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XLIV*. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE ADDUCT OBTAINED FROM QUADRICYCLANE AND DI- μ -CHLOROTETRACARBONYLDIRHODIUM(I)

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Summary

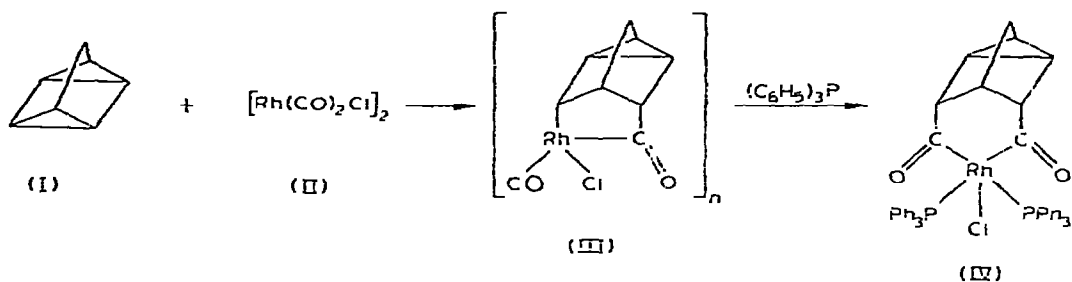
The structure of the adduct obtained from the reaction of tetracyclo[3.2.0.0^{2,7}.-0^{4,6}]heptane (quadricyclane with di- μ -chlorotetracarbonyldirhodium(I) has been established on the basis of chemical evidence. The structure proposed by Cassar and Halpern was confirmed on the basis of the tricyclic alcohol isolated from the lithium aluminum deuteride reduction of the initially formed rhodium containing adduct.

In 1970, Cassar and Halpern suggested that the addition of quadricyclane (I) to di- μ -chlorotetracarbonyldirhodium(I) (II) produced a 1/1 adduct (III) in which only one of the C-C bonds of the quadricyclane had been broken [2]. This structural assignment was based on elemental analysis, infrared data, the reported conversion of III to IV on treatment with triphenylphosphine, and analogy [3]. In view of our own deep involvement in the area of transition metal complex promoted rearrangements of strained ring systems [4] and the extensive interest of numerous groups in the rearrangement of quadricyclanes [5], we felt that the observations of Cassar and Halpern were of sufficient significance to merit a more rigorous verification of the structure of III. Our interest in this verification was strengthened by our inability to repeat the conversion of III into IV as reported. (We have since learned that the conversion of III into IV in

* For part XLIII see ref. 1.

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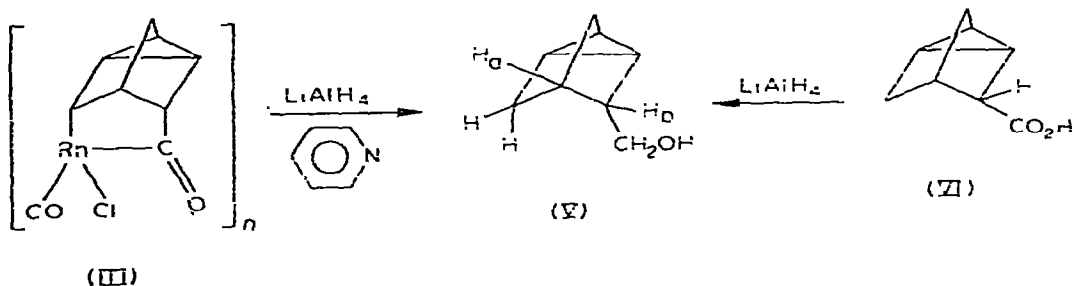
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the presence of triphenylphosphine will occur only if the reaction is carried out under a carbon monoxide atmosphere.)

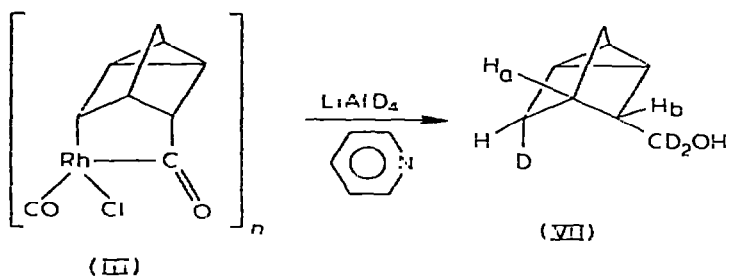
The preparation of III was accomplished as reported. In order to confirm the formation of a carbon-carbon bond between the carbonyl group and the seven-carbon skeleton, the complex was reduced with lithium aluminum hydride* to give 3-norbornylcarbinol (V) [7]. The alcohol was identical in all respects to that obtained via the reduction of the norbornene carboxylic acid (VI) [8].

The formation of V from III established that one of the carbonyl groups of II had become bonded to the modified quadricyclyl skeleton. However, it did not provide any information about the presence or position of the postulated bond from the modified quadricyclyl skeleton to the rhodium. Reduction of III with lithium aluminum deuteride in pyridine gave a sample of V containing three deuterium atoms (VII). The NMR spectrum of this compound established that two of the deuterium atoms reside on the carbinol moiety, as was anticipated. Unfortunately, the exact position of the third deuterium atom could not

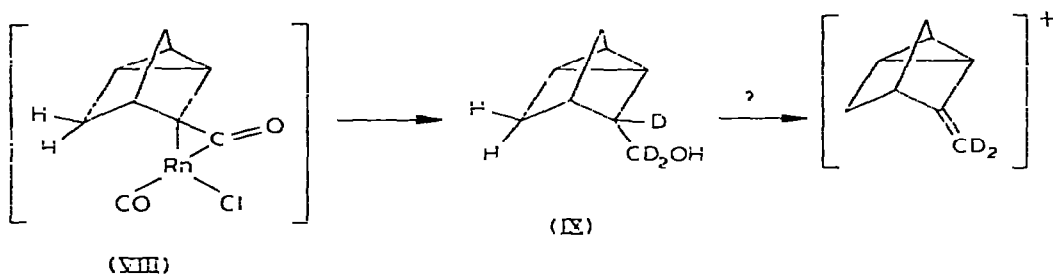


be established unequivocally on the basis of a comparison of the NMR spectra of V and VII. Attempts to establish the position of the third deuterium atom by mass spectroscopy provided an additional complication. A major peak for VII was *P*-19. It was established that this major fragmentation pattern involved loss of DOH which raised the question of whether the originally isolated complex had structure III as postulated, or whether a hydrogen shift had occurred to produce VIII which would have been reduced to IX. The loss of DOH from IX would appear to be preferable to the loss of DOH from VII. In order to resolve this apparent ambiguity, compounds IX and X were prepared. The synthesis of X was

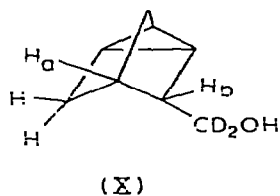
* The reductive cleavage of carbon-rhodium bonds with sodium borohydride has been previously reported [6]. However sodium borohydride failed to produce the desired reduction of III in our hands.



accomplished via the lithium aluminum deuteride reduction of VI. In order to prepare IX, VI was first treated with an excess of lithium diisopropyl amide to



give a dianion, which on quenching with deuterium oxide, gave the α -deuterated carboxylic acid (XI). Reduction of this material with lithium aluminum deuteride



gave IX. The IR and NMR spectra of IX were different from those of the reduction product obtained from the rhodium containing adduct, which eliminated VIII as a possible structure.

A comparison of the NMR spectra and mass spectral cracking patterns of V, VII, IX and X firmly established VII as the structure of the deuteride reduction product obtained from the rhodium containing adduct. As shown in Table 1, the mass spectral cracking patterns show the loss of water (or deuterated water) and of the carbinol moiety. The pattern for IX showed retention of all of the deuterium atoms in the m/e 109 peak. This indicated that the loss of water involved neither an α - nor a β -elimination. Since VII lost HOD, it is required that the deuterium atom come from a position other than the positions α - or β - to the hydroxyl group. Barring a major rearrangement of the hydrocarbon skeleton (which was ruled out by the comparison of V with an authentic sample), the most likely position remaining for loss of a deuterium atom as labeled water would be as shown in VII.

The NMR spectra of V, VII, IX and X showed the bridgehead hydrogen,

TABLE I

COMPARISON OF MASS SPECTRAL FRAGMENTATION PATTERNS OF THE 3-NORTRICYCLYL-CARBINOLS (RELATIVE INTENSITIES OF m/e 127-80)

m/e	V	VII	IX	X
127		36	50	
126				42
124	29			
109			33 ^a	
108		25 ^c		39 ^a
106	30 ^a			
94		100 ^d	100 ^d	
93	79 ^b	58	32	100 ^d
92		68	47	26
91	100			56
80	25	42	32	26

^a - HOH. ^b - CH₂OH. ^c - HOD. ^d - CD₂OH.

H_a, as a broad singlet at τ 8.09 \pm 0.01. The α -proton, H_b, appeared as a triplet at τ 8.27 for V, a singlet at τ 8.28 for X, and a singlet at τ 8.26 for VII. For IX, no signal was observed in this region.

We feel that the data presented above conclusively establish the presence of a carbon-rhodium bond and a new bond between the modified quadricyclyl skeleton and one of the carbonyl groups of II. Our findings tend to support the structure of the 1/1 adduct of quadricyclane and di- μ -chlorotetracarboxyldirrhodium(I) originally postulated by Cassar and Halpern*. The exact mechanistic detail whereby the "oxidative addition" [2] product is formed remains to be elucidated.

Experimental

Quadricyclane (I) was prepared by the method of Smith [9], di- μ -chlorotetracarboxyldirrhodium(I) (II) was prepared by the method of McCleverty and Wilkinson [10], and 3-bromonortricyclane was prepared by the method of Roberts and coworkers [8].

Di- μ -chlorotetracarboxyldirrhodium(I)-quadricyclane adduct (III)

In a three-necked, 250 ml round-bottomed flask, equipped with a magnetic stirrer, condenser, argon atmosphere and an ice bath, was placed 3.6 g (9.25 mmol) of II and 200 ml of purified technical pentane. Quadricyclane (2.5 g, 27.2 mmol) was added dropwise and after a brief induction period of ca. 2 min a bright yellow precipitate formed. The reaction mixture was stirred for an additional 2 h with an increased argon flow to reduce the pentane volume to ca. 75 ml. The bright yellow adduct III was collected by vacuum filtration, washed with pentane, and dried under vacuum to afford 4.76 g (90%) of the adduct. An infrared spectrum in KBr (Perkin-Elmer Model 457) showed carbonyl bands at 2070, 2010 (sh) cm^{-1} , and a band at 1735 cm^{-1} which was attributed to the inserted carbonyl (lit. [2] 2070 and 1750 cm^{-1}).

* Subsequent to the completion of this study, we have learned that a similar conclusion concerning the correctness of this structural assignment has been reached on the basis of X-ray crystallography. We wish to thank Prof. G. Christoph for informing us of his results prior to publication.

Attempted preparation of the di-inserted carbonyl rhodium—quadricyclane complex (IV) with triphenylphosphine

A solution of 1.35 g (2.35 mmol) of the previously prepared adduct (III) in 20 ml of purified chloroform was treated with a solution of 2.38 g (9.1 mmol) of triphenylphosphine in ca. 12 ml of chloroform. The reaction mixture was stirred for 2 h, the volume of chloroform was reduced to 15 ml, and 40 ml of purified technical pentane was added to precipitate a bright yellow product, which was vacuum filtered and washed with pentane to afford 1.19 g of product. The solvent was evaporated to yield another 1.34 g of product. Infrared spectra of both products showed them to be carbonylchlorobis(triphenylphosphine)rhodium by comparison with a previously prepared sample. The second product showed several hydrocarbon bands which were attributed to polymer formation. The formation of carbonylchlorobis(triphenylphosphine)rhodium under similar conditions was previously noted in the work of McQuillin and Powell [6].

Reduction of the adduct III with lithium aluminum hydride

Purified pyridine (20 ml) was added to 1.0 g (1.8 mmol) of III in a three-necked, 100 ml, round-bottomed flask, equipped with a condenser, drying tube and magnetic stirrer. The bright yellow solution was cooled with an ice-salt bath and purged with argon. To the solution was slowly added 0.6 g (16.0 mmol) of lithium aluminum hydride. The solution gradually turned very dark and was stirred for 24 h at room temperature. Hydrochloric acid (4 ml, 10%) was added dropwise and the reaction mixture was transferred to a separatory funnel and extracted with a total of 300 ml of ether. The ether was extracted with 10% hydrochloric acid until the extract was distinctly acidic, and the organic phase was dried over anhydrous magnesium sulphate. After filtration, the ether was removed by slow distillation through a glass helices packed column to afford ca. 1.5 ml of residue, which by gas chromatography (1/8 in X 10 ft, 15% diethylene glycol succinate on 60/80 Chromosorb P at 90-100°C) showed the composition to be ca. 30% ether, 35% 3-nortricyclylcarbinol (V) and 30% dimers. The IR spectrum of V was identical to the one obtained from the previously prepared alcohol and was quite different from the corresponding spectrum of 4-norborn-2-enylcarbinol. The sample was analyzed by GC-MS along with the 3-nortricyclylcarbinol prepared from VI and the 4-norborn-2-enylcarbinol which confirmed the formation of the 3-nortricyclylcarbinol (V). The dimers had molecular weights of 186 (C₁₄H₁₈) and 188 (C₁₄H₂₀).

Reduction of the adduct III with lithium aluminum deuteride

Purified pyridine (40 ml) was added to 2.0 g (3.5 mmol) of III in a three-necked, 250 ml, round-bottomed flask, equipped with a condenser, drying tube, magnetic stirrer, and argon atmosphere. The yellow solution was cooled with an ice-acetone bath (ca. -8 °C). To the solution was slowly added 1.35 g (32.2 mmol) of lithium aluminum deuteride. The solution gradually turned very dark and was stirred 20 h at room temperature and ca. 40 ml of deuterium oxide was added dropwise to quench the reaction. The reaction mixture was transferred to a separatory funnel and extracted with a total of 500 ml of ether. The ether was extracted with 10% hydrochloric acid until the water phase was distinctly acidic., the organic phase was dried over anhydrous magnesium sulphate,

filtered, and the ether was removed by slow distillation through a glass helices packed column to afford 1.35 g of residue. Gas-liquid chromatography (DEGS column) showed ca. 15% ether, 54% alcohol (VII), and 13% dimer. GC-MS, NMR, and IR analyses confirmed the formation of the trideuterated alcohol. IR (neat): 2.98, 3.25, 3.39, 3.46, 4.52 w, 4.79 w, 9.12, 12.39, and 12.60 μ ; NMR (100 MHz): τ 6.52 (br, s), 7.72 (s), 8.10 (s), 8.26 (s), and 8.40-9.20 (m); mass spec. determined mol. wt. found: 127.1074. $C_8H_9D_3O$ calcd.: 127.1076.

3-Carboxynortricyclane (VI)

A solution of 90 g (0.52 mol) of 3-bromonortricyclane in 200 ml of anhydrous ether was slowly added to a rapidly stirred suspension of 15.8 g (0.65 mol) of magnesium turnings and several drops of ethylene dibromide in 400 ml of ether under an argon atmosphere. The reaction mixture was gently refluxed for 1 h and then force filtered into a suspension of ca. 400 g of dry ice in 400 ml of ether, and stirred for 10 h under argon. Hydrochloric acid (200 ml, 10%) was added, the ether layer was separated and extracted with 100 ml of 10% hydrochloric acid and the combined water phases were extracted with 100 ml of ether. The ether was dried over anhydrous magnesium sulphate and removed by rotary evaporation to yield an oily solid. Recrystallization from purified technical pentane was unsatisfactory. The oily solid was taken up in 150 ml of ether and treated with 400 ml of 7% sodium hydroxide. The water phase was separated, extracted with 100 ml of ether, acidified with 10% hydrochloric acid, extracted with 400 ml of ether, dried over anhydrous magnesium sulphate, and filtered. The ether was removed by rotary evaporation to afford 62.3 g (86%) of VI, m.p. 42-46 °C (lit. [8] m.p. 40-50.6 °C or 43-45 °C). IR (neat): 3.37, 5.83, 7.04, 7.82, 8.08, 10.64, 12.31, and 12.50 μ ; NMR (60 MHz): τ 8.60 (m, 7H), 7.74 (s, 1H), 7.50 (s, 1H) and -1.70 (s, 1H).

3-Nortricyclylcarbinol (V)

To a slurry of 1.5 g of lithium aluminum hydride in ether was slowly added 4.5 g (33 mmol) of VI in 25 ml of ether. The reaction mixture was stirred for 20 h at 25 °C and 5 ml of 10% hydrochloric acid was added to destroy the excess lithium aluminum hydride. The ether layer was separated and the water phase was extracted with a total of 75 ml of ether. The ether was dried over anhydrous magnesium sulphate, filtered and distilled through a Vigreux column. The residue was vacuum distilled to yield 3.5 g (85%) of V, b.p. 72-74 °C/2.5 mm [lit. [7] 92-95.5 °C/9.5 mm]. IR (neat): 2.84, 3.22, 3.36, 3.46, 9.59, and 12.42 μ ; NMR (100 MHz): τ 6.03 (s), 6.50 (m), 8.10 (s), 8.27 (t), and 8.40-9.20 (m).

α -Deuterio-3-carboxynortricyclane (XI)

In a 100 ml Schlenk reaction vessel equipped with a magnetic stirrer, rubber septum, addition funnel and argon atmosphere, was placed 60 ml of anhydrous tetrahydrofuran and 3.03 g (30 mmol) of diisopropylamine. The solution was cooled to -12 °C and 37 mmol of n-butyllithium in 22 ml of hexane was slowly added. The solution was stirred for 0.5 h and 2.0 g (14 mmol) of VI in 15 ml of tetrahydrofuran was added dropwise. The temperature was maintained at < -10 °C for 18 h, deuterium oxide was added, the solution was stirred for 1.5 h at room temperature, and 15 ml of 8% hydrochloric acid was added. The organic

solvents were removed by rotary evaporation and the residue was extracted with ether, dried over anhydrous magnesium sulphate, filtered and the ether removed. NMR analysis indicated ca. 60% mono-deuterium incorporation. The above sequence was repeated on this material and the acid was purified by extraction with 5% sodium hydroxide, acidification and ether extraction to yield 1.2 g (60%) of the α -mono-deuterated acid. NMR analysis indicated 92% mono-deuterium incorporation, confirmed by mass spectroscopy which showed 94% mono-deuterium incorporation

Lithium aluminum deuteride reduction of XI

To a slurry of 0.5 g of lithium aluminum deuteride in anhydrous ether (cooled to -8°C) was slowly added 1.0 g (7.2 mmol) of α -deuterio-3-carboxy-nortricyclane (XI) in 10 ml of ether. The reaction mixture was stirred for 70 h at room temperature and 40 ml of 7% hydrochloric acid was added. The ether layer was separated and the water phase was extracted with 75 ml of ether. The ether was dried over anhydrous magnesium sulphate, filtered, and the solvent removed by rotary evaporation to yield a slightly yellow oil which was vacuum distilled to afford 0.78 g (85%) of the tri-deuterated alcohol IX. IR (neat): 2.96, 3.23, 3.38, 3.48, 4.52 w, 4.72 w, 10.30, and 12.50 μ ; NMR (100 MHz): τ 6.23 (s), 8.09 (s) and 8.40-9.20 (m).

Lithium aluminum deuteride reduction of VI

Utilizing the method described above for the preparation of V and IX, VI was reduced with lithium aluminum deuteride to produce X in an 80% yield. IR (neat): 2.95, 3.12, 3.38, 3.45, 4.52, 4.74, 8.68, 9.12, 10.15, 10.40, and 12.52 μ ; NMR (100 MHz): τ 6.69 (s), 8.10 (s), 8.28 (s), and 8.40-9.20 (m).

Acknowledgement

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