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INTRAMOLECULAR HYDROGEN TRANSFER OF AMINOCARBENE COMPLEXES LEADING TO IMINES

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SUMMARY

Displacement of the amino carbene ligand from complexes of the type $[(CO)_5CrC(R)NHR']$ [R = Ph; R′ = Ph, NHPh; R = Me, R′ = 2-(3-indolyl)ethyl] with a coordinating base such as pyridine, affords the corresponding imine, RCH=NR′, as a result of intramolecular hydrogen transfer. The intermediacy of a hydrazinocarbene complex in the reaction of an alkoxy carbene complex with hydrazines to give a coordinated nitrile is established.

INTRODUCTION

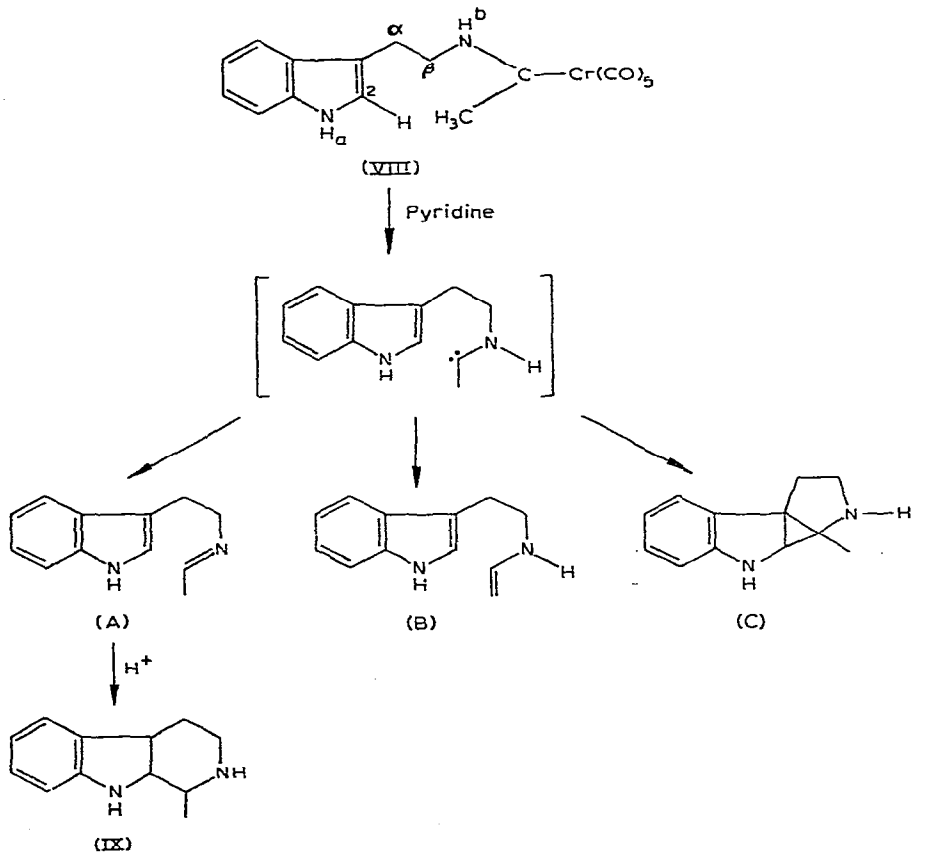
Mono- and dialkylcarbenes rearrange both by means of intramolecular α-hydrogen migration giving olefins and by internal insertion into C–H bonds giving cycloalkanes. The ratio of olefin to cycloalkane product is determined by the availability and proximity of primary, secondary and tertiary C–H bonds and by the manner in which the carbene is generated[1]. Arylalkylcarbenes, such as methylphenylcarbene, produce olefins in high yield as a result of α-hydrogen migration[2].

Ethyl vinyl ether is the only organic product isolated from the reaction of pyridine with the complex [ethoxy(methyl)carbene]pentacarbonylchromium in cyclohexene[3]. The methyl protons in this complex are acidic[4], so that a concerted nucleophilic attack by pyridine at either the carbene carbon or chromium atoms followed by release of the carbene and simultaneous migration of hydrogen seems the most likely reaction path. In any event, rearrangement of the carbene must be occurring more rapidly than either dimerisation to give an olefin or addition to the solvent to form a norcarane as neither of these products were observed. Thermolysis of the complex [methoxy(phenyl)carbene]pentacarbonylchromium, (I), at 135° afforded the carbene dimer, α,α-dimethoxystilbene[5], apparently without hydrogen migration. In view of these contrasting observations, we have investigated the migratory aptitude of hydrogen attached to nitrogen in aminocarbene compounds of the type $[(CO)_5CrC(R)NHR']$.

RESULTS AND DISCUSSION

When the complex [$(CO)_5CrC(Ph)NHPh$], (II), was treated with an excess of pyridine in refluxing hexane, the steady precipitation of *fac*-[$(C_5H_5N)_3Cr(CO)_3$] (III) indicated the progress of the reaction. After 18 hours the sole organic product (71% yield of pure material) was *N*-benzylideneaniline, (IV).

The addition of a slight excess of phenylhydrazine to the complex [$(CO)_5CrC$-(Ph)OEt], (V), in ether solution at room temperature results in a rapid reaction. The isolation of benzylidenephenylhydrazine (20%) (VI) confirms the existence[6] of an unstable hydrazinocarbene intermediate, [$(CO)_5CrC(Ph)NHNHPh$], in the reaction which leads, as a result of cleavage of the carbene ligand and subsequent internal rearrangement, to the principal products of the reaction which are aniline and the benzonitrile complex [$(CO)_5CrNCPh$], (VII).



These results show that the base induced displacement of an aminocarbene ligand containing an α-hydrogen atom attached to nitrogen, results in the formation of an imine as a result of the migration of that hydrogen to the carbene carbon atom. This process is assisted by resonance stabilisation of the product from the aromatic

substituents. When an α-hydrogen atom is not available, as in the thermolysis of the aminocarbene complex $[(CO)_5CrC(Ph)NMe_2]$, the carbene carbon atom will scavenge a hydrogen atom, presumably from the methyl groups, giving rise to the vicinal diamine, $Ph(Me_2N)CHCH(NMe_2)Ph$, which was isolated as a complex of the type $[L_2Cr(CO)_4]$[7].

Treatment of the complex {[2-(3-indolyl)ethylamino](methyl)carbene}pentacarbonylchromium, (VIII) with an excess of pyridine at reflux (115°), followed by an acidic work-up process gave tetrahydroharman (IX) as the only isolable organic product. In the light of the foregoing evidence we believe that (IX) is formed via the methyl imine (A) (Scheme) which rearranges in acid. The transfer of hydrogen from the methyl group will give the enamine, (B), which would be unstable under the basic conditions of the reaction. The brown residue remaining after a preparative TLC separation of (IX) probably contains the decomposition products arising from (B). There is no evidence of carbene addition to the indolic double bond to give (C), a cyclopropane. The formation of (IX) as a result of direct intramolecular insertion of the carbene into the indole olefinic α-CH bond is discounted as improbable. These findings indicate that the transfer of hydrogen is a very rapid process and occurs before the carbene ligand, if it ever becomes truly free from the metal as such, can react even with a potential intramolecular substrate.

Although the preparation of (II) from (I) using the published procedure[8] is straightforward, we find that if the complex (V) is used in place of (I), then the reaction with aniline affords an adduct (X) having the composition $[(CO)_5CrC(Ph)NHPh\cdot PhNH_2]$. All attempts to remove the aniline from (X) whether by heating, by quaternisation (HCl and MeI) or by chromatography were completely unsuccessful. When (X) was treated with pyridine in a manner similar to (II), the formation of (III), (IV) and aniline was observed.

The preparation of (VIII) followed from the addition of tryptamine to $[(CO)_5CrC(Me)OEt]$. Examination of the NMR spectrum of (VIII) showed the α-CH_2 group (see Scheme) as a triplet (J 6 Hz) which is not further split by coupling to 2-H. The β-CH_2 group appears as a multiplet because of coupling with both the α-CH_2 group and the amino hydrogen, H_b. Irradiation of the amino hydrogen signal, H_a (τ 3.27 in C_6D_6 solution) caused the doublet arising from 2-H at τ 3.59 (J 4 Hz) to collapse to a singlet thus establishing the former signal as being due to the indolic amino hydrogen. Both H_a and H_b exchange very rapidly with D_2O.

EXPERIMENTAL

The complex (V) was prepared by a standard method and obtained as red prismatic crystals (87% yield), m.p. 33-34° (lit.[9] m.p. 29°).

Preparation of the adduct $[(CO)_5CrC(Ph)NHPh\cdot PhNH_2]$, (X)

Aniline (1.1 g, 11.8 mmole) was added to (V) (1.63 g, 5.0 mmole) dissolved in benzene (15 ml) and the mixture stirred at room temperature overnight. After removal

of the solvent, recrystallisation of the yellow residue from hexane/benzene (1/1 v/v) gave yellow needle shaped crystals of (X) (1.91 g, 4.1 mmole), m.p. 76-78°. (Found: C, 61.3; H, 4.0; N, 6.2. $C_{24}H_{18}CrN_2O_5$ calcd.: C, 61.8; H, 3.9; N, 6.0%.)

Reaction of $[(CO)_5CrC(Ph)NHPh]$, *(II), with pyridine*

To (II) (0.736 g, 1.97 mmole) dissolved in hexane (20 ml) contained in a 50 ml round bottom flask fitted with a condenser and mercury guard tube, pyridine (2.0 ml, 24.8 mmole) was added and the solution stirred under reflux for 18 h. After 15 min reflux the yellow solution had become orange in colour and after 30 min it was deep red with a red solid present. The amount of solid increased as the reaction progressed. At the end of the reaction the solid was isolated, washed with hexane (3 × 5 ml) and dried under vacuum to give red crystals of $[(C_5H_5N)_3Cr(CO)_3]$, (III) (0.692 g, 94% yield). (Found: C, 57.6; H, 4.3; Cr, 14.2; N, 10.7. $C_{18}H_{15}CrN_3O_3$ calcd.: C, 57.9; H, 4.0; Cr, 13.9; N, 11.2%.) ν(CO) 1895(s), 1760(s) (Nujol) cm^{-1}. The liquid fractions were combined and evaporated to dryness. The residue was twice crystallised from 80% ethanol to give PhCH=NPh, (IV), (0.254 g, 71% yield), m.p. 50-51° (lit.[10] m.p. 51-52°). (Found: C, 86.1; H, 6.1; N, 7.7. $C_{13}H_{11}N$ calcd.: C, 86.2; H, 6.1; N, 7.7%.)

Reaction of $[(CO)_5CrC(Ph)OEt]$, *(V), with phenylhydrazine*

To a solution of (V) (0.888 g, 2.72 mmole) in dry ether (5 ml) was added freshly distilled phenylhydrazine (0.607 g, 3.10 mmole). After standing for 15 min at room temperature the solution became orange in colour. All the volatile material was transferred under vacuum to a trap cooled with liquid nitrogen. The red residue was mixed with ether and then extracted with 0.2 *N* hydrochloric acid (2 × 5 ml). The ethereal solution was dried (Na_2SO_4) and then chromatographed (alumina, grade III; ether) following concentration. This gave a single fraction which on evaporation of the yellow solution and crystallisation from hexane/ether (1/4 v/v) afforded pale yellow crystals of $[(CO)_5CrNCPh]$, (VIII), (0.535 g, 1.8 mmole, 67% yield,) m.p. 114-115° (lit.[11] m.p. 117°). (Found: C, 49.2; H, 1.9; Cr, 17.3; N, 4.7. $C_{12}H_5CrNO_5$ calcd.: C, 48.8; H, 1.7; Cr, 17.6; N, 4.8%.) ν(CO) 2074(m), 1949(s), 1922(m) (CS_2) cm^{-1}. The acidic aqueous phase was rapidly made alkaline and then extracted with ether (4 × 5 ml). After drying (Na_2SO_4) and evaporation of the ethereal solution to dryness, a buff coloured solid was obtained which was crystallised from 95% ethanol to give PhCH=NNHPh (0.101 g, 19% yield), m.p. 154–156° (lit.[12] m.p. 157-158°). (Found: C, 79.4; H, 5.8; N, 13.9. $C_{13}H_{12}N_2$ calcd.: C, 79.6; H, 6.1; N, 14.3%.) Analysis for the distillate by GLC (5% Carbowax, 20m, AW-DMDS on Chromosorb G80-100) showed that it contained only aniline, excess phenylhydrazine and solvent ether.

Preparation of {[2-(3-indolyl)ethylamino](methyl)carbene}*pentacarbonylchromium, (VIII)*

Tryptamine hydrochloride[13] (0.967 g, 4.94 mmole) was dissolved in 5% aqueous potassium hydroxide solution (10 ml) and the free base then extracted into

ethyl acetate (3 × 5 ml). The ethyl acetate solution of tryptamine was dried (Na_2SO_4) filtered and added dropwise at room temperature to [$(CO)_5CrC(Me)OEt$] (1.162 g 4.4 mmole) in ether (10 ml). After 1 h the reaction mixture was worked up to give yellow needle shaped crystals of (VIII) (1.07 g, 2.83 mmole, 64% yield), m.p. 112-113°. (Found: C, 54.0; H, 3.7; Cr, 13.8; N, 7.3. $C_{17}H_{14}CrN_2O_5$ calcd.: C, 54.0; H, 3.7; Cr, 13.8; N, 7.4%) λ_{max} nm (log ε): 248 (4.62), 290 (4.11), 354 (3.84). ν_{max} 3475s, 3335m, 3080w, 2940w, 2914w, 2058m, 1971w, 1938s, 1925ssh, 1624w, 1520sbr, 1460m, 1440m, 1420m, 1356m, 1334m, 1254w, 1240w, 1230w, 1130w, 1103s, 1094s, 1073w, 1014m, 945w, 835w, 804w, 765m, 741s, 678s (hexane, $CHCl_3$, CS_2) cm^{-1}. NMR spectrum τ (ppm): (*i*) C_6D_6 solution: 8.16 (3H, s, CH_3), 7.30 (2 H, t, α-$C\underline{H}_2$), 7.37 (2 H, m, β-CH_2), 3.59 (1 H, d, 2-$\underline{H}$), 3.27 (1 H, s, $N\underline{H}_a$), 1.75 (1 H, s, $N\underline{H}_b$), 2.85 (4 H, m); (*ii*) $CDCl_3$ solution: 7.56 (3 H, s, $C\underline{H}_3$), 6.94 (2 H, t, α-CH_2), 6.37 (2 H, m, β-$C\underline{H}_2$), 2.98 (1 H, d, 2-$\underline{H}$), 2.03 (1 H, s, $N\underline{H}_a$), 1.30 (1 H, s, $N\underline{H}_b$), 2.48, 3.75 (4 H, m); (*iii*) $(CD_3)_2CO$ solution: 7.57 (3 H, s, $C\underline{H}_3$), 6.89 (2 H, t, α-$C\underline{H}_2$), 6.17 (2 H, m, β-$C\underline{H}_2$), 2.85 (1 H, d, 2-H), 0.01 (1 H, s, NH_a), −0.22 (1 H, s, NH_b), 2.48, 2.68, 2.97 (4 H, m). Mass spectrum (*m/e*, *I*): 378, 4 (M^+); 350, 3; 322, 0.3; 294, 14; 266, 4; 238, 100; 130, 142; 108, 34; 103, 14; 95, 19.

Reaction of (VIII) with pyridine

The complex (VIII) (0.30 g, 0.79 mmole) was dissolved in pyridine (0.5 ml, 6.2 mmole) and the solution heated under reflux for 16 h in an atmosphere of nitrogen. The solution was then extracted into 1 *N* hydrochloric acid (5 ml) leaving a yellow solid residue. The residue was isolated and purified to give *cis*-[$(C_5H_5N)_2Cr(CO)_4$] (0.207 g, 0.64 mmole, 80% yield). The orange aqueous phase was extracted with ethyl acetate, made alkaline with 1 *N* sodium hydroxide and the free bases extracted with ethyl acetate again (4 × 10 ml). The combined extracts were dried ($MgSO_4$), filtered and evaporated to dryness. The buff solid remaining was purified by preparative TLC (silica; EtOAc + 5% Et_3N). The band having R_f 0.3 was removed, leaving a brown residue on the baseline, R_f 0.0. The former fraction was shown to be tetrahydroharman, (IX), (0.025 g, 17% yield), m.p. 173-175° (lit.[14] m.p. 174-176°), by comparison with an authentic sample.

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