Methyl 5,6-Dideoxy-2,3-*O*-isopropylidene-β-L-*ribo*-hex-5-enofuranoside (13). Methyl 2,3-*O*-isopropylidene-5,6-di-*O*-methanesulfonyl-α-D-talofuranoside (**12**, 12.5 g, 32 mmol), 35 g of sodium iodide, and 275 mL of 2-butanone were heated under reflux for 26 h. The mixture was worked up in a similar manner as in the preparation of **5** to afford 4.33 g (67.5% yield) of a clear, colorless liquid after distillation: bp 85–87 °C (3 mmHg), $[\alpha]^{25}{}_{\rm D}$ +61.0° (*c* 1.53, chloroform). The IR and NMR spectra of **13** were identical with **5**.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.92; H, 7.94.

9-(5,6-Dideoxy-β-L-*ribo*-hex-5-enofuranosyl)adenine (14). The preparation of 14 from **13** proceeded exactly as already described for the preparation of **9**. From 2.5 g of **13**, 4.89 g of methyl 2,3-di-*O*-benzoyl-5,6-dideoxy-β-L-*ribo*-hex-5-enofuranoside was obtained and this was acetolyzed to 1-*O*-acetyl-2,3-di-*O*-benzoyl-L-*ribo*-hex-5-enofuranose (4.16 g). Both of these compounds had NMR spectra which were virtually identical with their enantiomers. The 1-*O*-acetate (4.16 g, 10.5 mmol) was condensed with 6.2 g (13.1 mmol) of 6-benzamidochloromercuripurine in 450 mL of 1,2-dichloroethane as described for the synthesis of **9**. After workup, 4.48 g of tan foam was obtained. The blocking groups were removed with sodium methoxide, the methyl benzoate was removed as a water azeotrope, and the product was purified on a column[16] (33 × 2 cm) as described before.[31] The contents of the tubes containing the main UV peak were combined and crystallization from ethanol gave 1.201 g in two crops. Two recrystallizations from acetone yielded 0.998 g (36% from the 1-*O*-acetate) of needles, mp 191–191.5 °C. The sample required drying to 100 °C under high vacuum in a drying pistol (phosphorus pentaoxide) to remove traces of acetone and water. The IR spectrum of 14 was identical with **9**.

Anal. Calcd for $C_{11}H_{13}N_5O_3$: C, 50.18; H, 4.98; N, 26.60. Found: C, 49.79; H, 5.00; N, 26.46.

Registry No.—**1**, 2595-97-3; **2**, 28642-53-7; **3**, 28642-54-8; **4**, 65969-34-8; **5**, 29325-28-8; **6**, 65969-35-9; **7**, 65969-36-0; **8**, 66008-58-0; **9**, [65969-37-1; **10**, 65969-38-2; **11**, 2595-98-4; **12**, 65969-39-3; **13**, 65969-40-6; **14**, 65969-41-7; 1,2:5,6-di-*O*-isopropylidene-2-D-glucofuranose, 582-52-5; 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofurano-3-ulose, 2847-00-9; 6-benzamidochloromercuripurine, 17187-65-4; methyl 2,3-*O*-isopropylidene-α-D-talofuranoside, 65969-42-8; methyl 2,3-di-*O*-benzoyl-5,6-dideoxy-β-L-*ribo*-hex-5-enfuranoside, 65969-43-9; 1-*O*-acetyl-2,3-di-*O*-benzoyl-5,6-dideoxy-L-*ribo*-hex-5-enofuranose, 65969-44-0.

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(1) This work was supported by Grant CA 13802 from the National Cancer Institute, National Institutes of Health.

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(19) It should be noted that this method was worked out for ribofuranose nucleosides and may not be applicable here. For example, some discrepancies have been found when C-5′ has a substituent.[18]

(20) Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich., or by the Baron Consulting Co., Orange, Conn. Moist organic solutions were dried over anhydrous magnesium sulfate and evaporations were performed on a rotary evaporator under reduced pressure with a bath temperature of 40–45 °C unless specified otherwise. TLC was performed on silica gel G plates of 0.25-mm thickness, prepared with Desaga equipment. The NMR spectra were recorded on a Varian T-60A spectrometer with Me_4Si as the internal reference. IR and UV spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer and a Beckman DK-2 spectrophotometer, respectively. Optical rotations were determined with a Rudolph polarimeter. A Kofler micro hot stage was used to determine melting points as corrected values.

(21) Ruthenium dioxide hydrate was purchased from Engelhard Industries, Newark, N.J. It was used without any special treatment or activation.

(22) 1,2:5,6-Di-*O*-isopropylidene-β-D-glucofuranose was purchased from Pfanstiehl Laboratories, Inc., Waukegan, Ill.

(23) If this step is omitted, the colored material will distill with **5**.

(24) The resin was suspended in methanol and after 15 min the solvent was decanted. This process was repeated three times before the resin was used.

(25) If water was used, a large amount of benzoic anhydride was formed. The latter could be removed by treatment with methanol–pyridine solution for several days to form methyl benzoate.

(26) It is advisable to use a jacketed column in order to apply heat, if necessary, because the nucleoside tends to crystallize during early stages of chromatography. A hot-air blower (hair drier) was found to be a useful alternative for heating just the upper regions of the column.

(27) D-Galactal was purchased from Raylo Chemical, Ltd., Edmonton, Alberta, Canada.

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(29) Extraction of the aqueous layer using a separatory funnel with either chloroform or ethyl acetate produced a hopeless emulsion. It was desirable not to add salts so that the sugar in the aqueous layer could be easily recycled through the reaction sequence.

(30) Seed crystals were originally obtained from a small-scale reaction by scratching the product in a mixture of methanol and water.

(31) No significant crystallization of the nucleoside in the methanolysis solution occurred in this case, therefore, only one column was necessary.

Diels–Alder Approach to Naphthocyclobutenes and Anthrocyclobutenes

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The [2 + 4] cycloaddition of benzyne with 1,2-dimethylenecyclobutane or 1-vinylcyclobutene leads to the formation of an adduct which can be dehydrogenated with DDQ to provide naphtho[*b*]cyclobutene or naphtho[*a*]cyclobutene, respectively. Similar reaction of 2,3-dehydronaphthalene with these same two dienes provides analogous cycloadducts which can then be oxidized to anthro[*a*]cyclobutene and anthro[*b*]cyclobutene. Pyrolysis of 1,4-dihydronaphtho[*b*]cyclobutene provides a ring-opened diene which can undergo further cycloaddition. Other oxidative routes to naphtho[*b*]cyclobutene are presented.

The preparation of annelated aromatic systems is often best accomplished by the utilization of synthetic techniques in which the fused ring portion of the molecule comprises one of the initial reacting partners. This species can then undergo cycloaddition or condensation reactions to build up the aromatic nucleus. We have demonstrated the utility of this ap-

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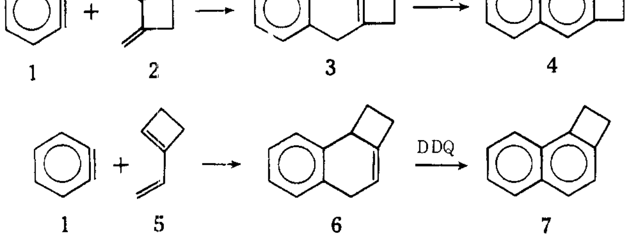
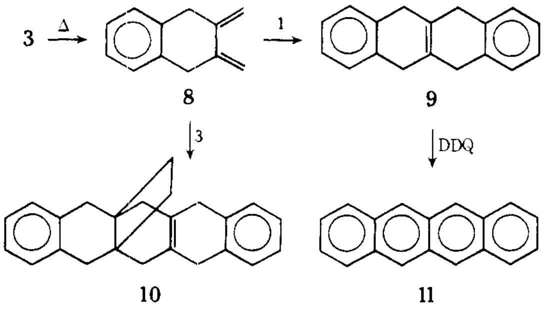
proach in the preparation of mono- and bisannelated benzenes[1] and pyridines.[2] When a Diels–Alder sequence is utilized to establish the molecular framework, the nature of the aromatic portion very often depends upon the dienophile which is employed. This paper will discuss how the [2 + 4] addition of 1,2-dimethylenecyclobutane and 1-vinylcyclobutene to a dehydroaromatic species can lead to the facile two-step preparation of cyclobutene-fused polynuclear aromatics.

The reaction of 1,2-dimethylenecyclobutane with excess benzyne (generated from anthranilic acid and isoamyl nitrite in tetrahydrofuran) in refluxing dichloromethane for 2 h resulted in a 25% yield of 1,4-dihydronaphtho[*b*]cyclobutene (**3**) after chromatography on silica gel: mp 69–70 °C; NMR ($CDCl_3$) δ 7.15 (s, 4 H, ArH), 3.3 (s, 4 H, $ArCH_2$), and 2.6 (s, 4 H, cyclobutyl **H**). Treatment of **3** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene provides naphtho[*b*]cyclobutene in 81% yield, mp 85–86 °C (lit.[3] mp 86.5 °C). A similar Diels–Alder reaction between benzyne and 1-vinylcyclobutene provided a 25% yield of adduct **6** which showed a characteristic olefinic resonance at 5.5 ppm. This material was contaminated by an equivalent amount of a phenyl-substituted triene whose precise structure could not readily be determined. Treatment of the mixture with DDQ resulted in the disappearance of **6** and the formation of naphtho[*a*]cyclobutene (**7**) which was isolated in 35% yield by chromatography on silica gel.



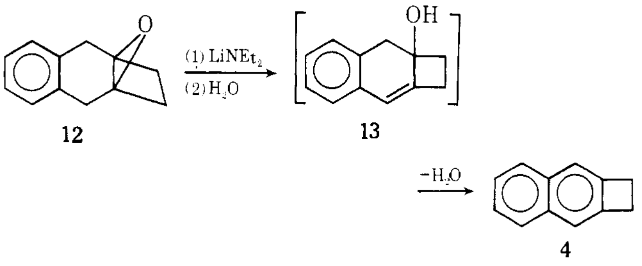
Cava and co-workers have reported the synthesis of both naphtho[*a*]cyclobutene[4] (**7**) and naphtho[*b*]cyclobutene[3] (**4**) by the extrusion of sulfur dioxide from the corresponding dihydronaphthothiophene dioxides. This elimination is accomplished by a pyrolysis reaction and suffers the disadvantage of incorporating a good deal of steric strain in the final step. Our Diels–Alder approach to these two molecules incorporates the strain into the species undergoing cycloaddition, thereby enhancing reactivity through the release of steric strain. The final step involves the aromatization of a benzene ring and is thus driven by the resonance energy gained by the system.

Pyrolysis of **3** through a spiral glass tube heated to 300 °C (0.05 mm) provides the ring-opened diene **8**: mp 64 °C; NMR (CCl_4) δ 7.04 (s, 4 H, ArH), 5.30 (m, 2 H, $=CH_2$), 4.88 (m, 2 H, $=CH_2$), and 3.50 (s, 4 H, $ArCH_2$). If this diene is allowed to react with a second equivalent of benzyne, 5,6,11,12-tetrahydronaphthacene (**9**) can be prepared: mp 160–165 °C; NMR (CCl_4) δ 7.1 (s, 8 H, ArH) and 3.45 (s, 8 H, $ArCH_2$). Oxidation of **9** with DDQ afforded naphthacene which was identical with a commercial sample.

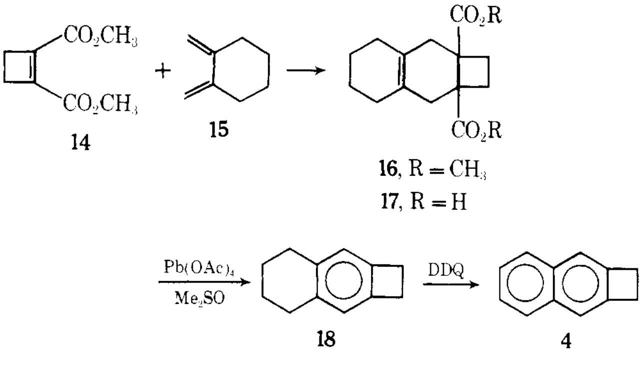


When the pyrolysis of **3** is carried out in a sealed tube at 200 °C, a dimer is formed in 70% yield as the result of diene **8** adding in a [2 + 4] fashion to its precursor **3**. Compound **10** (mp 119–121 °C) exhibited a parent ion at *m/e* 312 as well as a base peak at *m/e* 156 indicating that retro-Diels–Alder reaction is facile in the mass spectrometer. Cava has observed a similar dimer upon heating the analogous quinone to 200 °C.[5]

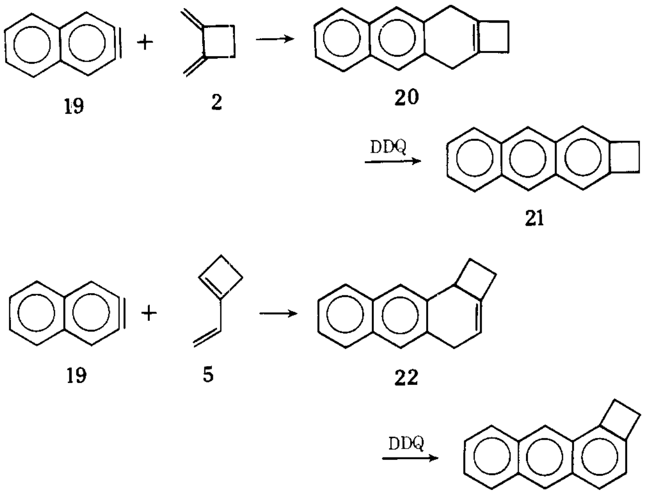
Oxidation of **3** with *m*-chloroperbenzoic acid results in the formation of the corresponding epoxide **12**. When this epoxide is treated with lithium diethylamide, the only product obtained is naphtho[*b*]cyclobutene. Abstraction of a benzylic proton accompanied by epoxide ring opening would lead to the formation of a tertiary allylic alkoxide which could dehydrate after hydrolysis or lose lithium hydroxide to aromatize directly.[6] The intermediate alcohol **13** was not observed.



Naphtho[*b*]cyclobutene may also be prepared by aromatization of the other six-membered ring. The synthesis of 5,6,7,8-tetrahydronaphtho[*b*]cyclobutene (**18**) was accomplished by a well-established cycloaddition route.[1] The addition of 1,2-dimethylenecyclohexane (**15**) to dimethyl 1,2-cyclobutenedicarboxylate (**14**) provides 64% of an adduct **16** which may be readily hydrolyzed to the corresponding diacid **17**. Bisdecarboxylation of this diacid and oxidation of the resulting 1,4-cyclohexadiene were accomplished by treatment with 2 equiv of lead tetraacetate in dimethyl sulfoxide. If **18** is then allowed to react with DDQ in benzene at room temperature for 16 h, smooth conversion to naphtho[*b*]cyclobutene occurs.

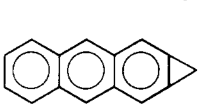


When 2,3-dehydronaphthalene (**19**) is substituted for benzyne in the cycloaddition reactions described above, the corresponding ring-fused 1,4-dihydroanthracenes may be obtained. Diazotization of 3-amino-2-naphthoic acid, followed by gentle pyrolysis, leads to the formation of **19**. Addition of 1,2-dimethylenecyclobutane to this species provides the adduct **20** which can then be aromatized by DDQ to anthro[*b*]cyclobutene (**21**) in good yield. Reaction of 1-vinylcyclobutene with **19** provides a complex mixture from which **22** may be isolated by preparative gas chromatography. The NMR spectrum of this molecule is very similar to that of compound **6**. The DDQ promoted oxidation of **22** proceeds much more slowly than that of **20** but after 3 days at 45 °C conversion to **23** is complete. It has been noted in a number of related cases that the position of ring fusion plays an important role in determining the rate of aromatization. These findings will be presented in a later paper.[7]



23

It is interesting to note that the cyclopropene-fused analogues of 21 and 23 are as yet unknown. Billups[8] and Garratt[9] have attempted preparation of anthro[*b*]cyclopropene 24 by



24

similar routes without success. Garratt has suggested that the apparent instability of this molecule might indicate a higher degree of bond fixation than in the corresponding naphtho[*b*]cyclopropene. For the present, it appears that the cyclobutene-fused anthracene derivatives which we have described here represent the outer limit of ring strain which will be tolerated by this polynuclear aromatic system.

Experimental Section

Dimethyl sulfoxide was distilled under vacuum from calcium hydride. Pyridine was distilled from barium oxide. Just prior to use, lead tetraacetate was recrystallized from acetic acid and protected from oxygen and light. DDQ was recrystallized from benzene/chloroform. Proton and carbon nuclear magnetic resonance spectra were obtained on a Varian Associates T-60 or XL-100 spectrometer and chemical shifts are reported in ppm downfield from Me_4Si. Infrared spectra were obtained on a Beckman IR-4250 spectrometer. Mass spectra were obtained by direct sample introduction into a Hewlett Packard 5933 A GC–mass spectrometer system. High-resolution mass spectral analyses were performed by Dr. R. Grigsby at the Department of Biochemistry and Biophysics, Texas A & M University, on a CEC21-110B double-focusing magnetic sector spectrometer at 70 eV. Exact masses were determined by peak matching. All melting points are uncorrected.

1,4-Dihydronaphtho[*b*]cyclobutene (3). Treatment of 9.5 g (0.07 mol) of anthranilic acid with 14 g (0.12 mol) of isoamyl nitrite in 50 mL of dry tetrahydrofuran at 20 °C for 1.5 h provided benzenediazonium 2-carboxylate as a tan precipitate.[10] This material was collected by filtration and combined with 100 mL of dichloromethane to which was added 2.2 g (0.028 mol) of 1,2-dimethylenecyclobutane.[11] The mixture was refluxed for 2 h until gas evolution had ceased. It was then cooled, washed three times with saturated sodium bicarbonate solution, and dried over magnesium sulfate. Filtration and evaporation of the solvent gave a yellow oil which was chromatographed on 35 g of silica gel, eluting with petroleum ether, to provide 1.10 g (25%) of 1,4-dihydronaptho[*b*]cyclobutene: mp 69–70 °C; NMR ($CDCl_3$) δ 7.15 (s, 4 H, ArH), 3.3 (s, 4 H, $ArCH_2$), and 2.6 (s, 4 H, cyclobutyl protons); IR (KBr) 3070, 2945, 2910, 2885, 2830, 1495, 1430, 1286, 1175, and 737 cm^{-1}.

1,4-Dihydronaphtho[*a*]cyclobutene (6). Following the above procedure, 25 mmol of benzenediazonium 2-carboxylate was reacted with 1.0 g (12 mmol) of 1-vinylcyclobutene.[1c] Chromatography of the crude product on 10 g of silica gel, eluting with petroleum ether, provided 0.98 g (50%) of a colorless oil. Analysis of this material by VPC (10 ft × ⅛ in. 10% Carbowax 20 M on Chromosorb W 60/80 mesh at 112 °C and 30 mL/min) showed two equal area peaks with retention times of 9.7 and 16.5 min. Both of these peaks were isolated by preparative VPC. The first peak showed: NMR (CCl_4) δ 7.25 (broad s, 5 H, ArH), 6.55 (m, 3 H), and 5.6–5.0 (overlapping m, 4 H); IR (thin film) 3100, 1498, 1452, 916, and 700 cm^{-1}. The IR did not correspond to 2-vinylnaphthalene and thus the material was considered to be an isomer of phenylhexatriene. Isolation of the second peak provided 1,4-dihydronaphtho[*a*]cyclobutene as a colorless oil: NMR (CCl_4) δ 6.98 (s, 4 H, ArH), 5.5 (broad S, 1 H, = CH), 3.8 (broad m, 1 H), 3.2 (m, 2 H), 2.8–2.3 (m, 3 H), and 2.0 (m, 1 H); IR (thin film) 3025, 2985, 2870, 1486, 1457, 1433, 1215, 1005, and 816 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 156 (92, parent), 141 (92), 128 (100), and 115 (36).

Naphtho[*b*]cyclobutene (4). To a stirred solution of 0.29 g (1.3 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in 25 mL of dry benzene was added 0.10 g (0.64 mmol) of **3**. The reaction mixture was stirred at room temperature for 1 h by which time the peak corresponding to **3** had disappeared by VPC. The mixture was filtered and the benzene was evaporated to give a black residue which was chromatographed on 10 g of silica gel, eluting with petroleum ether to provide 0.08 g (81%) of **4**: mp 85–86 °C; lit mp 86.5 °C;[3] NMR ($CDCl_3$) δ 7.5 (m, 6 H, ArH) and 3.28 (s, 4 H, $ArCH_2$); IR (KBr) 3060, 2920, 870, and 740 cm^{-1}.

Naphtho[*a*]cyclobutene (7). To a stirred solution of 1.43 g (6.3 mmol) of DDQ in 50 mL of dry benzene was added 0.49 g of 50% pure **6** (1.57 mmol). The reaction mixture was refluxed for 30 min and filtered and the benzene was evaporated. The black residue was dissolved in petroleum ether and filtered and the solvent was evaporated to give 0.17 g of a yellow oil. This oil was first distilled in a Kugelrohr apparatus (bp 20–70 °C (0.1 mm)) and then chromatographed on 35 g of silica gel, eluting with petroleum ether, to afford 0.048 g (20%) of **7** as a colorless oil: NMR ($CDCl_3$) δ 7.45 (m, 6 H, ArH) and 3.25 (m, 4 H, $ArCH_2$); IR (thin film) 3060, 2930, 1595, 1365, 810, 775, and 732 cm^{-1}.

2,3-Dimethylene-1,2,3,4,-tetrahydronaphthalene (8). A pyrolysis apparatus was constructed from a 12 in. long 1-in. diameter spiral of 0.25 in. (o.d.) Pyrex tubing. At the bottom end of this tube was attached a 15-mL round-bottom flask equipped with a side arm for the introduction of nitrogen. At the top of the tube was a trap cooled in a dry ice–acetone bath and connected to the vacuum line. The spiral tube was heated to 300–310 °C in a vertical tube furnace and evacuated to 0.05 mm. A 1.50-g (9.6 mmol) sample of 1,4-dihydronaphtho[*b*]cyclobutene (**3**) placed in the 15-mL flask was rapidly forced into the hot zone by heating with a microburner. After all the sample had evaporated from the pot, a slow bleed of nitrogen was continued until no further material collected in the cold trap. The pyrolyzed material (1.30 g) was collected and subjected to a second pyrolysis under the same conditions to ultimately yield 1.00 g (67%) of a white solid which NMR analysis showed to consist of a mixture of 30% of unreacted **3** and 70% of diene **8**. Pure **8**, mp 64 °C, was isolated by preparative VPC (6 ft × 0.25 in. 2% OV-101 on Chromosorb W 80/100 mesh at 100 °C and 30 mL/min): NMR (CCl_4) δ 7.04 (s, 4 H, ArH), 5.3 (broad s, 2 H, $=CH_2$), 4.88 (broad s, 2 H, $=CH_2$), and 3.50 (s, 4 H, $ArCH_2$); IR (thin film) 3013, 2920, 2870, 2820, 1501, 1460, 1425, 888, and 743 cm^{-1}.

5,6,11,12-Tetrahydronaphthacene (9). A 0.10-g (0.64 mmol) sample of **3** was subjected to a double pyrolysis as described above. The crude pyrosylate was taken up in 20 mL of dichloromethane to which was added 1.28 mmol of benzenediazonium 2-carboxylate generated as described above. The mixture was refluxed for 2 h and cooled and the dichloromethane was removed under vacuum. The residue was chromatographed on 60 g of silica gel, eluting with petroleum ether, to yield 0.04 g (27%) of **9** as a white solid: mp 160–165 °C; NMR ($CDCl_3$) δ 7.1 (s, 8 H, ArH) and 3.45 (s, 8 H, ArCH); IR (KBr) 2980, 2910, 1540, 1305, 1075, and 785 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 232 (60, parent), 229 (30), 217 (31), and 104 (100). Treatment of a small sample of **9** with DDQ in refluxing benzene resulted in the formation of a material which had an R_f identical to that of naphthacene.

Sealed Tube Pyrolysis of 3. In a small, heavy-wall tube was placed 0.10 g (0.64 mmol) of 1,4-dihydronaphtho[*b*]cyclobutene (**3**). The tube was sealed and heated to 200 °C for 8 h. After cooling, the resulting yellow oil was chromatographed on 35 g of silica gel, eluting with petroleum ether, to afford 0.04 g (40%) of adduct **10**: mp 133–134 °C;

NMR (CCl_4) δ 7.0 (8, H, Ar**H**) and 3.2, 2.7, 2.05, 1.9 (overlapping m, 16 H); IR (KBr) 3060, 3020, 2930, 1500, 1490, 1440, and 750 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 312 (54, parent), 284 (4), 156 (100), 141 (74), 128 (36), and 114 (34).

1,4-Dihydronaphtho[*b*]cyclobutene Oxide (12). A solution of 0.20 g (1.28 mmol) of 1,4-dihydronaphtho[*b*]cyclobutene in 15 mL of dichoromethane under nitrogen was cooled in an ice bath. A solution of 0.30 g (1.47 mmol) of *m*-choroperbenzoic acid in 10 mL of dichloromethane was then slowly added. The reaction mixture was stirred for 1 hour and then allowed to warm to room temperature and stirred an additional 23 h. The organic phase was then washed with 10% sodium thiosulfate, 5% sodium bicarbonate, water, and saturated sodium chloride solution. Drying over magnesium sulfate and evaporation of the solvent provided 0.18 g (80%) of epoxide **12:** mp 94–95 °C; NMR ($CDCl_3$) δ 7.08 (s, 4 H, ArH), 3.27 (s, 4 H, $ArC\mathbf{H}_2$), and 2.10 (s, 4 H, cyclobutyl **H**); IR (KBr) 2950, 2850, 1440, 1155, and 765 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 172 (58, parent), 144 (23), 130 (50), 129 (100), 128 (66), 116 (74), and 115 (79).

Reaction of 12 with Lithium Diethylamide. To a stirred, ice-cold mixture of 0.04 g (0.58 mmol) of diethylamine in 3 mL of anhydrous ether was added 0.3 mL of 2.4 M *n*-butyllithium in hexane. The solution was stirred for 10 min and 0.05 g (0.29 mmol) of epoxide **12** was added. The reaction mixture was stirred at 4 °C for 20 min and for an additional 2 h at room temperature. It was then poured into 30 mL of H_2O and extracted with ether. The ether extracts were dried over magnesium sulfate, filtered, and evaporated to provide a material which showed an NMR spectrum identical with that of naphtho[*b*]-cyclobutene (**4**).

Dimethyl Tricyclo[8.2.0.0^{3,8}]dodec-3(8)-ene-1,10-dicarboxylate (16). In a heavy-wall glass tube were placed 1.75 g (0.0162 mol) of 1,2-dimethylenecyclohexane (15),[12] 0.05 g of hydroquinone, and 2.76 g (0.0162 mol) of dimethyl-1,2-cyclobutene dicarboxylate (14).[13] The tube was sealed and heated in an oil bath to 85 °C for 18 h. The tube was then cooled and opened and the crude product was purified on 100 g of 60/200 mesh silica gel, eluting with 1:5 ether/petroleum ether to provide 2.91 g (64%) of the Diels–Alder adduct: mp 64–66 °C: NMR (CCl_4) δ 3.63 (s, 6 H, $CO_2C\mathbf{H}_3$) and 2.55–1.42 (m, 16 H); IR (KBr) 2910, 1720, 1440, 1330, 1280, 1265, 1220, 1100, and 1038 cm^{-1}.

Tricyclo[8.2.0.0^{3,8}]dodec-3(8)-ene-1,10-dicarboxylic Acid (17). To a solution of 2.90 g (0.0105 mol) of diester **16** in 40 mL of methanol was added a solution of 4.7 g (0.084 mol) of potassium hydroxide in 5 mL of water. The mixture was refluxed overnight, poured into 200 mL of saturated NaCl solution, and acidified with concentrated hydrochloric acid. The aqueous solution was extracted with ether and the extracts were dried over anhydrous sodium sulfate. Filtration, removal of solvent, and drying under vacuum provided 2.27 g (87%) of the corresponding dicarboxylic acid: mp 145–155 °C: NMR (Me_2SO-d_6) δ 2.6–1.4 (m, 16 H); IR (KBr) 3100 (6), 2940, 1734, 1405, 1295, 1240, 1178, 1150, and 1110 cm^{-1}.

5,6,7,8-Tetrahydronaphtho[*b*]cyclobutene (18). To a solution of 2.1 g (8.4 mmol) of diacid **17** and 3.3 g (42 mmol) of pyridine in 25 mL of dry dimethyl sulfoxide under nitrogen was added 8.2 g (18.5 mmol) of lead tetracetate. An exothermic reaction was observed with the evolution of gas. The reaction mixture was stirred at room temperature for 75 min and then poured into 125 mL of saturated NaCl solution and extracted five times with ether. The ether solution was washed first with cold, dilute hydrochloric acid and then with water, dried over anhydrous sodium sulfate, and filtered; the solvent was removed under vacuum to provide 0.52 g of a yellow liquid. This crude product was purified on 30 g of 60/200 mesh silica gel, eluting with 1:5 ether/petroleum ether to provide 0.343 g (26%) of pure hydrocarbon **18:** NMR (CCl_4) δ 6.45 (s, 2 H, Ar**H**), 2.98 (s, 4 H), 2.60 (m, 4 H), and 1.62 (m, 4 H); IR (thin film) 3010, 2935, 2860, 2840, 1478, 918, and 864 cm^{-1}. Anal. Calcd for $C_{12}H_{14}$: *m/e* 158.1096. Found: *m/e* 158.1089.

DDQ Oxidation of 18. To a solution of 20 mg of 5,6,7,8-tetrahydronaphtho[*b*]cyclobutene (**18**) in 5 mL of dry benzene was added 50 mg of DDQ and the reaction mixture was stirred at room temperature for 10 h. The resulting yellow solution was passed through a small silica gel column, eluting with petroleum ether. Removal of the solvent gave a white solid, mp 78–80 °C, which showed an NMR spectrum identical to that of naphtho[*b*]cyclobutene (**4**).

1,4-Dihydroanthro[*b*]cyclobutene (20). In a 100-mL round-bottom flask were placed 0.5 g (2.7 mmol) of 3-amino-2-naphthoic acid,[14] 0.5 mL of concentrated HCl, 20 mL of tetrahydrofuran, and 0.63 g (5.4 mmol) of isoamyl nitrite. The mixture was stirred for 1 h and the resulting orange precipitate was collected by filtration and washed with dioxane (distilled from sodium). The wet precipitate was transferred to a 100-mL round-bottom flask to which was added 30 mL of dioxane, 0.2 mL of propylene oxide, and approximately 0.5 g (6.3 mmol) of 1,2-dimethylenecyclobutane. This mixture was rapidly heated to 100 °C in an oil bath and stirred for 1 h until no further gas evolution was observed. The red solution was cooled and filtered through 30 g of silica gel, washing with 200 mL of dichloromethane. The oil obtained by evaporation of solvent was taken up in petroleum ether and removed from a tarry precipitate. The petroleum ether was evaporated and the resulting yellow oil was chromatographed on 30 g of silica gel eluting with petroleum ether. A white solid (50 mg, 9% yield) was obtained which appeared to be 85% pure by NMR. This material was subjected to preparative TLC (SilicAR TLC-7GF) eluting with petroleum ether to provide 40 mg of **20:** mp 135–136 °C; NMR ($CDCl_3$) δ 7.8–7.2 (m, 4 H), 7.60 (d, 2 H, $J = 2.5$ Hz), 3.50 (broad s, 4 H, cyclobutenyl **H**), and 2.67 (broad s, 4 H, ArC**H**); IR (KBr) 3050, 2935, 2908, 2865, 2830, 868, and 746 cm^{-1}.

Anthro[*b*]cyclobutene (21). In a 5-mm NMR tube was placed 40 mg of **20** and 0.5 mL of carbon tetrachloride. To this solution was added 0.10 g of DDQ and the tube was heated in a water bath at 40 °C. The reaction was followed by NMR. After 16 h the peaks corresponding to **20** had completely disappeared while those corresponding to **21** had grown in. The solution was filtered through silica gel and the solvent was removed to provide a white solid: mp 245–247 °C; NMR ($CDCl_3$) δ 8.35 (s, 2 H, $H_{9,10}$), 7.95 (m, 2 H, $H_{5,8}$), 7.56 (s, 2 H, $H_{1,4}$), 7.33 (m, 2 H, $H_{6,7}$), and 3.38 (s, 4 H, $ArC\mathbf{H}_3$); IR (KBr) 3060, 2965, 2935, 1415, 1290, 995, 902, and 740 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 204 (100, parent), 203 (42), 202 (41), 101 (46), 89 (18), and 88 (18). Anal. Calcd for $C_{16}H_{12}$: *m/e* 204.0939. Found: *m/e* 204.0932.

1,4-Dihydroanthro[*a*]cyclobutene (22). The same procedure as for **20** utilizing 0.5 g (2.7 mmol) of 3-amino-2-naphthoic acid[18] and 0.5 g (6.3 mmol) of 1-vinylcyclobutene[1c] was followed. After workup as outlined for **20** above there was obtained 30 mg (5.4%) of solid material, mp 98–101 °C, which was identified as **22** by its spectral properties: NMR ($CDCl_3$) δ 7.9–7.2 (m, 6 H, Ar**H**), 5.67 (broad s, 1 H, =C**H**), 4.05 (broad s, 1 H, ArC**H**), 3.40 (broad s, 2 H, $ArC\mathbf{H}_2$), and 3.0–2.0 (overlapping m, 4 H, cyclobutyl **H**); IR (KBr) 2955, 1659, 1562, 1510, 880, and 755 cm^{-1}.

Anthro[*a*]cyclobutene (23). A solution of 30 mg of **22** and 0.10 g of DDQ in 0.5 mL of $CDCl_3$ was placed in a 5-mm NMR tube. The tube was warmed to 45 °C in a water bath and the reaction was followed by NMR. After 3 days the upfield peaks corresponding to **22** had disappeared. The solution was filtered through silica gel, the solvent was evaporated, and the residue was purified by preparative TLC (SilicAR TLC-7GF) eluting with petroleum ether to provide 20 mg of **23:** mp 103–105 °C: NMR ($CDCl_3$) δ 8.42 and 8.25 (singlets, 2 H, H_9 and H_{10}), 8.1–7.7 (m, 3 H, H_4, H_5, H_8), 7.6–7.2 (m, 3 H, H_3, H_6, H_7), and 3.35 (m, 4 H, cyclobutyl **H**); IR (KBr) 2950, 2920, 1260, 1095, 900, and 795 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 204 (100, parent), 203 (48), 202 (46), 101 (47), 100 (20), and 88 (20). Anal. Calcd for $C_{16}H_{12}$: *m/e* 204.0939. Found: *m/e* 204.0930.

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Reductive Coupling of Carbonyl Compounds to Olefins by Tungsten Hexachloride–Lithium Aluminum Hydride and Some Tungsten and Molybdenum Carbonyls

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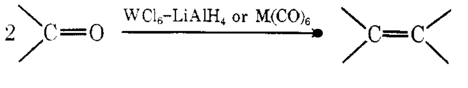
The WCl_6–$LiAlH_4$ system and some zerovalent metal carbonyls such as $W(CO)_6$, $W(CO)_5L$ (L = PPh_3, $NH_2C_6H_{11}$, $CPh(OCH_3)$, and Cl), and $Mo(CO)_6$ have been found to cause reductive coupling of carbonyl compounds. The reactivity of the WCl_6–$LiAlH_4$ system is almost the same as that of the WCl_6–BuLi system. The WCl_6–$LiAlH_4$ reagent is also capable of reducing epoxides to olefins. A mechanism involving a carbene–W complex is proposed for the carbonyl coupling.

The reductive coupling of carbonyl compounds by transition metal complexes is an important method for the formation of C–C bonds.[2] Sharpless et al. have reported that a new class of reagents derived from the interaction of tungsten(VI) hexachloride (WCl_6) and *n*-butyllithium (BuLi) causes coupling of carbonyl compounds.[3] We were interested in this tungsten-induced coupling for two reasons, because of its synthetic utility and because of its relationship to the significant olefin metathesis reaction caused by VIB group metals, especially tungsten.

We have found that the WCl_6–$LiAlH_4$ system and also hexacarbonyltungsten(0) ($W(CO)_6$) show similar reactivities to that of the WCl_6–BuLi system for coupling.



We have reported that these reagents are also effective for dehalogenative coupling of gem dihalides and related compounds.[4] In this paper we describe the reductive coupling of carbonyl compounds by tungsten compounds and hexacarbonylmolybdenum(0) and also the reductions of epoxides to olefins by tungsten compounds.[5]

Results and Discussion

WCl_6–$LiAlH_4$ System. The WCl_6–$LiAlH_4$-promoted coupling of carbonyl compounds was carried out using equimolar amounts of WCl_6 and $LiAlH_4$ and 0.5 equiv of the carbonyl compound in tetrahydrofuran (THF) under nitrogen atmosphere at room temperature. The reaction was rapid and complete within 1 h. The results are summarized in Table I. In contrast to the reaction with WCl_6–BuLi, it was important to use equimolar amounts of WCl_6 and $LiAlH_4$ to obtain optimum yield.[3] Substitution of other cocatalysts such as $NaAlH_4$, $NaBH_4$, LiH, CaH_2, Mg, or Zn or other solvent systems resulted in inferior yields (Tables II and III). As can be seen from Table I, aliphatic systems underwent coupling in poor yield. The reactivity of this reagent was almost the same

Table I. Coupling of Carbonyl Compounds by WCl_6–$LiAlH_4$ or $W(CO)_6$[a,d]

Carbonyl compd	Registry no.	Product	Yield, %[b] *E*	Yield, %[b] *Z*	Reagent[c]
Benzaldehyde	100-52-7	Stilbene	73	5	A
			21	21	B
p-Methoxybenzaldehyde	123-11-5	*p,p'*-Dimethoxystilbene	76	6	A
			39	24	B
p-Chlorobenzaldehyde	104-88-1	*p,p'*-Dichlorostilbene	63	2	A
			36	26	B
p-Methylbenzaldehyde	104-87-0	*p,p'*-Dimethylstilbene	57	3	A
			29	14	B
Benzophenone	119-61-9	Tetraphenylethylene	43		A
			3		B
Acetophenone	98-86-2	1,2-Dimethylstilbene	20	13	A
			3	4	B
Propionaldehyde	123-38-6	3-Hexene	18 (*E,Z*)		A
Cyclohexanone	108-94-1	Cyclohexylidenecyclohexane	55		A
			0.2		B

[a] Reaction was performed charging 0.8 mmol of WCl_6, 0.8 mmol of $LiAlH_4$, and 0.4 mmol of the carbonyl compound in 10 mL of THF (for reagent A) or CH_2Cl_2 (for reagent B) with stirring for 6 h at room temperature under nitrogen atmosphere. [b] Based on the starting carbonyl compound. [c] A, reagent WCl_6–$LiAlH_4$; B, reagent $W(CO)_6$. [d] Registry No.—WCl_6, 13283-01-7; $LiAlH_4$, 16853-85-3; $W(CO)_6$, 14040-11-0.

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