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A Novel Cyclocarbonylation Reaction: Synthesis of 1,2,8,9-Tetrahydrocyclohepta[1,2,3-*fg*:4,5,6-*f'g'*]diacenaphthylene-5-one

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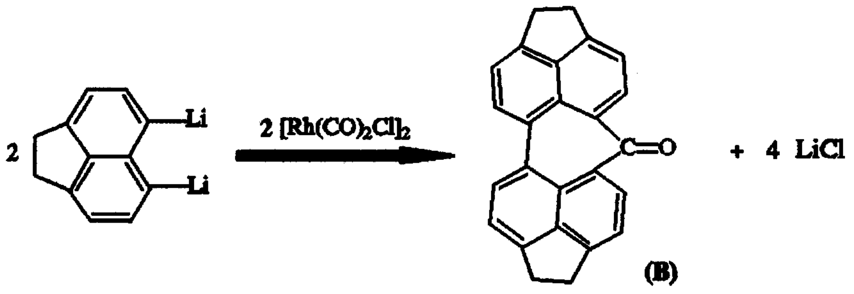
Abstract: 1,2,8,9-Tetrahydrocyclohepta[1,2,3-*fg*:4,5,6-*f'g'*]diacenaphthylene-5-one (**B**) was synthesized by the reaction of 5,6-dilithioacenaphthene with $[Rh(CO)_2Cl]_2$. X-ray crystallography shows that **B** is a cycloheptatrienone flanked by two acenaphtho groups.

The stoichiometric reaction between $[Rh(CO)_2Cl]_2$ and ArHgCl produced Ar_2CO.[1] However, with excess ArHgCl, Ar_2CO and the coupling product Ar_2 were obtained. This indicates that $[Rh(CO)_2Cl]_2$ can function as both a carbonylation and a coupling reagent.[1] A stoichiometric reaction between a dicarbanion and $[Rh(CO)_2Cl]_2$ in which $[Rh(CO)_2Cl]_2$ carbonylated one carbanion, while the other carbanion was intramolecularly coupled producing an odd-membered cycloketone, would be of considerable interest.

The coupling of 5,6-dilithioacenaphthene to give 1,2,7,8-tetrahydrodicyclopenta[1,2,3-*cd*:1',2',3'-*lm*]perylene (A) using $Ni(acac)_2$ or $CoCl_2$ as catalyst has been reported.[2] It is also known that reaction of 5,6-dilithioacenaphthene with pyracenequinone, followed by oxidation with $Pb(OAc)_4$, gave 1,2,8,9-tetrahydroocta[1,2,3-*fg*:5,6,7-*f'g'*]diacenaphthylene-5,12-dione.[3] However, 1,2,8,9-tetrahydrocyclohepta[1,2,3-*fg*:4,5,6-*f'g'*]diacenaphthylene-5-one (**B**) has not been synthesized, probably because of the strong steric repulsion of the two acenaphtho groups which prevents insertion of the carbonyl group.

Treatment of 5,6-dilithioacenaphthene with one equivalent of $[Rh(CO)_2Cl]_2$ afforded **B** in 30 % yield according to equation 1. The yield was the same when the reaction was performed under one atmosphere of CO. The reaction produced only two compounds, unlike the coupling reaction for preparing A from 6,6'-dibromo-5,5'-diacenaphthene, which produced as many as 18 compounds.[2] The two products were **B** and acenaphthene. They were easily separated by column chromatography. Mass spectra and microanalysis established the formula of the orange crystals of **B** as $C_{25}H_{16}O$. However, the $\upsilon(C=O)$ absorption in the infrared spectrum occurred at extremely low frequency (1620 cm^{-1}), and the ^{13}C NMR signal was at very high field (173.6 ppm) for an aromatic carbonyl group (the ^{13}C NMR data are shown in Figure 1). Therefore, the structure of **B** was determined by X-ray diffraction. An ORTEP plot is shown in Figure 2. It is seen that in reaction 1 two acenaphtho groups have been coupled through the 6,6' position, and a carbonyl



(1)

group has been inserted in the 5,5′ position. The C(25)—O distance was 1.245 (13) Å, which is consistent with the expected C=O distance of 1.23 (1) Å.[4] The carbonyl group has distorted the seven membered ring. The C(7)—C(11) distance (1.515 (10) Å) was 0.08 Å longer than the analogous distance in A of 1.437 Å.[5] This lengthening was due to steric repulsion, which also twisted the two acenaphtho rings. The angle between planes 1 and 4 (25.2° (14)) was smaller than the angle between planes 2 and 3 (33.0° (11), see Table 1), whereas in A all of the carbons lay in the same plane.[5]

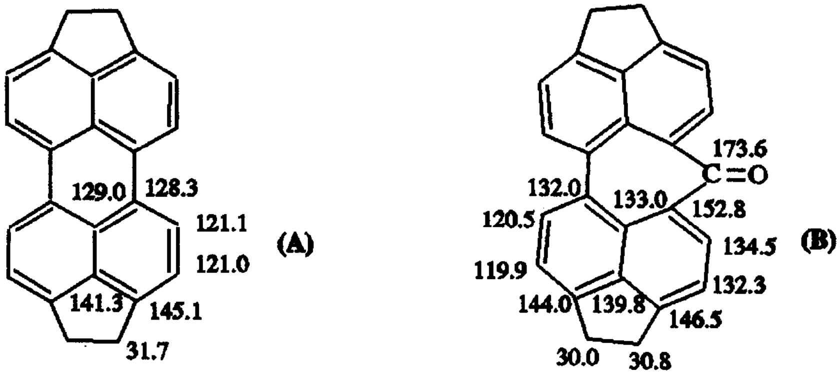


Figure 1. ^{13}C NMR of A and B.

EXPERIMENTAL

General. The reaction was carried out under nitrogen. Ether was dried by refluxing over sodium benzophenone and was distilled directly onto the reactants. 5,6-Dilithioacenaphthene[3] and $[Rh(CO)_2Cl]_2$[6] were prepared by literature methods. Column chromatography was carried out on silica gel (230-400 mesh) using CH_2Cl_2/petroleum ether (30-60 °C, 1/3 v/v) as eluent. NMR spectra were recorded in $CDCl_3$ solution using a JEOL FX-100 NMR spectrometer, and referenced internally to Me_4Si. Infrared spectra were recorded as KBr pellets on a Carl Zeiss/Specord-75 infrared spectrometer. The mass spectrum was obtained on an AEI MS-50 instrument. The electronic spectrum was recorded on a Hitachi-340 Spectrometer.

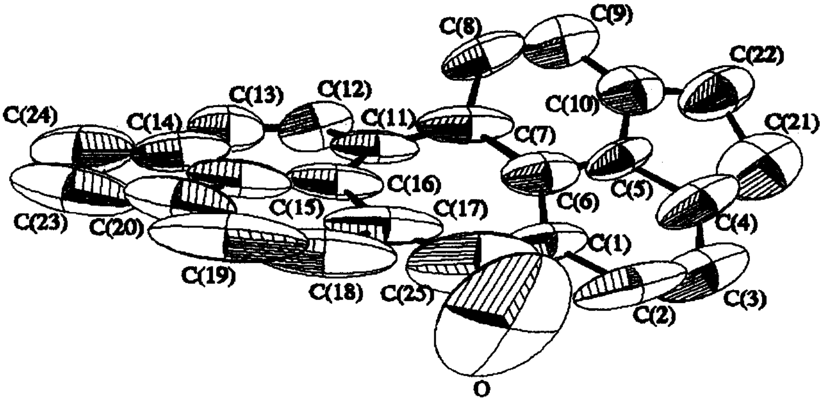


Figure 2. Molecular structure of **B**.

Table 1 Angles between Planes in **B** (°)[a]

	Plane 1	Plane 2	Plane 3	Plane 4
Plane 1	0	6.2 (13)	29.4 (13)	25.2 (14)
Plane 2	6.2 (13)	0	33.0 (11)	29.8 (13)
Plane 3	29.4 (13)	33.0 (11)	0	7.2 (12)
Plane 4	25.2 (14)	29.8 (13)	7.2 (12)	0

[a] Plane 1: C(1), C(2), C(3), C(4), C(5), C(6); plane 2: C(5), C(6), C(7), C(8), C(9), C(10); plane 3: C(11), C(12), C(13), C(14), C(15), C(16); plane 4: C(15), C(16), C(17), C(18), C(19), C(20).

Preparation of 1,2,8,9-Tetrahydrocyclohepta[1,2,3-*fg*:4,5,6-*f'g'*]diacenaphthylene-5-one (B). To a freshly prepared solution of 5,6-dilithioacenaphthene-TMEDA complex[3a] (5.21 mmol, 70 cm^3) in an icebath (-5 to -10 °C) was added dropwise 50 cm^3 of an ether solution of freshly sublimed $[Rh(CO)_2Cl]_2$ (2.00 g, 5.14 mmol). The solution changed color from orange to brown, then became a black-brown suspension. The mixture was stirred and warmed to room temperature over 2 hours. The ether was removed under vacuum to give a yellow-brown solid, which was extracted with CH_2Cl_2. The CH_2Cl_2 solution was washed with water (2 × 100 cm^3), then separated by column chromatography. A pink fluorescent band (R_f = 0.25) was collected and dried to give orange **B** (0.255 g, 30% based on 5,6-dibromoacenaphthene). The product was recrystallized from $CHCl_3$/petroleum ether (60-90 °C, 1/1, v/v) to give orange needles (0.120 g, 15 %). Mp: 225.5 - 228.0 °C. Anal.: Calcd. for $C_{25}H_{16}O$: C, 90.3; H, 4.9 %. Found: C, 89.9; H, 4.6 %. EI-MS, (m/z, int., M^+): 332, 100, $[C_{25}H_{16}O]^+$; 304, 20, $[C_{25}H_{16}O - C_2H_4]^+$; 276, 3, $[C_{25}H_{16}O - 2C_2H_4]^+$. IR (KBr pellet): 1620 cm^{-1} $\upsilon(C{=}O)$. NMR ($CDCl_3$, δ ppm): ^1H: 3.38 (8H, s, 4CH_2 of C(21)-C(24)); 7.30 (2H, d, J = 8.0 Hz, H(9) and H(13)); 7.34 (2H, J = 8.0 Hz, H(3) and H(19)); 7.72 (2H d, J = 8.0 Hz, H(8) and H(12)); 8.58 (2H, d, J = 8.0 Hz, H(2) and H(18)). ^{13}C: see Figure 1. UV (hexane), λ_{max} (nm): 441; 420; 400 (sh); 327; 248 (sh); 212.

X-ray Crystallography and Crystal data for B. The X-ray diffraction experiment was carried out on a NICOLET R3m/E diffractometer. The radiation was Mo Kα (λ = 0.71073 Å). The scan mode for the data collection was $\omega/2\theta$ with $2\theta \leq 44°$. The structure was refined by using the SHLEXTL program suite, supplied by NICOLET and implemented on an Eclipse/S140 computer, with scattering factors taken from the program. The structure was solved by direct methods to give the positions of all non-hydrogen atoms. These were refined anisotropically with fixed C—C distances for the four benzene rings. Hydrogen atoms were included as fixed contributors to the final least square refinement. Crystal data: $C_{25}H_{16}O$, M_r 332.4; triclinic, $P\bar{1}$; $\underline{a}$ = 7.604 (1), $\underline{b}$ = 8.695 (2), $\underline{c}$ = 14.037 (4) Å, $\underline{\alpha}$ = 83.64 (2), $\underline{\beta}$ = 75.35 (2), $\underline{\gamma}$ = 64.11 (1) °; V = 807.8 (3) Å^3; $\underline{Z}$ = 2. The crystal used was a small block of dimensions 0.32 × 0.24 × 0.24 mm. The number of unique reflections collected was 674, with 670 being observed by the criteria $\underline{I} > 3\,\sigma(\underline{I})$. Final $\underline{R}_F$ = 0.077; $\underline{R}_w$ = 0.077 and GoF = 1.32, with 235 refined parameters.

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Supplementary Material: Atomic coordinates and thermal parameters, bond distances and angles.

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