detection limit in the matrix experiments described above.

Shorter wavelength irradiation ($\lambda > 400$ nm) of **4** gives complete rearrangement to 2,5-oxepinedione (**5**), characterized IR and mass spectroscopically.[18] The lactone band at 1753 cm^{-1} (37-cm^{-1} isotopic shift) and the ketone band at 1660 cm^{-1} (no isotopic shift) are observed close to the corresponding bands in α-pyrone (1752 cm^{-1}) and γ-pyrone (1678 cm^{-1}). A small amount of **5** was isolated from the cold window after evaporating the matrix. The mass spectrum obtained from this sample[18] confirmed the assignment given above.

Chemiluminescence, observed in other thermal carbene oxidations[6,16,19] was not found. Quinone **6** does not show any fluorescence or phosphorescence on irradiation in Ar at 9 K, and thus chemiluminescence is not expected.

Experimental Section

p-Benzoquinone diazide (**2**) and *p*-benzoquinone-d_4 diazide[9] were synthesized by treating *p*-diazophenol hydrochloride with silver oxide according to the literature procedure.[20] *p*-Aminophenol-d_4 hydrochloride was synthesized by H-D exchange with D_2O at 220 °C.[21] The deuterium content was >95% (by mass spectroscopy).

Matrix experiments were performed by standard techniques,[6b,16] using an Air Products CSW-202 Displex closed cycle helium cryostat. The temperature of the matrix was controlled by a Lake Shore DRC 81 C controller (silicon diode sensor) interfaced to a HP 86 microcomputer. Argon (Messer Griesheim, 99.9995%), oxygen (Messer Griesheim, 99.998%), and [$^{18}O_2$]oxygen (Ventron, 99.8% isotopic purity) were mixed in a gas-handling system by standard manometric techniques. Infrared spectra were recorded on a Perkin Elmer PE 580 and UV–vis spectra on a Varian Cary 17D spectrometer. Both instruments were interfaced to a Hewlett Packard 86 microcomputer.

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Registry No. **1**, 113567-56-9; [$^2H_4$]-**1**, 113567-58-1; [$^{18}O_2$]-**1**, 113567-57-0; [$^2H_4$,$^{18}O_2$]-**1**, 113567-59-2; **2**, 932-97-8; [$^2H_4$]-**2**, 113567-96-7; **3**, 3225-37-4; **4**, 113567-94-5; **5**, 113567-95-6.

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(18) **5**: IR (Ar, 9 K) 1769 (w), 1753 (m), 1748 (m), 1660 (m), 1638 (w), 1330 (s), 1296 (m), 1141 (m), 1048 (m), 869 (m) cm^{-1}; MS, *m/z* (relative intensity) 124 (M^+, 46), 96 ($M^+ - CO$, 100), 69 (55), 68 (43), 54 (41), 39 (32). [$^{18}O_2$]-**5**: IR (Ar, 9 K) 1716 (s), 1664 (s), 1647 (m), 1337 (w), 1320 (s), 1288 (s), 1132 (s), 1028 (m), 871 (m) cm^{-1}.

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Selective Halogenation of Aromatic Hydrocarbons with Alumina-Supported Copper(II) Halides

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Copper(II) halides have been used to halogenate aromatic hydrocarbons under heterogeneous conditions in nonpolar solvents. For example, anthracene and pyrene react with copper(II) chloride and bromide in heterogeneous conditions to give excellent yields of 9-haloanthracenes and 1-halopyrenes.[1,2] However, the process is not generally applicable for halogenation of all aromatic hydrocarbons. Aromatic hydrocarbons with ionization potentials (IP) higher than approximately 7.55 eV were found to be entirely unreactive toward chlorination with copper(II) chloride.[3] Even under reflux with copper(II) chloride in high-boiling solvents, e.g., nitrobenzene and chlorobenzene, chlorination of naphthalene (IP = 8.10[4]) or phenanthrene (IP = 8.03[4]) was not successful.[1,5]

Table I. Chlorination of Polycyclic Aromatic Hydrocarbons with $CuCl_2/Al_2O_3$[a]

aromatics	°C/h	products	total yield, %	ratio of products, % mono-Cl	ratio of products, % di-Cl
naphthalene	130/2	1-Cl, 1,4-Cl_2	94	94	6
1-methylnaphthalene	130/2	4-Cl	100	100	0
phenanthrene	130/2	9-Cl, 9,10-Cl_2	94	94	6
fluorene	130/1	2-Cl, 2,7-Cl_2	93	83	17
anthracene	50/1[b]	9-Cl, 9,10-Cl_2	99	95	5
	80/7[b]	9,10-Cl_2	99	0	100

[a] $CuCl_2$/aromatic = 5; solvent: chlorobenzene. [b] Carbon tetrachloride.

Previously, we reported that copper(II) halides supported on alumina halogenated phenylacetylene selectively to give 1-halo-2-phenylacetylene or 1,1,2-trihalo-2-phenylethylene in nonpolar solvents under mild conditions.[6] In the present paper, we report that aromatic hydrocarbons with ionization potentials higher than 7.55 eV were easily halogenated by alumina-supported copper(II) halides to give mono- or dihalogenated products. For example, while reaction of naphthalene, phenanthrene, and fluorene with copper(II) chloride in refluxing chlorobenzene produced negligible yields of chlorinated products, similar reaction with alumina-supported copper(II) chloride produced monochlorinated compounds in high yields, Table I. To examine what factors influence product yields, we examined the chlorination of naphthalene in more detail. Empirical testing of five supports (alumina, silica gel, molecular sieve, graphite, and Kieselguhr) revealed that alumina was most effective in activating copper(II) chloride. Kieselguhr was entirely ineffective. We postulated a reaction mechanism with participation of an aromatic radical cation which was formed by one electron transfer from an aromatic hydrocarbon to copper(II) chloride. Activated alumina has electron-acceptor properties, and formation of a radical cation of an aromatic hydrocarbon adsorbed on alumina has been observed by ESR.[7] Therefore, it seemed to us that alumina as a support facilitates the generation of the radical cation of the aromatic hydrocarbon.

Copper(II) bromide was more reactive than copper(II) chloride toward the aromatic hydrocarbons. Bromination of aromatic hydrocarbons proceeded in carbon tetrachloride to give the corresponding bromo compounds with high selectivity, Table II. Mono- or dibromo compounds were selectively obtained in high yield depending upon the reaction conditions. For instance, 1-bromonaphthalene was obtained from the reaction run at 80 °C in carbon

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Table II. Bromination of Aromatic Hydrocarbons with $CuBr_2/Al_2O_3$[a]

aromatics	°C/h	products	total yield, %	ratio of products, % mono-Br	ratio of products, % di-Br
naphthalene	80/2	1-Br	98	100	0
	130/1[b]	1-Br, 1,4-Br_2	100	8	92
1-methylnaphthalene	50/2	4-Br	100	100	0
	80/16	2,4-Br_2	100	0	100
phenanthrene	80/2	9-Br	95	100	0
fluorene	80/2	2-Br	95	100	0
	80/6	2,7-Br_2	98	0	100
toluene	80/8	2-Br, 4-Br	65	100[c]	0
p-xylene	80/1.5	2-Br, 2,6-Br_2	95	85	15
mesitylene	50/1	2-Br, 2,4-Br_2	98	99	1

[a] $CuBr_2$/aromatic = 5; solvent: carbon tetrachloride. [b] Chlorobenzene. [c] Mixture (1:1) of *o*- and *p*-bromotoluene.

tetrachloride and 1,4-dibromonaphthalene was obtained from the reaction run at 130 °C in chlorobenzene. Halogenation of alkylbenzenes with metal halides gave mixtures of nuclear-halogenated compounds and side-chain-halogenated compounds.[8-10] In contrast, in similar reactions using alumina-supported copper(II) bromide, only nuclear bromination occurred and no side-chain brominated compounds were obtained. The reaction of toluene with alumina-supported copper(II) bromide gave mixture of *o*- and *p*-bromotoluene. *p*-Xylene and mesitylene were also susceptible to nuclear bromination, and the corresponding monobromo compounds were obtained in high yields. Reactivity of the alkylbenzenes toward copper(II) bromide increased with increasing number of alkyl groups, as follows: mesitylene > *p*-xylene > toluene.

The advantages of this procedure are simple workups, mild reaction conditions, and higher selectivities. Products can be isolated in good yield by simple filtration and solvent evaporation, and no extraction steps are required.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. Neutral alumina was purchased from ICN Biomedicals (Woelm N-Super 1). Carbon tetrachloride was dried with calcium chloride and distilled. All ^1H NMR, IR, and mass spectra were recorded by using JEOL FX-90Q, JASCO A-302, and JEOL DX-303 spectrometers, respectively. Product mixtures were analyzed by GLC on a Hitachi Model 163 flame ionization instrument equipped with a SE-30 on Chromosorb WAW column.

Preparation of Copper(II) Chloride Adsorbed on Alumina (Reagent 1). To a solution of copper(II) chloride dihydrate (10 g) in distilled water (30 mL) was added neutral alumina (20 g, Woelm N-Super 1) at room temperature. The water was evaporated by using a rotary evaporator at 80 °C under reduced pressure. The resulting reagent was then dried under vacuum (4 Torr) at 100 °C for 15 h. Preparation of alumina-supported copper(II) bromide (reagent **2**) was similar to that described above.

1-Chloronaphthalene: General Procedure for Chlorination of Aromatic Hydrocarbons. A 100-mL round-bottomed flask was charged with **1** (7.14 g) and naphthalene (0.345 g, 3 mmol) dissolved in chlorobenzene (30 mL). A Teflon-coated stirring bar was added and the mixture stirred vigorously at 130 °C for 2 h. Analysis by GLC indicated the complete disappearance of naphthalene. The product mixture was filtered, and the reagent was washed with chlorobenzene (10 mL).

2,7-Dibromofluorene: General Procedure for Bromination of Aromatic Hydrocarbons. A mixture of fluorene (1.5 g, 9 mmol), **2** (30 g), and carbon tetrachloride (80 mL) was placed in a 200-mL round-bottomed flask and stirred with a Teflon-coated magnetic stirring bar at 80 °C for 5 h. The product mixture was filtered, and the spent reagent was washed with carbon tetrachloride (30 mL). Evaporation of solvent from the combined filtrate under reduced pressure yielded 2.84 g (97%) of 2,7-dibromofluorene as a pale yellow solid having ^1H NMR and IR spectra identical with those of an authentic sample, mp 157-159 °C (lit.[11] mp 162-163 °C). The purity was >96% (GLC).

Registry No. Alumina, 1344-28-1; naphthalene, 91-20-3; 1-methylnaphthalene, 90-12-0; phenanthrene, 85-01-8; fluorene, 86-73-7; anthracene, 120-12-7; toluene, 108-88-3; *p*-xylene, 106-42-3; 1,3,5-trimethylbenzene, 108-67-8; 1-chloronaphthalene, 90-13-1; 1,4-dichloronaphthalene, 1825-31-6; 4-chloro-1-methylnaphthalene, 17075-39-7; 9-chlorophenanthrene, 947-72-8; 9,10-dichlorophenanthrene, 17219-94-2; 2-chlorofluorene, 2523-44-6; 2,7-dichlorofluorene, 7012-16-0; 9-chloroanthracene, 716-53-0; 9,10-dichloroanthracene, 605-48-1; 1-bromonaphthalene, 90-11-9; 1,4-dibromonaphthalene, 83-53-4; 4-bromo-1-methylnaphthalene, 6627-78-7; 1-methyl-2,4-dibromonaphthalene, 3278-84-0; 9-bromophenanthrene, 573-17-1; 2-bromofluorene, 1133-80-8; 2,7-dibromofluorene, 16433-88-8; 2-bromotoluene, 95-46-5; 4-bromotoluene, 106-38-7; 2-bromo-1,4-dimethylbenzene, 553-94-6; 2,6-dibromo-1,4-dimethylbenzene, 66788-13-4; 2-bromo-1,3,5-trimethylbenzene, 576-83-0.

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Intramolecular [4 + 1] Pyrroline Annulation via Azide-Diene Cycloadditions. 2. Formal Stereoselective Total Syntheses of (±)-Platynecine, (±)-Hastanecine, (±)-Turneforcidine, and (±)-Dihydroxyheliotridane

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Introduction

A functional approach to simple pyrrolizidine bases such as a supinidine, trachelanthamidine, and isoretronecanol has been realized by the intramolecular cyclization of azido dienes.[2,3] In analogy with similar ring closures of carbenoids,[4] these cyclizations, combined with the subsequent thermolysis of vinylaziridines, provided a reliable pyrroline annulation technology representing a formal [4 + 1] union of a nitrene with a 1,3-diene. Following the necessary investigations of conditions of rearrangements of vinylaziridines, we decided to adapt this methodology to the preparation of pyrrolizidines oxygenated in both rings. Herein we report the synthesis of several pyrrolizidine alkaloids of the retronecine type via a fully general approach and a common set of intermediates, Figure 1.

Results and Discussion

Pyrrolizidine alkaloids enjoy popularity in the synthetic community for two reasons. First, they are the basic constituents of many cytotoxic lactones,[5] and second, they

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