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Molten Salt Catalyzed Transfer Hydrogenation of Polycyclic Aromatic Hydrocarbons. Selective Hydrogenation of Anthracene and Naphthacene by Tetralin in Molten Antimony Trichloride[†]

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Anthracene and naphthacene are selectively hydrogenated by tetralin to 9,10-dihydroanthracene and 5,12-dihydronaphthacene, respectively, in a reaction that is catalyzed by molten $SbCl_3$ at 80 °C. In situ ^1H NMR studies indicate that under similar conditions, phenanthrene and pyrene do not react, while perylene is partially oxidized to a persistent radical cation. For the tetralin transfer hydrogenation of anthracene and naphthacene, product analysis shows that no naphthalene is formed, but that the dehydrogenated tetralin reacts with itself and unreacted arene to give alkylated products. These transfer hydrogenation reactions can best be explained by a redox initiated ionic mechanism involving the arene radical cation and the 1-tetralyl cation (1,2,3,4-tetrahydro-1-naphthalenylium ion) as key intermediates.

Introduction

Hydroaromatics have been widely investigated as hydrogen donor solvents for direct coal liquefaction. Research on coal or coal model compounds[1-4] has generally occurred under high-temperature pyrolysis conditions in which the hydroaromatic, such as tetralin (1,2,3,4-tetrahydronaphthalene), acts as a hydrogen donor for thermally generated radicals. Transfer hydrogenations can often be performed at much lower temperatures by employing a heterogeneous or homogeneous catalyst.[5] Molten metal halides such as $ZnCl_2$ are known to be effective catalysts for hydrocracking coal,[6] and a recent study has shown that in combination with tetralin as a hydrogen donor, a protonic $ZnCl_2$ melt (10% H_2O added) catalyzes the liquefaction of subbituminous coal at quite moderate temperatures (250–300 °C),[7] presumably by means of proton assisted Friedel–Crafts catalysis. With the tetralin present the degree of coal conversion was only slightly influenced by the presence of hydrogen gas.

During our basic studies of molten salt catalysis, we found that molten, anhydrous $SbCl_3$ (another effective molten salt hydrocracking catalyst for coal[8]) is an active medium for hydrogen redistribution reactions for polycyclic aromatic hydrocarbons (arenes) at low temperatures, 100–130 °C.[9-12] Under aprotic conditions we observed both catalytic[9,10] and stoichiometric[11,12] involvement of $SbCl_3$ resulting from redox chemistry in the melt in which Sb^{3+} is an oxidant. This redox function has also been suggested as playing a role in hydrocracking reactions catalyzed by anhydrous $ZnCl_2$.[13] In this investigation we examine whether tetralin can act as a hydrogen donor in $SbCl_3$ melts to a group of arenes of widely varying oxidizability under conditions in which arene radical cations are believed to be reactive intermediates.

Results

Anthracene. The ^1H NMR spectrum of an equimolar

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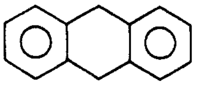
(1) Tsai, M.-C.; Weller, S. W. *Fuel Process Technol.* **1979**, 2, 313.
(2) Franz, J. A.; Camaioni, D. M. *Prepr., Div. Fuel Chem., Am. Chem. Soc.* **1981**, *26*(1), 105.
(3) Collins, C. J.; Raaen, V. F.; Benjamin, B. M.; Kabalka, G. W. *Fuel* **1977**, *56*, 107.
(4) Benjamin, B. M.; Raaen, V. F.; Maupin, P. H.; Brown, L. L.; Collins, C. J. *Fuel* **1978**, *57*, 269.
(5) Brieger, G.; Nestrick, T. J. *Chem. Rev.* **1974**, *74*, 567.
(6) Zielke, C. W.; Struck, R. T.; Evans, J. M.; Costanza, C. P.; Gorin, E. *Ind. Eng. Chem. Process Des. Dev.* **1966**, *5*, 151, 158; Zielke, C. W.; Klunder, E. B.; Maskew, J. T.; Struck, R. T. *Ibid.* **1980**, *19*, 85.
(7) Grens, E. A., II; Hershkowitz, F.; Holten, R. R.; Shinn, J. H.; Vermeulen, T. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 396.
(8) Wald, M. M. U.S. Patent 3542655, 1970.
(9) Dworkin, A. S.; Poutsma, M. L.; Brynestad, J.; Brown, L. L.; Gilpatrick, L. O.; Smith, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5299.
(10) Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P.; Buchanan, M. V.; Olerich, G. *Fuel* **1981**, *60*, 694.
(11) Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. *J. Am. Chem. Soc.* **1980**, *102*, 5262.
(12) Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. *J. Org. Chem.* **1981**, *46*, 471.
(13) Morita, M.; Hirosawa, K.; Sata, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1256 and references therein.

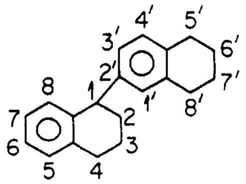
0022-3263/82/1947-0603$01.25/0

solution of anthracene and tetralin in molten $SbCl_3$ at 80 °C shows the immediate formation of 9,10-dihydroanthracene (DHA), whose spectrum gradually increases in intensity with time. No initial broadening of the anthracene spectrum is observed (vide infra). The ^1H NMR spectrum of DHA in $SbCl_3$ is characterized by a peak at δ 3.99 for the aliphatic protons and several peaks for the AA′BB′ pattern centered at δ 7.33 for the aryl protons which are resolved from the anthracene spectrum in which no peaks are further upfield than δ 7.5. Under similar conditions, anthracene in $SbCl_3$ without tetralin gives a highly broadened NMR spectrum of anthracene with the band broadening in the order $H_{9,10} > H_{1,4,5,8} > H_{2,3,6,7}$. This ordering also corresponds to the relative magnitude of the hyperfine coupling constants in the anthracene radical cation, and the broadening in the NMR spectrum is attributed to electron exchange between anthracene and small amounts of its radical cation. At longer reaction periods (>30 min) anthracene begins to slowly disproportionate via Scholl condensation as previously reported.[9] NMR also indicates that tetralin, alone, in $SbCl_3$ is totally unreactive over the temperature range studied, 80–125 °C.



A solution of tetralin and anthracene-d_{10} in $SbCl_3$ at 80 °C also shows the ^1H NMR midfield peak for the aliphatic protons of DHA, indicating that the tetralin is acting as the hydrogen donor. Also, anthracene ^1H peaks are observed to grow in slowly, implying that some proton–deuterium exchange is occurring in the melt.

The reaction coproducts and stoichiometry were determined from larger scale reactions run in Schlenk glassware under argon. GC analysis of the organic products from a reaction of equimolar anthracene and tetralin in $SbCl_3$ at 80 °C for 30 min shows that DHA is formed in 30% yield based on original anthracene. The DHA yield increases to 49% for a 165-min reaction period. GC–MS shows that no other hydroanthracenes are produced; therefore, the transfer hydrogenation is selective. Surprisingly, the dehydrogenated tetralin does not yield naphthalene as expected, but, instead, two main products incorporating the tetralyl moiety are observed by GC–MS and have masses of 262 and 308. One product (mass = 262) was collected by GC and identified by MS and ^1H and ^{13}C NMR as 1,2,3,4,5′,6′,7′,8′-octahydro-1,2′-binaphthalene (**1**). The other product (mass = 308) was separated by HPLC and identified by MS and ^1H NMR as 2-(1,2,3,4-tetrahydro-1-naphthyl)anthracene (**2**). DHA, **1**, **2**, unreacted anthracene, and tetralin account for better than 96% of the total organics. The remainder is comprised of several products with the largest two having masses of 308 and 310 from GC–MS. The former compound appears to be an isomer of **2**, probably substituted in the anthracene 1-position (vide infra), and the latter compound appears to be a dihydro derivative of **2**. No products resulting from the possible Scholl condensation reaction of anthracene[9] are observed for the 30-min reaction period. Even at the longer reaction time (165 min), only a minor amount of Scholl condensation is observed as indicated by the presence of ~2% 2,9′-bianthracene.



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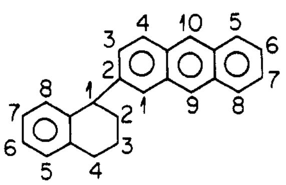

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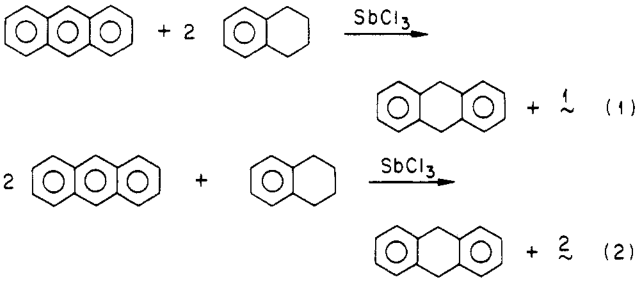
Table I. Influence of Tetralin Concentration on the Anthracene-Tetralin-$SbCl_3$ Reaction[a]

anthracene, mmol	tetralin, mmol	$SbCl_3$, mmol	DHA % yield[b]	1/2 yield,[c] mole ratio
1.40	0	34.2		
1.40	0.70	34.2	20	0.15
1.40	1.40	34.2	30	0.50
1.40	2.80	34.2	39	1.5
1.40	5.60	34.2	38	3.5
0.39	37.8	9.52		

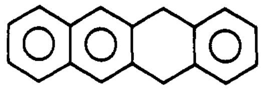
[a] Reactions were run at 80 °C for 30 min. [b] Based on original anthracene (±2%). [c] Based on GC area ratios.

Although the types of products do not change, the relative amounts of DHA, **1**, and **2** formed depend on the concentration of tetralin initially present as shown for a 30-min reaction period in Table I. Anthracene conversions range from 36% for an initial tetralin/anthracene mole ratio of 0.5 to 46% for an initial ratio of 4.0. The yield of DHA increases as the concentration of tetralin increases to a maximum of 39% at a tetralin/anthracene ratio of 2.0. No effort was made to maximize the DHA yield by optimizing other reaction parameters such as time, temperature, or anthracene concentration. The mole ratio of **1**/**2** also varies dramatically as a function of initial tetralin concentration (Table I) and increases with increasing concentration of tetralin. The overall reaction stoichiometry at any given tetralin/anthracene ratio can be represented as the sum of two limiting equations. Reaction 1 predominates at high tetralin/anthracene ratios, while reaction 2 predominates at low tetralin/anthracene ratios.

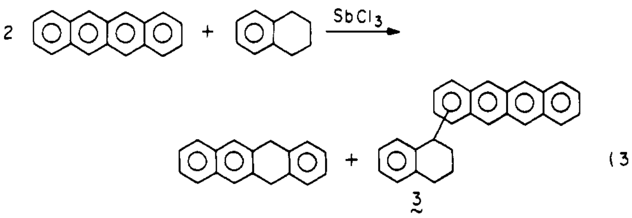


It should be noted that the presence of $SbCl_3$ is necessary for this transfer hydrogenation reaction to occur. Moreover, as the last entry in Table I indicates if tetralin is present in large excess such that it is actually the solvent and $SbCl_3$ is present as a homogeneous catalyst (with the same $SbCl_3$/anthracene ratio), no reaction takes place. It appears that the catalytic activity of the $SbCl_3$ resides in the $SbCl_3$ melt and not in molecular $SbCl_3$ dissolved in the organic solvent.

Naphthacene. The ^1H NMR at 80 °C of a solution of naphthacene in $SbCl_3$ without tetralin indicates that significant quantities of radical cation are formed and undergo electron exchange with the parent arene. In place of the naphthacene lines a very weak, broad absorption from about 7–9.5 ppm is observed. After several hours at 80 °C, naphthacene begins to disproportionate via Scholl condensation as did anthracene.[9] However, in the presence of an equimolar concentration of tetralin there is no perceptible line broadening in the NMR, and naphthacene reacts very rapidly at 80 °C. The formation of 5,12-dihydronaphthacene (DHN) can be immediately observed as evidenced by its characteristic midfield peak in the melt at δ 4.09 for the aliphatic protons.



Products have been identified from a larger scale reaction performed at 80 °C for 30 min with a tetralin/naphthacene mole ratio of 2 and the same molar concentration of naphthacene as was used in the anthracene experiments. The initial tetralin/naphthacene ratio chosen is the stoichiometry that maximizes the DHA yield in the anthracene reaction with tetralin (Table I). Naphthacene is found to be much more reactive than anthracene, and GC and HPLC-UV analyses show a 97% conversion of the naphthacene. GC-MS analysis reveals that the transfer hydrogenation is again very selective with DHN the only hydronaphthacene detected. Quantitative results from GC and HPLC-UV show that DHN is produced in 51 ± 2% yield based on initial naphthacene. The GC-MS results again show that no naphthalene is formed and that essentially all of the remainder of the organics can be accounted for by three compounds which incorporate the tetralyl moiety. These compounds include **1** and two isomers of a tetrahydronaphthyl-substituted naphthacene (**3**; mass = 358). The two isomers of **3** are formed in approximately equal amounts and are probably substituted at the 1- and 2-positions of naphthacene by analogy with the anthracene products. The mole ratio of **1**/**3** is about 0.12 rather than the 1.5 observed for **1**/**2** in the analogous anthracene reaction (Table I). Therefore, the reaction stoichiometry is represented principally by eq 3 (even in the presence of excess tetralin) with a small contribution from the naphthacene analogue to eq 1.



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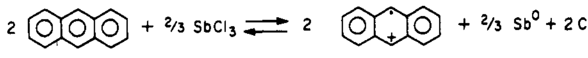
Phenanthrene and Pyrene. The ^{1}H NMR spectrum of an equimolar solution of phenanthrene or pyrene with tetralin in $SbCl_3$ shows no evidence for any chemical reaction in the melt over the temperature range studied (80–130 °C). The spectra of these arenes remain well resolved and similar to those obtained in conventional organic solvents like $CDCl_3$. Furthermore, these spectra show no line broadening suggestive of the presence of arene radical cation. These arenes also do not undergo the $SbCl_3$-catalyzed Scholl condensation reaction.[9]

Perylene. Perylene behaves in a still different manner. The ^{1}H NMR spectrum of an equimolar solution of perylene and tetralin in $SbCl_3$ at 80 °C shows only the signals attributable to tetralin. There is apparently an appreciable concentration of the perylene radical cation produced, and electron exchange with the neutral perylene results in the broadening of the perylene spectrum beyond detection. The NMR spectrum of this deeply colored solution (brown to green) does not change even after prolonged heating at 130 °C, suggesting that the perylene radical cation is quite persistent in the melt even in the presence of tetralin.

Discussion

The transfer hydrogenation reactions presented here appear to be initiated by the oxidation of the arene to its radical cation by the $SbCl_3$ melt. The arenes under study span a wide range of oxidizability in the melt with phenanthrene the most difficult to oxidize and naphthacene the easiest ($E_{1/2}$ values are shown in parentheses[14]): phenanthrene (0.9 V), pyrene (0.59 V), anthracene (0.51 V), perylene (0.24 V), and naphthacene (0.21 V). An earlier ESR study of dilute solutions of arenes in $SbCl_3$ melts demonstrated that anthracene, perylene, and naphthacene are oxidized to their corresponding radical cations, while pyrene is not oxidized.[15] Phenanthrene, which has an $E_{1/2}$ similar to that of naphthalene, has also been found not to be oxidized in $SbCl_3$. The correlation between the ESR results in $SbCl_3$ and the reactivity pattern observed for the arenes with tetralin in $SbCl_3$ suggests that only the arenes that can be oxidized by $SbCl_3$ to radical cations are capable of undergoing the transfer hydrogenation reaction. Although perylene is not hydrogenated, the ^{1}H NMR of the melt does indicate that, as expected, perylene is partially oxidized to its radical cation. However, the radical cation is surprisingly unreactive even at elevated temperatures and does not react with tetralin. The reason for the kinetic stability of the perylene radical cation in molten $SbCl_3$ is not known, but this behavior has been previously observed.[9]

The mechanism for the catalytic transfer hydrogenation of arenes by tetralin in $SbCl_3$ can be simply described in terms of a redox driven sequence of reactions as shown in eqs 4–9 for the particular example of anthracene. In the first step (eq 4) the reduced form of antimony in the melt is shown for convenience to be the metal. However, we now know that antimony can exist in stable oxidation states in the melt between 3+ and the metal.[16] These as yet unidentified lower oxidation states can serve as homogeneous electron carriers, and this ability to form lower oxidation states of antimony in the melt may contribute to the fact that the transfer hydrogenation reaction is catalyzed by $SbCl_3$ melts and not by molecular $SbCl_3$ dissolved in tetralin as solvent.



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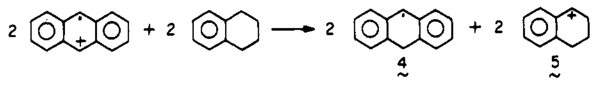

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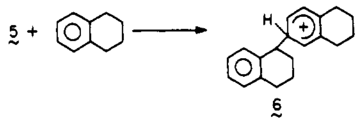

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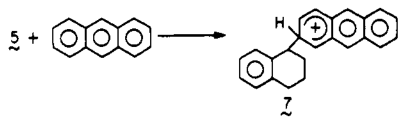

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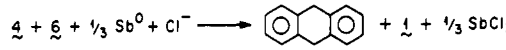

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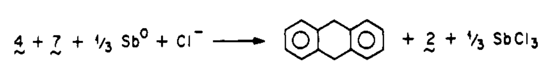

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It can be seen from eq 4 that the reduction of $SbCl_3$ liberates chloride. Therefore, the oxidizing power of the $SbCl_3$ melt can be decreased by addition of chloride donors

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[14] $E_{1/2}$ vs. $Sb^0/SbCl_3$ ($KSbCl_4$, saturated) at 99 °C; from Bauer, D.; Beck, J. P.; Texier, P. *Collect. Czech. Chem. Commun.* **1971**, *36*, 940. $E_{1/2}$ for phenanthrene is estimated from a correlation with $E_{1/2}$ values for arenes measured in acetonitrile from Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124.

[15] Buchanan, A. C., III; Livingston, R.; Dworkin, A. S.; Smith, G. P. *J. Phys. Chem.* **1980**, *84*, 423.

[16] Sørlie, M.; Smith, G. P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 931.

and increased by the addition of chloride acceptors as we have demonstrated previously.[15] Moreover, decreasing or increasing the oxidizing power of the $SbCl_3$ melt has been shown to respectively decrease[9] or increase[10] the catalytic activity of the melt. Consistent with these earlier observations we find that the addition of the chloride donor KCl to $SbCl_3$ drastically lowers the transfer hydrogenation reaction rate. For example, the reaction of anthracene and tetralin (1:2 mole ratio) in an $SbCl_3$ melt containing 8 mol % KCl at 80 °C results in only a 2% yield (rather than 39%) of DHA after the standard 30-min reaction period. Therefore, all our observations strongly indicate that reaction 4, the oxidation of the arene to its radical cation by $SbCl_3$, is the initial reaction step.

The radical cation thus generated must then abstract hydride from the tetralin 1-position (eq 5) to give the anthracenyl radical (**4**) and the 1-tetralyl cation (**5**). The observed selectivity in the formation of the alkylated products **1** and **2** and the dependence of their relative yields on the initial stoichiometry (Table I) implies that **5** then undergoes competitive electrophilic attack on tetralin (eq 6) and unreacted parent arene (anthracene in eq 7). The net reaction stoichiometry will then depend on the relative rates of reactions 6 and 7. As we showed earlier for the tetralin/anthracene mole ratios examined, reaction 7 is favored at mole ratios ≤ 1, while reaction 6 becomes favored when excess tetralin is present. For the case of the more reactive arene, naphthacene, the analogous reaction corresponding to eq 7 predominates even when excess tetralin is present. The selectivity for the formation of the particular isomers of **1** and **2** is also consistent with the known Friedel–Crafts alkylation chemistry of tetralin and anthracene. For tetralin the selectivity of the positional isomers formed upon alkylation depends on the nature of the catalyst, the size of the electrophile, and the reaction temperature.[17] With Lewis acid catalysts and bulky electrophiles, substitution at the tetralin 6-position is highly favored[17] as we have observed. For anthracene, alkylation with cyclohexyl cation yields only 1- and 2-substituted products with substitution at the 2-position highly favored.[18,19] The high selectivity for the formation of **2** from the attack of the 1-tetralyl cation on anthracene is again in agreement with these results from Friedel–Crafts alkylation studies. In the naphthacene reaction with tetralin, nearly equal amounts of two isomers of the alkylated product **3** were found, and these are assumed to be the 1- and 2-substituted naphthacenes by analogy with the anthracene chemistry.

Once intermediates such as **6** and **7** are formed, the ipso protons on the charged rings should be highly acidic, and these species should be rapidly deprotonated to yield the observed products **1** and **2**, respectively. The nature of the reoxidation step for the lower valent antimony species (necessary for the reaction to be catalytic in $SbCl_3$) is not known, and this process has been lumped together with the proton transfer in eq 8 and 9 to give the observed DHA.

Summary

Anthracene and naphthacene are selectively hydrogenated by tetralin at low temperatures in a reaction that is catalyzed by molten $SbCl_3$. Two key steps in the reaction mechanism appear to be the oxidation of the arene to its radical cation by Sb^{3+} and the transfer of hydride from tetralin to the arene radical cation. The resulting tetralyl cation does not ultimately yield naphthalene, but undergoes electrophilic aromatic substitution on unreacted tetralin and arene molecules.

Our studies of the chemistry of model compounds for some of the structural units in coal in $SbCl_3$ melts have shown that $SbCl_3$ is a very active catalyst for transferring hydrogen from one molecule to another even at low temperatures and without added hydrogen gas. This ability to catalyze hydrogen shuttling could play an important role in the liquefaction of coal in molten $SbCl_3$, especially in the presence of hydrogen donor solvents and at temperatures below those required for coal pyrolysis.

Experimental Section

Materials. $SbCl_3$ (mp 73 °C) was purified by sublimation and distillation as previously described.[11] The resulting material was further purified by repeated zone refining. The arenes were commercial reagents of the highest purity (99+ %) and were subsequently sublimed. Tetralin was distilled prior to use while anthracene-d_{10} (98+ atom % D, Aldrich) was used without further purification.

NMR. Reactions were studied in situ by ^1H NMR in 5-mm o.d. tubes (1-mm wall) filled with 0.016–0.023 g of the arene, 0.010–0.017 g of tetralin, and 0.8–1.0 g of $SbCl_3$, with the arene and tetralin at equimolar concentrations. The NMR tube was filled with the arene and $SbCl_3$ in a controlled atmosphere glove box whose argon atmosphere was continuously purified and monitored for moisture and oxygen content which amounted to <1 ppm each. Tetralin was added to the tube outside the glovebox by means of a calibrated syringe while the NMR tube was being purged with argon. The tube was then sealed under a reduced pressure of argon on a vacuum line.

^1H NMR measurements were made at 200.17 MHz on a Nicolet NT-200 Fourier transform, superconducting magnet spectrometer. The chemical shifts were referenced externally to $(CH_3)_4NCl$ (δ 3.12) in $SbCl_3$, which was itself separately referenced to $(CH_3)_4Si$ in the melt.

Separation and Identification. Products from the reactions of anthracene and naphthacene with tetralin in $SbCl_3$ were identified from larger scale reactions performed in Schlenk glassware under argon. For example, for an equimolar anthracene/tetralin reaction, 0.250 g (1.40 mmol) of anthracene, 0.185 g (1.40 mmol) of tetralin, and 7.80 g (34.2 mmol) of $SbCl_3$ were used. The reaction mixture was stirred at 80 °C for 30 min and then allowed to cool to room temperature. The reaction mixture was then hydrolyzed in 3 M HCl, and the organics were extracted into CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$, filtered, and then concentrated to ~50 mL by distillation at 39 °C under argon.

The organic products were analyzed by GC on a Bendix 2200 gas chromatograph with a flame ionization detector and a column containing Dexsil 300 on 80/100-mesh Chromosorb G-HP. GC–MS were obtained on a Hewlett-Packard 5985 GC–mass spectrometer using electron-impact ionization at 70 eV, and the chromatographic separations made on a 30 m × 0.25 mm i.d. glass capillary column coated with OV-101 liquid phase. HPLC was performed on a Waters liquid chromatograph with UV detection at 270 nm. Separations were made on a 50 × 0.94 cm i.d. Whatman Partisil M9-ODS-3 column with a $CH_3OH–H_2O$ mobile phase.

For the anthracene reactions, quantitative analyses for tetralin, anthracene, and DHA were made by GC, using hexamethylbenzene as an internal standard, and the results were corrected for differences in detector response. For the naphthacene reaction, naphthacene and DHN were quantitatively analyzed by GC, using 9,10-dimethylanthracene as an internal standard. Tetralin (and also naphthacene and DHN) were collected by HPLC, and quantitative results were calculated from their corresponding UV spectra obtained on a Cary 14 spectrophotometer.

Compounds 1 and 2. The CH_2Cl_2 layer from an anthracene–tetralin reaction was evaporated to dryness, and the organics

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[17] Patinkin, S. H.; Friedman, B. S. in "Friedel–Crafts and Related Reactions"; G. A. Olah, Ed.; Interscience: New York, 1964; Vol. 2, Part 1, pp 68–74.

[18] Saidova, F. M.; Sidorova, N. G. *Dokl. Akad. Nauk. Uzb. SSR* **1968**, *25*, 37; *Chem. Abstr.* **1969**, *70*, 57512t.

[19] It is possible that the initial attack of the electrophile occurs at the more reactive 9-position followed by isomerization.

were fractionated by sublimation. Compound 1 was collected as a colorless oil by preparative GC of a sublimation fraction (80 °C, 2×10^{-3} mmHg) on a 6 ft × 0.25 in. column packed with 5% SE-30 on Hal F-720. Approximately 1 mg of 1 was collected, dissolved in 50 μL of CD_2Cl_2, and transferred to a 1.7-mm o.d. NMR tube. The ^1H and ^{13}C NMR spectra of 1 were obtained on a JEOL FX-90Q spectrometer using a $^{13}C/^1H$ dual microprobe system and an internal ^2H lock. The ^1H spectrum was measured at 89.56 MHz, and the chemical shifts were referenced to the residual proton resonance at δ 5.31 (relative to Me_4Si) of CD_2Cl_2. The ^{13}C spectrum was measured at 22.50 MHz, and the chemical shifts were referenced to the CD_2Cl_2 ^{13}C resonance at δ 53.74 (relative to Me_4Si).

The ^1H chemical shifts (multiplicity, number of protons, and assignment are given in parentheses) for 1 are as follows: δ 6.6–7.3 (m, 7, H_{5-8} and $H_{1',3',4'}$), 3.99 (t, 1 H_1), 2.78 (m, 6, $H_{4,5',8'}$), 1.80 (m, 8, $H_{2,3,6',7'}$). The ^{13}C chemical shifts for 1 (with tentative assignments) are as follows: δ 45.6 (C_1), 33.6 (C_2), 21.5 (C_3), 30.1 (C_4), 137.9 (C_{4a}), 129.2 (C_5), 126.0 (C_6), 125.7 (C_7), 129.2 (C_8), 140.2 (C_{8a}), 130.3 ($C_{1'}$), 145.0 ($C_{2'}$), 126.3 ($C_{3'}$), 129.6 ($C_{4'}$), 135.1 ($C_{4a'}$), 29.3 ($C_{5'}$), 23.7 ($C_{6'}$), 23.7 ($C_{7'}$), 29.7 ($C_{8'}$), 137.2 ($C_{8a'}$). For comparison, the measured ^{13}C chemical shifts for tetralin were as follows: δ 29.7 ($C_{1,4}$), 23.6 ($C_{2,3}$), 137.5 ($C_{4a,8a}$), 129.3 ($C_{5,8}$), 125.6 ($C_{6,7}$). The mass spectrum (70 eV) of 1 is as follows: *m/e* (relative intensity) 262 (M^+, 24), 234 (8), 131 (19), 130 (100), 129 (19).

Compound 2 was found to be concentrated in the residue from the fractional sublimation. It was collected from the HPLC separation of this fraction on a 50 × 0.94 cm i.d. Whatman Partisil M9-ODS-3 column using a MeOH–H_2O (98:2) mobile phase. The ^1H NMR of approximately 1 mg of this white solid in CD_2Cl_2 was obtained with the JEOL microprobe system described above. The ^1H chemical shifts for the anthracene portion of **2** (with assignments by analogy with those reported for 2-methylanthracene[20]) are as follows: δ 8.37 (s, 1, H_{10}), 8.30 (s, 1, H_9), 7.93 (m, 3, $H_{4,5,8}$), 7.64 (s, 1, H_1), 7.42 (m, 2, $H_{6,7}$), 7.23 (d, 1, H_3). For the tetralin portion of **2**, the ^1H chemical shifts are as follows: δ 7.00 (m, 4, H_{5-8}), 4.31 (t, 1, H_1), 2.90 (m, 2, H_4), 1.94 (m, 4, $H_{2,3}$). The mass spectrum, (70 eV) of **2** is as follows: *m/e* 308 (M^+, 100), 309 (29), 280 (13), 279 (25), 278 (27), 178 (31), 139 (31), 132 (26), 131 (13), 130 (77), 129 (26).

Compound 3. Two isomers of **3** were observed by GC–MS and very similar mass spectra were measured. The mass spectrum (70 eV) of one isomer of **3** is as follows: *m/e* 358 (M^+, 100), 359 (30), 357 (14), 330 (12), 329 (18), 229 (10), 228 (32), 179 (10). The mass spectrum of the other isomer of **3** is as follows: *m/e* 358 (100), 359 (30), 357 (14), 330 (9), 329 (17), 229 (13), 228 (34), 179 (11).

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Registry No. 1, 80082-89-9; **2**, 80082-90-2; **3** (isomer 1), 80082-91-3; **3** (isomer 2), 80082-92-4; anthracene, 120-12-7; naphthacene, 92-24-0; tetralin, 119-64-2; $SbCl_3$, 10025-91-9.

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(20) Caspar, M. L.; Stothers, J. B.; Wilson, N. K. *Can. J. Chem.* **1975**, *53*, 1958.

Platinum-Catalyzed Racemization of 1,1′-Binaphthyl

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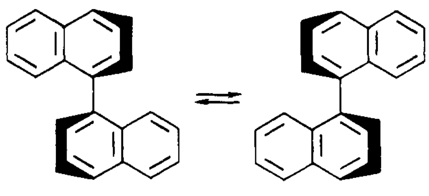
The racemization of 1,1′-binaphthyl in ethanol is subject to heterogeneous catalysis by platinum (prepared by reduction of platinum oxide with hydrogen). The rate of catalyzed reaction is first order in binaphthyl but independent of platinum concentration over a limited range. First-order rate constants at 25 °C decrease with increased binaphthyl concentration and are up to 12-fold that for the uncatalyzed racemization. Catalysis by platinum is stopped momentarily by the injection of air and is diminished by injection of cyclohexene or cyclohexane into the solution. Racemization therefore occurs on active sites which are also capable of reducing oxygen or cyclohexene. It is suggested that, for racemization of binaphthyl, these sites are acting as electron donors rather than hydrogen atom donors.

Racemization of 1,1′-binaphthyl is homogeneously catalyzed by formation of its radical anion[1–5] and heterogeneously catalyzed by active carbons or by electron-donor surfaces such as potassium–graphite compounds.[5] The heterogeneous catalysis on various carbon surfaces has been suggested to occur via adsorption on relatively large graphitic planes.[6] Such adsorption could lead to a planar intermediate state which most simply accounts for the racemization.

However, it has recently been shown that Raney nickel is also a catalyst for the racemization of binaphthyl.[7]



S enantiomer *R* enantiomer

Kinetic studies of this heterogeneous racemization were severely limited by its erratic character. Nevertheless, Raney nickel not only reduces binaphthyl to a biphenyl derivative but, with a suitably poisoned catalyst, also can racemize binaphthyl without any concurrent reduction. Adsorption to form a planar molecule, as suggested on carbon, seems unlikely on the more irregular surface of nickel. It was therefore of interest to determine more generally if another hydrogenation catalyst such as Adam's

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(1) O. Ito and M. Hatano, *Chem. Lett.*, 39 (1976).

(2) O. Eisenstein, J. P. Mazaleyrat, M. Tordeux, and Z. Welvart, *J. Am. Chem. Soc.*, **99**, 2230 (1977).

(3) M. Irie, T. Yorozu, K. Yoshida, and K. Hayashi, *J. Phys. Chem.*, 81, 973 (1977).

(4) M. F. M. Post, J. Langelaar, and J. D. W. Van Voorst, *Chem. Phys. Lett.*, **46**, 331 (1977).

(5) L. G. Hutchins and R. E. Pincock, *J. Org. Chem.*, **45**, 2414 (1980).

(6) R. E. Pincock, W. M. Johnson, and J. Haywood-Farmer, *Can. J. Chem.*, **54**, 548 (1976).

(7) L. G. Hutchins and R. E. Pincock, *J. Catal.*, in press.