chloro-9,10-dihydroanthracene with Sodium Borohydride in TFA. To a solution of $NaBH_4$ (0.6 g, 15.8 mmol) in TFA (20 mL) kept at 0 °C was added a mixture of **6b** (1.0 g, 2.5 mmol) and CH_2Cl_2 in 10 min. The reaction mixture was poured into ice-cold potassium hydroxide and extracted with ether. After evaporation of solvent, the crude products were triturated with benzene–petroleum ether to afford 9-(diphenylmethylene)-10-methyl-9,10-dihydroanthracene (**34a**). The column chromatography of the mother liquor on alumina gave 9-(diphenylmethyl)-10-methylanthracene (**33a**).

Reaction of a Salt. To a solution of sodium azide (0.65 g, 10 mmol) in DMF (30 mL) was added **4b** (2.0 g, 3.3 mmol) during 2 min at 20 °C while a current of nitrogen was bubbled through (the dark green color of **4b** disappeared during the reaction). The mixture was poured into ice-cold potassium hydroxide and extracted with ether. The NMR and UV spectra of the crude products only showed the existence of the azide with anthracene structure **14b**. Column chromatography on silica gel afforded **14b** in a yield of 61%.

The reactions of a salt with $NaBH_4$ (6 molar equiv) in TFA, $NaBH_4$ (8 molar equiv) in diglyme, and NaOEt (3 molar equiv) in EtOH were performed as above (see also the conditions described in Table II–V).

Reaction of 9c with Sodium Methoxide. The reaction of **9c** with sodium methoxide (10 molar equiv) was performed at 20 °C for 10 min in benzene–methanol (1:1) as solvent. Trituration of the crude products with methanol afforded (10-isopropyl-anthracen-9-yl)benzyl methyl ether (**35c**). Column chromatography of the mother liquor on silica gel gave 9-benzylidene-10-isopropyl-10-methoxy-9,10-dihydroanthracene (**36c**).

Reaction of 3c with Potassium *tert*-Butoxide. To a solution of potassium *tert*-butoxide (2g, 17.9 mmol) in *tert*-butyl alcohol (50 mL) was added **3c** (1.0 g, 3 mmol) in one portion and the mixture was kept at 35 °C for 10 min. Column chromatography of the crude products on basic alumina gave 9-anthrylbenzyl *tert*-butyl ether (**20c**) and 9-benzylidene-10-*tert*-butoxy-9,10-dihydroanthracene (**21c**). Treatment of **21c** with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol for 2 h afforded 9-benzyl-10-*tert*-butoxyanthracene (**26c**).

Relative Thermodynamic Stabilities of Compounds with Anthracene Structure and with Quinoidal Structure. When a mixture of **19b** and potassium *tert*-butoxide (10 molar equiv) in *tert*-butyl alcohol was heated under reflux for 4 h, the UV absorption of **19b** disappeared completely. With the use of column chromatography on alumina the anthracene hydrocarbon **18b** was isolated quantitatively. Under the same conditions the quinoidal compounds **19c–e**, **34a,b**, and **28a–c** rearranged to the corresponding anthracene derivatives **18c–e**, **33a,b**, and **27a–c**, respectively. However, 9-benzyl-10-isopropyl-anthracene (**33c**) and 9-benzylidene-10-isopropyl-9,10-dihydroanthracene (**34c**) were inert under these conditions; when **33c** or **34c** was treated under the same conditions, the hydrocarbon was recovered quantitatively. The quinoidal hydrocarbon **34c** was recovered quantitatively even after treatment with butyllithium (5 molar equiv) in ether at 20 °C for 2 h, followed by workup with ethanol. The reaction of **34c** with *p*-toluenesulfonic acid in refluxing benzene gave the complex mixture. Under these conditions the anthracene hydrocarbon **33c** was stable.

The reaction of a mixture of 9-(*p*-methylbenzylidene)-10-ethoxy-9,10-dihydroanthracene (**13b**) and a trace amout of concentrated H_2SO_4 in refluxing ethanol afforded the anthracene derivative **12b** quantitatively. Under the same conditions the quinoidal ethyl ethers **13c–e** and **30a** rearranged to the anthracene derivatives **12c–e** and **29a**, respectively. When the reactions of the quinoidal methyl ethers **23c** and **36a** with a trace amount of concentrated H_2SO_4 in methanol were performed under reflux for 2 h, the corresponding methyl ethers with anthracene structures **22c** and **35a**, respectively, were obtained quantitatively.

A mixture of **29c** and small amounts of H_2SO_4 in ethanol was kept at 80 °C for 2 h. The UV and NMR spectra of the crude products showed that they contained **29c** (27%) and **30c** (73%). The reaction of **30c** under the same conditions gave the same mixture. Treatment of **35c** with a trace amount of H_2SO_4 in refluxing methanol for 2h gave the equilibrating mixture of **35c** (21%) and **36c** (79%). The same equilibrating mixture of **35c** and **36c** was also obtained from **36c** under the same conditions. When the quinoidal alcohol **10a** was treated with the same acid catalyst at 60 °C for 2 h, the anthracene derivative **8a** was obtained quantitatively. Similar behavior was observed in the reaction of **10b**. In contrast, the reaction of **8c** under the same conditions afforded **10c** quantitatively.

A solution of **15b** and sodium azide (1 molar equiv) in aqueous DMF was stirred at 60 °C for 3 h, from which was isolated **14b** in a yield of 90%. Column chromatography on silica gel or on alumina also compelled the rearrangement of **15b**. Similar behavior was observed in the cases of **15a**, **15c–e**, and **32a**. The rate of the rearrangement of **15e** was, however, very slow; the rearrangement was found to complete, when the reaction mixture was kept at 80 °C for 5 h. Under these conditions 63% of **31c** rearranged to **32c**.

Supplementary Material Available: A listing of the physical properties of the substrates and products (Table VIII) (9 pages). Ordering information is given on any current masthead page.