Alkali Metals as Hydrogenation Catalysts for Aromatic Molecules[1]

SIDNEY FRIEDMAN,* MARVIN L. KAUFMAN, AND IRVING WENDER

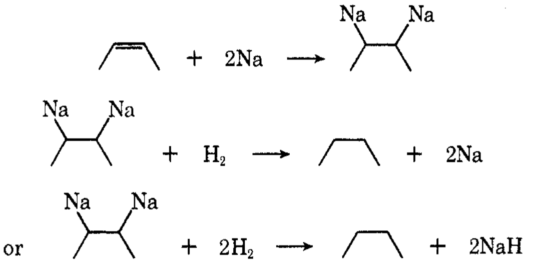
Pittsburgh Coal Research Center, Bureau of Mines,
U. S. Department of the Interior, Pittsburgh, Pennsylvania 15213

Alkali metals are hydrogenation catalysts for aromatic compounds at high temperatures and pressures. Catalytic activity increases from lithium to rubidium. It is unnecessary to use the more active metals as the free metal; mixtures of sodium metal and potassium carbonate produce results equivalent to those obtained with NaK alloy. The extent of hydrogenation depends on temperature and the metal used. Below 250°, polycyclics and polyphenyls can be reduced readily in benzene as solvent to compounds containing isolated benzene rings at initial hydrogen pressures of 1400 psig and temperatures of 180–250° with Na + Rb_2CO_3; above 250°, benzene forms hydrogenated dimers and higher polymers. *o*-Terphenyl hydrogenates and cyclizes to dodecahydrotriphenylene. Ethers are cleaved by the alkali metals as are some polycyclic heteroaromatic compounds. The use of amines as solvents permits hydrogenation at lower temperatures than with benzene.

Sodium in liquid ammonia has been used for many years as a reducing agent for aromatic systems,[2] and more recently both sodium and lithium in amines have become increasingly important.[3,4] In these reductions, the amines serve as proton donors; in liquid ammonia, an alcohol is usually added to furnish the hydrogen.[2]

There are also some instances known where ethers are used as solvents for reductions with alkali metals;[5] here, the alkali metal salt of the hydrocarbon is formed. Addition of water or alcohol then provides the necessary hydrogen to decompose the salt and form the reduced hydrocarbon. In these reactions, the alkali metal participates noncatalytically and is eventually converted to $M^+ B^-$, where M = Na or Li and B = OH, OR, or NR_2. The equivalent of an ionic carbon–metal bond is formed at some stage of the reaction.

Carbon–metal bonds, such as those formed in alkali metal reductions in nonpolar solvents, are known to hydrogenate readily.[6] Thus, if such a bond is formed in an atmosphere of hydrogen, reduction can take place to regenerate the metal or to form its hydride. The sodium hydride formed in eq 3 or 4 might also be capable of adding to a double bond,[7] providing an alternate pathway to the reduction product. In either case, these reactions would constitute a catalytic hydrogenation.

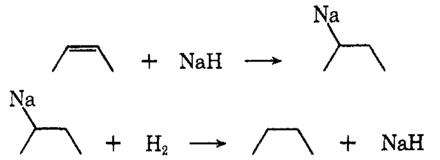


(1)

(2)

(3)

$$2NaH \rightleftharpoons 2Na + H_2 \qquad (4)$$



(5)

(6)

Several investigations have explored this catalytic system for hydrogenating aromatics, using alkali metals[8] and sodium hydride[7,9] as the initial catalysts, and in all cases hydrogenations have been achieved. However, most of the reported work has been confined to the reduction of naphthalene to tetrahydronaphthalene. We have investigated the system in more detail, studied the effects of other alkali metals and of other solvents, and applied it to compounds other than naphthalene, especially compounds of the type one might find in coal or coal tar.

Discussion

Initially, a series of reactions was conducted in which sodium metal, an aromatic hydrocarbon, and a solvent (benzene or toluene) were heated with hydrogen in a rocking autoclave to a specified temperature. The reaction product contained some white solid in suspension. Addition of isopropyl alcohol caused considerable reaction, with evolution of gas, presumably hydrogen from decomposition of NaH. Examination of the products by mass spectrometry and gas chromatography gave the results shown in Table I. These results indicated that sodium (or NaH) was a hydrogenation catalyst, and that careful control of temperature and pressure might allow stepwise hydrogenation to be carried out.

Similar experiments showed that lithium, which is a better reducing agent than sodium in metal–amine systems,[4] is a much poorer catalyst than sodium for hydrogenation of naphthalene. Lithium, due to its low density, floats on the surface of the reaction mixture and appears to be poorly dispersed during the reaction. Even at 325°, only 4% of the naphthalene is reduced. Limitations of the equipment prevented going to higher temperature.

Liquid sodium–potassium alloy (NaK), which probably behaves like potassium, was more active than sodium. As shown in Tables I and II, most of the hydrocarbons tried were hydrogenated to mixtures of products, with a few exceptions. The reductive cyclization of *o*-terphenyl to give *sym*-dodecahydrotriphenylene as a major product is one of the best available methods for

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[1] Presented before the Division of Fuel Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 30–Sept 4, 1964.

[2] A. J. Birch, *Quart. Rev.*, **4**, 69 (1950).

[3] G. W. Watt, *Chem. Rev.*, **46**, 317 (1950).

[4] (a) R. A. Benkeser, *Advan. Chem. Ser.*, **23**, 58 (1959). (b) L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).

[5] S. E. Hunt and A. S. Lindsey, *J. Chem. Soc.*, 2227 (1958); H. Mohler and J. Sorge, *Helv. Chim. Acta*, **22**, 229 (1939).

[6] H. Gilman, A. L. Jacoby, and H. Ludeman, *J. Amer. Chem. Soc.*, **60**, 2336 (1938).

[7] S. M. Blitzer and T. H. Pearson, U. S. Patent 2,987,558 (1961).

[8] F. W. Bergstrom and J. F. Carbon, *J. Amer. Chem. Soc.*, **63**, 2934 (1941). Guyot, *Chim. Ind. Spec.*, No. 410 (1928); *Chem. Abstr.*, **22**, 4522 (1928). N. A. Orlov and N. D. Likhachev, *Ber.*, **63B**, 2179 (1930).

[9] G. Hugel and Friess, *Bull. Soc. Chim. Fr.*, **49**, 1042 (1931); G. Hugel, *Can. Chem. Met.*, **13**, 5 (1929).

TABLE I

ALKALI METAL CATALYZED HYDROGENATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS

Compd	Catalyst	Temp, °C	Principal products[a] (%)
Naphthalene	Li	325	Naphthalene (96) 1,2,3,4-Tetrahydronaphthalene (4)
	Na	300	Naphthalene (30) 1,2,3,4-Tetrahydronaphthalene (62)
	NaK	250	1,2,3,4-Tetrahydronaphthalene (91) 1,1′,2,2′,3,3′,4,4′-Octahydro-2,2′-dinaphthyl (8)
	NaRb	180	1,2,3,4-Tetrahydronaphthalene (99)
	NaCs	200	1,2,3,4-Tetrahydronaphthalene (88)
Anthracene	Na	250	9,10-Dihydroanthracene (53) 1,2,3,4-Tetrahydroanthracene (38)
	NaK	250	1,2,3,4-Tetrahydroanthracene (37) Octahydroanthracene (53)[b]
	NaK	350	Octahydroanthracene (85)[b]
	NaRb	220	Octahydroanthracene (70)[b]
Phenanthrene	Na	250	9,10-Dihydrophenanthrene (23) 1,2,3,4-Tetrahydrophenanthrene (72)
	NaK	250	9,10-Dihydrophenanthrene (10) Octahydrophenanthrene (80)[b]
	NaRb	180	9,10-Dihydrophenanthrene (82) 1,2,3,4-Tetrahydrophenanthrene (5)
	NaRb	200	9,10-Dihydrophenanthrene (10) Octahydrophenanthrene (78)[b]
	NaCs	220	9,10-Dihydrophenanthrene (50) Octahydrophenanthrene (36)[b]
Naphthacene	NaK	250	5,12-Dihydronaphthacene (99)
	NaRb	300	5,12-Dihydronaphthacene (25) Hexahydronaphthacene (18) Octahydronaphthacene (36)
Chrysene	NaK	250	Hexahydrochrysene (40) Octahydrochrysene (24) Dodecahydrochrysene (23)
	NaRb	250	Dodecahydrochrysene (85)
Triphenylene	NaK	250	Triphenylene (12) *sym*-Dodecahydrotriphenylene (70)
Pyrene	NaK	250	Pyrene (45) 4,5-Dihydropyrene (42)
	NaK	350	Pyrene (50) Hexahydropyrene (10) Decahydropyrene (32)
	NaRb	250	Pyrene (43) Decahydropyrene (22) Dodecahydropyrene (14)
Perylene	NaRb	250	Perylene (10) Octahydroperylene (47) Dodecahydroperylene (30)
Fluorene	NaRb	250	Fluorene (60) 1,2,3,4-Tetrahydrofluorene (10) 1,2,3,4,4a,9a-Hexahydrofluorene (25)

[a] Percentage yields, based on recovered material, in parenthesis. [c] Approximately 2:1 mixture of symmetrical (1,2,3,4,5,6,7,8-octahydro) isomer and unsymmetrical (1,2,3,4,4a,9,9a,10-octahydroanthracene; 1,2,3,4,4a,9,10,10a-octahydrophenanthrene) isomer. All other unnumbered products were identified by mass spectral peaks and were not further characterized.

TABLE II

ALKALI METAL CATALYZED HYDROGENATIONS OF POLYARYL HYDROCARBONS

Compd	Catalyst	Temp, °C	Principal products[a]
Biphenyl	NaK	350	Biphenyl (20) Phenylcyclohexane (70) Benzene[b]
	NaRb	250	Biphenyl (20) Phenylcyclohexane (70) Benzene[b]
o-Terphenyl	NaK	350	*o*-Terphenyl (30) *sym*-Dodecahydrotriphenylene (50)
	NaRb	250	Biphenyl (60) Hexahydroterphenyl (10) *sym*-Dodecahydrotriphenylene (20) Benzene[b]
p-Terphenyl	NaK	350	Biphenyl (10) *trans*-1,4-Diphenylcyclohexane (40) Dodecahydroterphenyl (40)
1,3,5-Triphenylbenzene	NaRb	250	Hexahydroterphenyl (10) Hexahydrotriphenylbenzene (50) Dodecahydrotriphenylbenzene (30) Octadecahydrotriphenylbenzene (5)

[a] Percentage yields, based on recovered material, in parenthesis. [b] Yield not determined.

preparation of the latter compound.[10] The starting material is readily available, and the product is easily crystallized from the reaction mixture.

In the reduction of the polyaryls, scission of the bonds between the rings is indicated by the formation of traces of benzene, biphenyl, phenylcyclohexane, and traces of higher polyaryls. When benzene is heated to 250° with NaK and hydrogen, some biphenyl is formed; at 350°, hydrogen is absorbed with formation of hydrogenated dimers and higher polymers, as well as chars.[11] Toluene, though less reactive than benzene, reacts in a similar manner; there is some migration of methyl groups, with formation of benzene and small amounts of material with molecular weights corresponding to xylene, phenylcyclohexane, methylbiphenyl, and methylphenylcyclohexane. Because of this, tetralin or decalin was used as solvent for hydrogenations carried out above 250°, though they resulted in less extensive hydrogenation when compared to benzene at 250°.

Alkali Metal–Salt Combination Catalysts.—Since the reaction of alkali metals and alkali metal salts is an equilibrium reaction (eq 7), it was felt that NaK

$$\mathrm{Na} + \mathrm{KX} \rightleftharpoons \mathrm{NaX} + \mathrm{K} \tag{7}$$

could be formed *in situ* in a reaction vessel at elevated temperatures by using Na and the appropriate potassium salt. Potassium chloride–sodium mixtures fail to give results comparable to NaK at 250°; instead the mixture behaves like sodium. When K_2CO_3 or KOH is used with Na, however, hydrogenation of naphthalene,[12] phenanthrene, and pyrene proceeds to give products and yields similar to those obtained with NaK. In the absence of sodium, K_2CO_3 gives no hydrogenation.

The success of the potassium salt–sodium metal system suggested that the use of rubidium salts might allow the catalytic behavior equivalent to sodium–rubidium (NaRb) to be studied without the inconvenience of handling metallic rubidium. Experiments indicate this to be valid. Substitution of Rb_2CO_3 for K_2CO_3 results in lowering the temperature of a given hydrogenation

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[10] D. A. Scola, *J. Chem. Eng. Data*, **9**, 405 (1964).

[11] L. H. Slaugh, *Tetrahedron*, **24**, 4525 (1968). This reference incorrectly quotes the authors (ref 1) as stating that benzene does not react in the presence of alkali metals and hydrogen.

[12] G. L. O'Connor, H. E. Fritz, and M. A. Eccles, U. S. Patent 2,968,681 (1961). This patent, which covers the use of sodium with potassium salts for hydrogenation of naphthalene, appeared during the course of this work.

by 50° to 100°. In some cases, NaRb (prepared *in situ* from Na and Rb_2CO_3 in all experiments) causes more extensive hydrogenation than is observed with NaK. Varying the ratio of Na to Rb_2CO_3 from 1:2 to 2:1 had no observable effect on results. A single experiment using rubidium formate with sodium gave results comparable to those obtained with sodium itself.

Some of the observations reported in this paper may be the result of the heterogeneity of the system and the difficulty in obtaining reaction between a solid salt and a solid or molten metal immersed in a passive liquid phase, rather than to the chemistry of the materials themselves.

Hydrogenation of Heteroatom Compounds.—The presence in an aromatic molecule of oxygen-containing functional groups necessitates that sufficient catalyst be present to allow for the formation of an alkali metal salt of the hydroxyl group which may be formed. The results shown in Tables III and IV indicate that aromatic C–O bonds are readily hydrogenolyzed by NaRb; the products are predominantly those expected from hydrogenation of the deoxygenated compounds. Decarboxylation also occurs readily.

Table III

NaRb-Catalyzed Hydrogenations of Oxygenated Aromatic Compounds

Compd	Catalyst	Temp, °C	Principal products[a]
2-Methoxynaphthalene	NaRb	250	1,2,3,4-Tetrahydronaphthalene (80) 2-Naphthol (10) Dihydro- and tetrahydronaphthol (5)
2-Naphthol	NaRb	220	1,2,3,4-Tetrahydronaphthalene (50) 5,6,7,8-Tetrahydro-2-naphthol (45)
p-Phenylphenol	NaRb	250	Phenylcyclohexane (90)
2-Naphthoic acid	NaRb	250	1,2,3,4-Tetrahydronaphthalene (80)
Anthraquinone	NaRb	250	Octahydroanthracene (70)[b] *sym*-Octahydroanthranol (20)

[a] Percentage yields, based on recovered material, in parenthesis. [b] Approximately 2:1 mixture of symmetrical and unsymmetrical isomers.

Table IV

NaRb-Catalyzed Hyrogenations of Heterocyclic Aromatic Compounds

Compd	Catalyst	Temp, °C	Principal products[a]
Dibenzofuran	NaRb	250	Phenylcyclohexane (80) Biphenyl (10) Hexahydroterphenyl (5)
Dibenzothiophene	NaRb	250	Dibenzothiophene (50) Phenylthiophenol (20) Biphenyl (20)
Quinoline	NaRb	220	5,6,7,8-Tetrahydroquinoline (60) Dimers (30)
Acridine	NaRb	250	Acridine (30) 9,10-Dihydroacridine (30) Tetrahydroacridine (9) Octahydroacridine (25)[b]
Phenanthridine	NaRb	250	Octahydrophenanthridine (77)[b]

[a] Percentage yields, based on recovered material, in parenthesis. [b] Only unsymmetrical isomers detected.

Dibenzofuran (Table IV) at 250° is reductively cleaved; small amounts of hexahydroterphenyl are formed indicating reaction with the solvent, benzene. By contrast, dibenzothiophene is relatively inert toward both hydrogenation and cleavage in the presence of NaRb. This contrasts with Raney nickel or lithium–ethylenediamine reductions,[13] both of which bring about desulfurization. Added thianaphthene did not affect the NaRb-catalyzed hydrogenation of naphthalene, which indicates that the presence of sulfur compounds does not poison the alkali metal catalysts. Ring cleavage and decomposition are observed with nitrogen-containing heterocyclic aromatic compounds. Pyridine, when used as a solvent, forms a variety of products, including tar.

Several experiments to evaluate cesium as a catalyst were carried out in a manner similar to those involving rubidium (Table I), using cesium carbonate and sodium metal. Cesium proved to be a less active hydrogenation catalyst than rubidium and slightly more active than potassium in catalytic activity.

Effect of Solvents.—Initially, benzene and toluene were used as solvents because of their lack of reactivity toward alkali metals at room temperature. Since the work was directed primarily toward reductions of coal, it was apparent that a better coal solvent would be useful. Amines, which are good coal solvents, react with alkali metals to form amides.

$$M + RNH_2 \rightleftharpoons RNH^- + M^+ + {}^1/_2H_2$$

However, the reaction is probably reversible, so that, in the presence of hydrogen, some metal remains, probably in solution. In any event, the catalytic hydrogenation does proceed in amine and in benzene–amine solvents. Whereas 180° is the lowest temperature at which measurable hydrogen uptake occurs in benzene, in ethylenediamine or in butylamine–benzene (1:1) at 120°, phenanthrene is hydrogenated to octahydrophenanthrene with Na + Rb_2CO_3 (Table V). By lowering the initial hydrogen pressure to 100 psig, it is possible to prepare 1,2,3,4-tetrahydrophenanthrene in 80% yield in butylamine–benzene at 120°.

Similarly, other polycyclic hydrocarbons can be reduced at temperatures up to 200° in ethylenediamine and in ethylenediamine–benzene (1:1). The results are roughly comparable to those obtained at 250° when benzene is used as solvent.

Preliminary investigations have been carried out on coal and coal tar fractions. As many as 15 hydrogens per 100 C atoms have been added to a 90% carbon coal. The H_{arom}/H_{aliph} ratio (nmr) of a coal tar pitch was reduced from an initial 4.26 to 0.61 by hydrogenation with NaRb at 350°.

Experimental Section

Reagents.—The hydrocarbon solvents were dried over sodium. The ethylenediamine was refluxed with Na and freshly distilled before use. The reactants were obtained from standard suppliers. Where possible, reagent grade material was used.

The NaK (containing 76% potassium by weight, approximately 1:2 mol ratio) was a gift of the Mine Safety Appliance Research Corp. The liquid NaK was kept under N_2 and transferred by means of a hypodermic syringe. All NaRb was prepared *in situ* using sodium–Rb_2CO_3 weight ratios of 1:2 to 2:1.

Analyses of Products.—Products were analyzed by gas–liquid chromatography where possible, and by low-voltage mass spec-

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[13] L. Reggel, C. Zahn, I. Wender, and R. Raymond, *Bull. U. S. Bur. Mines*, No. 615, 36 (1965).

TABLE V

NaRb-CATALYZED HYDROGENATIONS IN AMINE SOLVENTS

Compd	Catalyst	Temp, °C	Solvent	Principal products[a]
Phenanthrene	NaRb	120	Ethylenediamine	Octahydrophenanthrene (91)
	NaRb	120	Butylamine–benzene (1:1)	Octahydrophenanthrene (97)
	NaRb	120[b]	Butylamine–benzene (1:1)	Dihydrophenanthrene (12) 1,2,3,4-Tetrahydrophenanthrene (80)
Pyrene	NaRb	200	Ethylenediamine	Tetrahydropyrene (28) Hexahydropyrene (23) Decahydropyrene (18)
Naphthacene	NaRb	200	Ethylenediamine–benzene (1:1)	Dihydronaphthacene (32) Hexahydronaphthacene (22) Octahydronaphthacene (29)
Fluoranthene	NaRb	200	Ethylenediamine	Dihydrofluoranthene (80) Tetrahydrofluoranthene (7)
o-Terphenyl	NaRb	120	Ethylenediamine	Hexahydroterphenyl (75) Dodecahydrotriphenylene (13)

[a] Percentage yields, based on recovered material, in parenthesis. [b] Gas pressure, 100 psi.

trometry routinely. This latter procedure provides a molecular weight distribution of products. In certain experiments, it was possible to isolate a specific component and identify it by infrared and ultraviolet spectrometry. In these instances, the products are suitably described.

When a product is identified without specific numbering of the substituted hydrogen, identification has been inferred from the molecular weight (obtained from mass spectral measurements).

Procedure.—The procedure for all experiments was similar. Two examples will be given to illustrate the procedure. Initial pressures were between 1200 psi and 1400 psi. Temperatures shown in Tables I to V represent minimum temperatures at which appreciable yields of the indicated products were observed. Benzene or toluene was used as solvent for all reactions up to 250°. In a few cases, reductions were carried out above 250° to achieve more extensive reaction. In those experiments, tetralin and decalin served as solvents. All runs were held at temperature for 4.5–5 hr. The quantity of reactants was 5 g, except for naphthalene (30 g) and the tetra- and pentacyclic hydrocarbons which were used in 2-g amounts due to limited solubility. Recoveries ranged between 80 and 100%, physical losses being proportionately greater for runs containing smaller amounts of substrate. All analytical results are reported on the basis of the percentage of the total recovered, isolated product.

Hydrogenation of Naphthalene.—A solution of 30 g of naphthalene in 150 ml of toluene was placed in a 0.5-l. Aminco[14] rocking autoclave with 2 g of NaK. Hydrogen was introduced into the autoclave at 1250 psi, and it was then heated to 250°. It took 2.5 hr for the autoclave to reach this temperature. The autoclave was kept at 250° for 4.5 hr and then allowed to cool overnight. The reaction mixture consisted of a white solid in suspension in the toluene solution. The solid reacted vigorously with the isopropyl alcohol added to dispose of excess NaK. The solution was extracted with water to remove the alkali hydroxides, and the organic layer was extracted with ether. The ether solution was distilled through a helix-packed column to remove all solvents. The residue, containing naphthalene and its reduction products, was examined by mass spectrometry and gas chromatography. It was found to consist of 91% tetrahydronaphthalene and 8% of dimeric product with mol wt 262, and a small amount with mol wt 260.

The dimer was isolated by chromatography on alumina after removal of the lower boiling material by distillation. The recrystallized material, mp 105–108°, had a tetralin-like ultraviolet spectrum and infrared and nmr spectra consistent with a structure of 1,1′,2,2′,3,3′,4,4′-octahydro-2,2′-dinaphthyl.[15,16] Dehydrogenation with palladium on charcoal gave 2,2′-dinaphthyl.

Hydrogenation of Phenanthrene.—A solution of 5 g of phenanthrene in 80 ml of benzene was placed in an Aminco rocking autoclave with 1.5 g of sodium and 2.0 g of rubidium carbonate. Hydrogen was introduced into the autoclave at 1400 psi, and it was then heated to 200°. It took 2 hr for the autoclave to reach this temperature, which was maintained for 5 hr. The autoclave was allowed to cool overnight, and isopropyl alcohol was added to decompose the metal hydrides. The solution was extracted with water to remove the metal hydroxides, and the organic layer was extracted with ether. The ether and benzene were removed by distillation and the residue was examined by mass spectrometry. The product contained 10% 9,10-dihydrophenanthrene and 78% octahydrophenanthrene, as well as smaller amounts of 1,2,3,4-tetrahydrophenanthrene and phenanthrene. Traces of dimeric products were also present. Gas chromatographic analysis of the octahydrophenanthrene indicated an approximate 2:1 ratio of 1,2,3,4,5,6,7,8-octahydrophenanthrene to 1,2,3,4,4a,9,10,10a-octahydrophenanthrene.

Registry No.—Naphthalene, 91-20-3; anthracene, 120-12-7; phenanthrene, 85-01-8; naphthacene, 92-24-0; chrysene, 218-01-9; triphenylene, 217-59-4; pyrene, 129-00-0; perylene, 198-55-0; fluorene, 86-73-7; biphenyl, 92-52-4; *o*-terphenyl, 84-15-1; *p*-terphenyl, 92-94-4; 1,3,5-triphenylbenzene, 612-71-5; 2-methoxynaphthalene, 93-04-9; 2-naphthol, 135-19-3; *p*-phenylphenol, 92-69-3; 2-naphthoic acid, 93-09-4; anthraquinone, 84-65-1; dibenzofuran, 132-64-9; dibenzothiaphene, 132-65-0; quinoline, 91-22-5; acridine, 260-94-6; phenanthridine, 229-87-8; fluoranthene, 206-44-0.

Acknowledgment.—We thank Miss Janet Shultz for mass spectral determinations.

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(14) Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

(15) E. J. Eisenbraun, D. V. Hertzler, R. C. Bansal, P. W. K. Flanagan, and M. C. Hamming, Preprints of Papers, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, PETR 017. The same compound is also reported in ref 12.

(16) L. Reggel, H. W. Sternberg, and I. Wender, *Nature*, **81**, 190 (1961), report what is apparently a diastereomer.