Scheme II

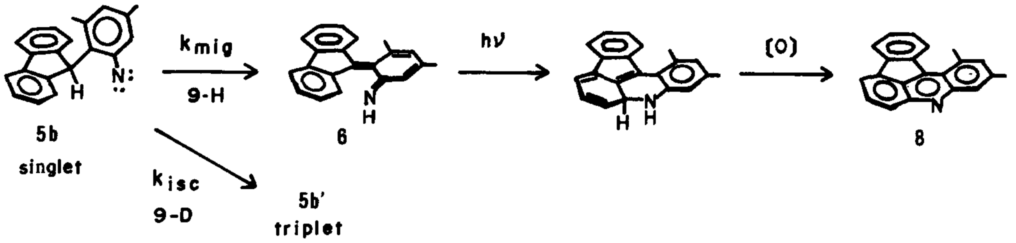

Table I. X,Y Band Positions of Various Triplet *o*-(9-Fluorenyl)phenylnitrenes at 4 K in Methylcyclohexane Glasses

precursor of nitrene	resonance position, G[a]	shifts, G
phenyl azide	6824[b]	0
1-azatriptycene (1)	6730	−94[c]
9-(2-azidophenyl)fluorene (3)	6750	−74
ap-9-(2-azido-4,6-dimethylphenyl)-fluorene (4a)	6722	−102
sp-9-(2-azido-4,6-dimethylphenyl)-9-deuteriofluorene (4b')	6745	−79

[a] The microwave frequency was normalized at 9.2196 GHz. The band positions were read with the aid of a gaussmeter (a Varian E-500 NMR gaussmeter). [b] The agreement with the literature data[6] is excellent. [c] The negative values correspond to downfield shifts relative to the signal position of phenylnitrene.

The above results provide, to our knowledge, the first example demonstrating a remarkable difference in reactivity between the well-defined conformers of a nitrene[10] and are explained in terms of the competition between the facile singlet reactions and intersystem crossing to the triplet nitrene in both conformers. In the singlet **5a**, the nitrene center is situated right above the fluorene ring, and therefore the addition to the double bond of the latter ring should be very favorable. Intersystem crossing to triplet **5a** can still compete to some extent. In singlet **5b**, since the hydrogen atom at the 9-position of the fluorene ring is so close to the univalent nitrogen, the 1,4-migration of the hydrogen becomes exclusive.[11] The reaction can be retarded by the deuterium isotope effect at the 9-position,[12] allowing intersystem crossing to the triplet to be competitive with the deuterium migration. *o*-Quinoid tautomer **6** obtained after the hydrogen migration undergoes conrotatory photocyclization to give the dihydro derivative of **8**.

We note that **5a** has the X,Y transition at lower magnetic field by 23 G than **5b'**. The difference corresponds to a slightly smaller zero-field splitting parameter *D*, which in turn indicates the longer average distance between the two odd electrons with parallel spin in **5a**. The probable explanation is that through-space interaction may be operating in delocalizing the p-type odd electron at the nitrenic center over the π-system of the fluorene ring lying underneath.

Turning lastly to a comparison with photochemistry of **1** and **3**, we collected the ESR data in Table I. The previous assignment of triplet nitrene **2** from **1** with low-field X,Y transition to the *ap* conformer and **2** from **3** with high-field signal to the *sp* form is consistent with the present results. The absorption spectral behaviors are also in accord with this assignment.

Registry No. 1, 197-45-5; **2**, 74357-27-0; **3**, 74357-30-5; **4a**, 85681-33-0; **5a**, 85681-34-1; **5b'**, 85681-35-2; **6**, 85681-36-3; **7**, 85681-38-5; **8**, 85681-37-4; phenyl azide, 622-37-7.

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(10) The presence of geometrical isomers in equilibrium is detected by ESR at cryogenic temperatures for naphthyl-, vinyl-, and quinolylcarbenes: (a) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129. (b) Hutton, R. S.; Roth, H. D.; Schilling, M. L. M.; Suggs, J. W. *Ibid.* **1981**, *103*, 5147. (c) Senthilnathan, V. P.; Platz, M. S. *Ibid.* **1981**, *103*, 5503.

(11) A similar scheme is presented for 1-methyl-8-nitrenonaphthalene: Platz, M. S.; Burns, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4425.

(12) Precedents for the isotope effect in the hydrogen abstraction reaction of biradicals and carbenes in matrices are found in the following: (a) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688. (b) Senthilnathan, V. P.; Platz, M. S. *Ibid.* **1980**, *102*, 7637.

Migration of Tricarbonylchromium Groups in Phenylanthracenes

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There are few reported examples of metal migration from one site on a coordinated organometallic ligand to another. Deprotonation of (fluorene)tricarbonylchromium [$C_{13}H_{10}Cr(CO)_3$] leads to an equilibrium mixture of the η^5 and η^6 complexes of the fluorenyl anion,[1] $C_{13}H_9Cr(CO)_3^-$. (η^6-Fluorene)tricarbonylmanganese cation, η^6-$C_{13}H_{10}Mn(CO)_3^+$, on deprotonation, gives η^6-$C_{13}H_9Mn(CO)_3$, which rearranges irreversibly to η^5-$C_{13}H_9Mn(CO)_3$.[2] We report the migration of a tricarbonylchromium group between two nonadjacent six-membered rings in phenylanthracenes.

(Anthracene)tricarbonylchromium (ATC) is a deep-purple complex in which the $Cr(CO)_3$ group bonds to a terminal ring.[3] (Biphenyl)tricarbonylchromium is yellow.[4] 9-Phenylanthracene incorporates biphenyl and anthracene systems in a single molecule. A refluxing solution of 9-phenylanthracene and $Cr(CO)_6$ in dioxane became purple. This solution, on standing overnight in the dark, turned yellow; heating to reflux temperature caused the solution again to become purple. From the cooled yellow solution were isolated yellow crystals of structure IIa[5] (Chart I). A solution of IIa in dioxane slowly became dark brown when heated to 100 °C, indicating a mixture of the yellow and purple compounds.

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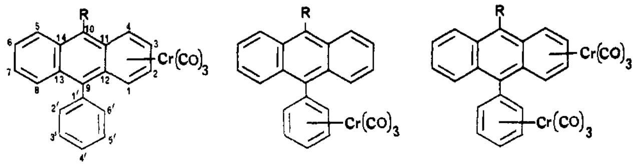
(4) Fischer, E. O.; Kriebitzsch, N.; Fischer, R. D. *Chem. Ber.* **1959**, *92*, 3214–3222.

(5) Anal. Calcd for $C_{23}H_{14}CrO_3$: C, 70.77; H, 3.61; O, 12.30. Found: C, 70.57; H, 3.56; O, 12.52. Mass spectrum, *m/z* 390 (M^+), 334 [$(M - 2CO)^+$] 306 [$(M - 3CO)^+$], 254 [$(M - Cr - 3CO)^+$], 52 (Cr^+, base peak), 28 (CO^+); ^1H NMR (60 MHz, CD_2Cl_2) δ 8.32 (s, 1 H), 7.60 (m, 9 H), 6.58 (m, 1 H), 6.15 (m, 1 H), 5.73 (m, 2 H); ^{13}C NMR (50.31 MHz, CD_2Cl_2) δ 138.4, 136.1, 133.2, 131.5, 130.8, 130.6, 128.7, 128.3, 127.9, 126.8, 126.6, 126.3, 105.7, 105.2, 93.2, 93.0, 90.9, 89.3.

0002-7863/83/1505-3724$01.50/0

Chart I



Ia, R = H
Ib, R = Ph

IIa, R = H
IIb, R = Ph

IIIa, R = H
IIIb, R = Ph

Use of di-*n*-butyl ether as solvent again produced a purple solution, which after 7 h of reflux (approximately 75% reaction by CO gas evolution) was quickly cooled; chromatography on silica gel under pressure (ca. 2 bar) at 3 °C (eluents: pentane, pentane–ether (2:1), and ether) yielded three fractions (weights ca. 5:5:1, overall yield 30–35%), which were purple, yellow, and purple respectively. The yellow fraction was shown to be IIa. The two purple fractions have structures Ia[6] and IIIa,[7] respectively. Complex IIIa is extremely labile, and satisfactory solution spectra were not obtained; oxidation or heat changes IIIa to IIa.

For Ia, the upfield shift in the ^{1}H NMR spectrum of signals δ 6.58–5.73 (4 H) and in the ^{13}C NMR of six signals (δ 105.7–89.3) indicates binding of the Cr(CO)$_3$ group to a terminal ring of the anthracene portion of the molecule. Carbonyl bands at 1960, 1899, and 1882 cm^{-1} (Et$_2$O) are comparable to those of ATC (1982, 1924, and 1897 cm^{-1} in cyclohexane[3]). The visible–UV spectrum shows a maximum at 514 nm (cf. 512 nm for ATC). For the free ligand, the aromatic absorptions (300–400 nm) contain at least five distinct bands, whereas only a single very broad band appears for complex Ia.

The signal at δ 5.75 (5 H) in the ^{1}H NMR spectrum of IIa indicates binding of the Cr(CO)$_3$ group to the external ring of the ligand (confirmed by four signals (δ 108.6–90.7) in the ^{13}C NMR spectrum). The signal at δ 9.45 is assigned to H(1) (or H(8)), which is deshielded by the Cr(CO)$_3$ group. This signal disappears on heating (dioxane-d_8) to 99 °C and reappears on cooling to ca. 80 °C. The signals at δ 5.75 are unchanged; this indicates that at 99 °C, the Cr(CO)$_3$ group is still bound to the external phenyl ring and that the changes observed at higher temperatures in the downfield region must be attributed to increased oscillation or rotation of the external phenyl ring about the C(9)–C(1′) bond. That there are more than eight signals in the normal aromatic region of the ^{13}C NMR spectrum also suggests restricted rotation about the C(1′)–C(9) bond. The visible–UV spectrum shows a band at ca. 433 nm, which appears as a shoulder on the aromatic absorptions in the 300–400-nm range.

The formation of Ia from IIa also occurs in *n*-Bu$_2$O. A boiling solution of IIa in *n*-Bu$_2$O changed over 6 h from yellow to dark purple. Quick cooling of this solution and chromatography yielded both Ia and IIa. Differential scanning calorimetry of IIa reveals first an exothermic irreversible process (probably a crystal modification) at 165–170 °C. Melting occurs at 215 °C, accompanied by endothermic conversion of IIa to Ia. At 223 °C exothermic decomposition occurs; thermogravimetric measurements indicate loss of three molecules of CO. In contrast, crystalline Ia undergoes decomposition at ca. 80 °C, with no evidence for formation of IIa. The equilibrium constant for the reaction IIa $\rightleftarrows$ Ia in molten 9-phenylanthracene has been determined. A mixture of IIa and ligand (mole ratio ca. 1:5.7) gave K_{eq} values of 1.37 ± 0.03 at 490 K and 1.25 ± 0.03 at 470 K; thus, $\Delta H = 9.0 \pm 4.0$ kJ/mol for the migration process.

The 9,10-diphenylanthracene system has also been studied. Compounds Ib, IIb, IIIb, and a bis(tricarbonyl)chromium complex in which the two Cr(CO)$_3$ groups are on the external rings have been isolated and characterized. Migration of the Cr(CO)$_3$ group transforming IIb to Ib has also been observed.

Further studies of the equilibria described are in progress, as are kinetic studies to elucidate the mechanism of Cr(CO)$_3$ group migration. It is probable that this migration is intermolecular,[8] as an intramolecular process seems unlikely on steric grounds.

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Registry No. Ia, 85629-62-5; Ib, 85629-63-6; IIa, 85629-64-7; IIb, 85629-65-8; IIIa, 85629-66-9; IIIb, 85629-67-0.

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[6] Anal. Calcd for C$_{23}$H$_{14}$CrO$_3$: C, 70.77; H, 3.61; Cr, 13.32. Found: C, 70.48; H, 3.68; Cr, 13.30. Mass spectrum, *m/z* 390 (M$^+$), 362 [(M – CO)$^+$], 334 [(M – 2CO)$^+$], 306 [(M – 3CO)$^+$], 254 [(M – Cr – 3CO)$^+$], 52 (Cr$^+$); ^{1}H NMR (60 MHz, CD$_2$Cl$_2$) δ 9.45 (m, 1 H), 8.65 (s, 1 H), 8.1 and 7.6 (m, 7 H), 5.75 (m, 5 H); ^{13}C NMR (50.31 MHz, CD$_2$Cl$_2$) δ 131.8, 131.0, 130.8, 129.0, 128.5, 128.1, 127.9, 126.1, 125.3, 125.0, 124.6, 108.6 (C1′), 99.0 (C3′, C5′), 93.5 (C4′), 90.7 (C2′, C6′); IR (Et$_2$O) 1969, 1900 cm^{-1}.

[7] Mass spectrum (field desorption ionization), *m/z* 526 (M$^+$), 470 [(M – 2CO)$^+$], 442 [(M – 3CO)$^+$], 390 [(M – Cr – 3CO)$^+$], 358 [(M – 6 CO)$^+$], 334 [(M – Cr – 5CO)$^+$], 306 [(M – Cr – 6CO)$^+$], 254 [(M – 2Cr – 6CO)$^+$], 52 (Cr$^+$).

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Stereochemistry of Hydroboration of α-Chiral Olefins and Reduction of α-Chiral Ketones. An Unusual Anti-Cram Selectivity with Dialkylboranes

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Prediction of the relative asymmetric induction for addition to chiral carbonyl compounds has been a subject of great interest from a synthetic and mechanistic point of view.[1] A variety of transition-state models based on steric approach control have been proposed for nucleophilic additions to chiral carbonyl compounds.[2] Although derived from different concepts, each model predicts the Cram product unless other factors such as metal chelation of the carbonyl group with a nearby oxygen or nitrogen are involved. However, we have discovered that different stereochemical pathways are involved in the reduction of chiral ketones with nucleophilic organoborohydrides and electrophilic organoboranes. As a result, either Cram or anti-Cram product can be predominantly produced. In a similar manner, hydroboration of the methylene compound derived from the ketone proceeds in a highly anti-Cram fashion. These results allow one to effectively control stereochemistry in an acyclic system.

During the investigation of the synthesis of steroid side chains,[3] we required an authentic mixture of a 22-hydroxy steroid epimeric at C-20. The mixture could be prepared by hydroboration of a 20(22)-methylene steroid. Since there was a discrepancy in the literature about the stereochemistry of such hydroborations,[4] we

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