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RHODIUM(I) CATALYSIS OF CYCLOPROP[*a*]ACENAPHTHYLENE ISOMERIZATIONS

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Summary

Cycloprop[*a*]acenaphthylene was found to rearrange to phenalene in the presence of rhodium dicarbonyl chloride dimer. Deuterium labeling of this molecule at C(7) (both *exo* and *endo*), at C(8), at C(7) (*exo*) and C(8) and at C(7) (*exo*), C(8), and C(8′) indicated that the C(7) (*exo*) deuterium was migrating stereospecifically. Furthermore, all of the isotopic label present in the cycloprop[*a*]acenaphthylene was found statistically distributed over positions 1, 3, 4, 6, 7, and 9 of the phenalene product. Control experiments established the need of the catalyst, the inability to achieve rearrangement of the *exo*-7-methyl derivative, and the susceptibility of a monodeuterated phenalene for extensive isotopic scrambling in its own right when exposed to rhodium(I). These results have been interpreted on the basis of oxidative addition by rhodium(I) into the central bond of cycloprop[*a*]acenaphthylene from above the "flap", followed by shifting of the C(7) (*exo*) hydrogen (or deuterium) to give a η^3-allylrhodium-(III) complex. The experimental data further support a mechanism involving subsequent rearrangement of this intermediate around the periphery of the phenalene ring. This process which is otherwise degenerate is thought to be facilitated by the special electronic features of the phenalenyl system.

Since the initial discovery a decade ago of transition-metal-catalyzed strained ring rearrangements, steady progress has been made in our understanding of these processes. Increasingly sophisticated synthetic applications of these novel and varied reactions also continue to make their appearance. Yet there remain substantial gaps in our knowledge. A particular case in point is the behavior of bicyclo[*n*.1.0]alkanes toward various catalysts [1,2]. The very highly strained (64 kcal/mol) [3,4] bicyclo[1.1.0]butane ring system, for example, enters

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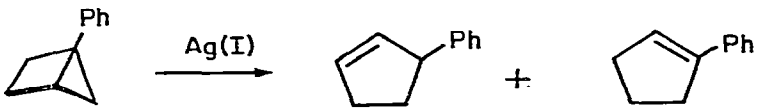
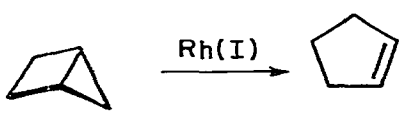
readily into isomerization with a rather wide selection of metal ions ranging from the noble silver(I) [5] and rhodium(I) [6] to the more mundane zinc(II) and mercury(II) [7]. Four mechanistically different pathways leading to 1,3-dienes, cyclobutenes, and vinylcyclopropanes have been experimentally defined [8].

In contrast, bicyclo[2.1.0]pentanes, molecules whose strain energy remain substantial (~54 kcal/mol), are generally unreactive toward silver(I) despite possible release of ca. 47 kcal/mol of strain energy through cleavage of the central bond [3,4,9]. The lone known exception is the 1-phenyl derivative (I) which gives a 28/72 ratio of II and III upon exposure to $AgBF_4$ [10]. The activating



(I) (II) (III)

effect of the aryl substituent is reflected further in the susceptibility of I to comparable rearrangement with Lewis acids such as ZnI_2. Despite the insensitivity of the parent hydrocarbon IV to soluble silver(I) catalysts at temperatures as high as 110°C [2,11] rhodium(I) is an excellent catalyst at room temperature

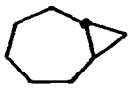


(IV) (V)

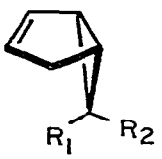
[11,12]. Further investigation has shown that deuterium substituents are randomly distributed in the cyclopentene product, the likely result of intervention by a metal hydride [12]. An additional notable aspect of this isomerization is the absence of rearrangement when the bicyclopentane nucleus carries a 5-*exo*-methyl or carbomethoxy substituent [11]. In yet other studies, Noyori has shown that bis(acrylonitrile)nickel(0) promotes [2 + 2] cycloaddition of the central bicyclopentane bond to electron-deficient olefins [13], the stereochemical course of which (double retention) is diametrically opposite to that realized under purely thermal conditions (double inversion) [14]. These results implicate a strong kinetic preference of these catalysts for attack to the topside of the "flap" in IV and its derivatives.

As the level of strain in such bicyclic molecules is further decreased as in bicyclo[3.1.0]hexane (VI), iridium(I) becomes the catalyst of choice [2]. However, the *trans*-fused ring juncture in VII and the additional double bond in VIII and IX are seemingly adequate to reinstate strain sufficient to provide a reasonable susceptibility to rhodium(I) [2,15]. As a test of the stereochemical and stereoelectronic consequences of C(6) substitution in the bicyclo[3.1.0]hex-2-enes, Barnett and coworkers qualitatively examined the rates of ring opening of the four esters illustrated. While the rearrangements of VIIIa and VIIIb in the presence of an oxidized $(Ph_3P)_3RhCl$ catalyst required 2 and 9 days, respectively, to go to completion, the more highly hindered IXa was entirely isomerized in 12 h! Under identical conditions, epimer IXb was recovered unchanged after 12 days. Furthermore, the dihydro derivatives of VIIIa and IXa remained intact

(VI)

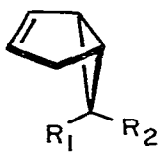


(VII)



VIII a , $R_1 = CO_2CH_3$, $R_2 = H$

VIII b , $R_1 = H$, $R_2 = CO_2CH_3$



IX a , $R_1 = CO_2CH_3$, $R_2 = CH_3$

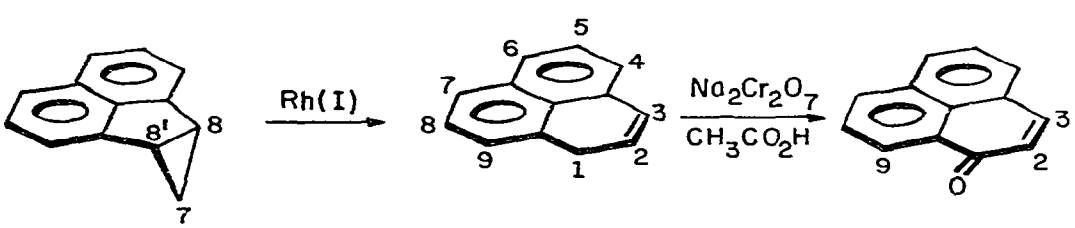
IX b , $R_1 = CH_3$, $R_2 = CO_2CH_3$

even after heating with this catalyst at 55—60° for several weeks [15].

In view of the obvious differences in reactivity separating bicyclo[2.1.0]-pentanes and bicyclo[3.1.0]hexanes and the still more remarkable behavior of VIII and IX, we have attempted to obtain more detailed mechanistic insight into the rearrangement of bicyclo[3.1.0]hexenyl systems through examination of the susceptibility of selected derivatives of cycloprop[*a*]acenaphthylene (X) to transition metal promoted rearrangement. Should the π-bond in VIII and IX play an important coordinative role in the simple bicyclo[3.1.0]hex-2-enes, then replacement by a naphthalene ring represents a substantial modification in this structural parameter. Also in order was an analysis of the possible relaxation of steric constraints to approach of catalyst with increasing ring size. The cyclo-prop[*a*]acenaphthylene frame was considered particularly well suited to these tests because of reasonable synthetic accessibility [16] and an anticipated acceptable level of reactivity in the central bond as a result of its connectivity to two benzylic carbons.

Results

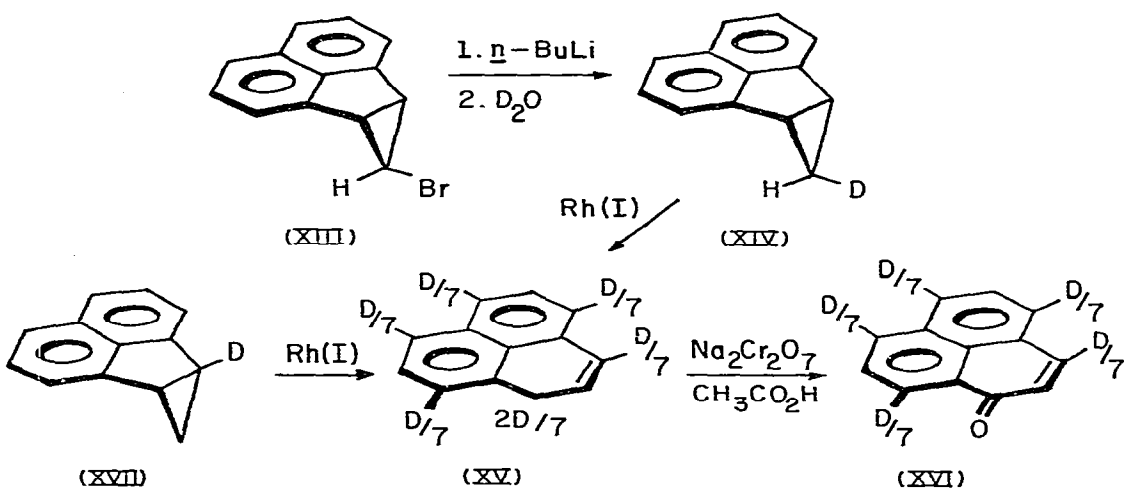
Although X proved unreactive toward soluble silver(I) salts under a variety of conditions, treatment with a catalytic quantity of rhodium dicarbonyl chloride dimer in benzene (or C_6D_6) resulted in complete rearrangement to phenalene (XI) after 5 h at 50°C. This isomerization could be conveniently monitored by



(X) (XI) (XII)

^{1}H NMR spectroscopy since the characteristic aliphatic proton signals of X [17] and those due to H(1)—H(3) in XI [18] are widely separated. Additional confirmation of structure was achieved through oxidation of XI with sodium dichromate in acetic acid [16] to give phenalenone (XII) whose identity was established by spectral means [18] and direct comparison with a commercial sample.

In order to obtain information on the stereochemical dependence of the apparent 1,2 shift, the *exo*-7-deuterio derivative (XIV) was prepared in ⩾95% isotopic purity (71% yield) from bromide XIII through application of Wittig's procedure [16]. When treated with the rhodium(I) catalyst as above, comparable quantitative conversion to monodeuterated phenalene was observed. Repeated integration of the 100 MHz ^{1}H NMR spectra of samples of XV isolated from several independent experiments revealed the protons in positions 1, 2, and 3 to be present in the ratio 1.85/1.00/0.91. These data immediately suggested that controlled scrambling of the deuterium label beyond the confines of the alicyclic ring in phenalene was likely occurring, a conclusion which was reinforced by the finding that exposure of XVII (⩾95% d_1) [16] to rhodium(I) also gave XV (1.78/1.00/0.90) with comparable isotopic substitution. But since the aromatic protons in phenalene are closely spaced and strongly overlapping [18], it is not possible to integrate select regions of the δ 6.7—8.0 ppm miltiplet with meaningful accuracy. The situation is vastly improved in phenalenone where H(2), H(3), and H(6)/H(7) appear at chemical shifts well separated from the

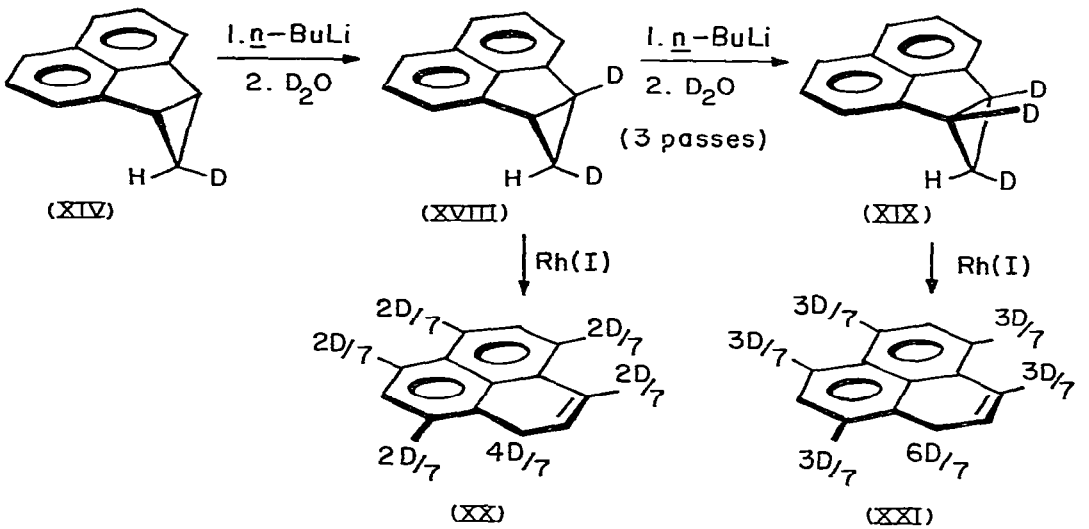


complex multiplet due to H(3), H(4), H(5) and H(8) [18]. Accordingly, XV was oxidized to XVI. Through integration of the H(2) and H(9) signals, it was possible to establish a ratio of 1.0/0.86 for these two sites. Also, the multiplicity of the H(2) absorption clearly indicated the presence of deuterium in low concentration at position 3.

Because the method of oxidation employed very possibly proceeds by transient generation of the phenalenyl cation and/or radical, both of which are extensively delocalized and endowed with three-fold rotational symmetry about an axis which passes through the internal carbon atom perpendicular to the molecular plane [19,20], full isotopic scrambling between alternate carbons

1, 3, 4, 6, 7, and 9 is to be expected in XVI *. Accordingly, one is forced to rely exclusively upon the nature of the first-formed phenalene product. If XV were isotopically labeled as indicated in the formula, then the intensities of the signals for H(1), H(2), and H(3) (assuming 95% isotopic purity) should be 1.71/1.00/0.85 if isotope effects are ignored. Although these values correspond suitably well with the experimental observations, we are forced to deal with small differences between rather larger numbers, a not particularly ideal situation. For this reason and to achieve greater precision, we next prepared XVIII and XIX.

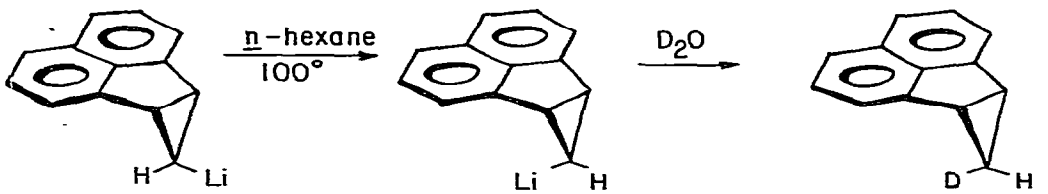
The 7,8-dideuterio derivative XVIII became available (39% yield) through deprotonation of a benzylic hydrogen in XIV with n-butyllithium, followed by D_2O quenching. Careful ^1H NMR analysis revealed the deuterium content at C(7) to be unchanged (≥95%) and that at C(8) to be 86%. The total deuterium content was therefore ≥81% d_2. Isomerization of XVIII using the now standard conditions furnished XX in high yield. The intensities of the signals due to those protons in positions 1, 2, and 3 were determined to be in the ratio 1.51/1.0/0.78. The ratio anticipated on the basis of completely staggered isotopic substitution resulting from stereospecific migration of *exo*-7-*d* as indicated by XX is 1.48/1.00/0.74.



By subjecting XIV to four sequential H/D exchanges comparable to that which served in the preparation of XVIII, triply labeled cycloprop[*a*]acenaphthylene XIX was isolated in 33% yield. The total deuterium content at the benzylic sites was determined to be 80%, while that at H(7) again remained at the 95% level. The phenalene obtained upon rearrangement of XIX showed the protons in positions 1, 2, and 3 to be partitioned in a ratio of 1.17/1.00/0.62. The relative integrated areas demanded by statistical scrambling of 4.25 protons over the seven positions indicated in XXI are 1.21/1.00/0.61. The agreement between theory and experiment in both instances is seen therefore to be excellent.

* In XVI, the theoretical ratio of H(2) to H(9) (assuming 95% isotopic purity) should be 1.0/0.84 in close agreement with experimental findings (1.0/0.86).

Although these results implicate a particularly labile role for the 7-*exo*-hydrogen (deuterium) in these isomerizations, the test remained incomplete. As concerns control experiments, it came as no surprise that XIV, XVIII, and XIX were stable when maintained at 50°C in C_6D_6 solution for periods of time well beyond that required for the catalyzed reactions. Secondly, study of the *endo*-7-*d* derivative was considered in order if definition of the reactivity pattern was to be made totally unambiguous. To evaluate this parameter, *exo*-7-lithiocycloprop[*a*]acenaphthylene (XXII) was partially epimerized by heating in n-hexane at 100°C (sealed tube conditions) according to the published method [16]. Addition of D_2O gave a 54/46 mixture of XXIII and XIV containing 80% of one deuterium (assumed to be the same for both isomers). The phenalene obtained by rearrangement of this mixture showed H(1), H(2), and H(3) to be partitioned in a 2.22/1.00/1.18 fashion. Since the ratio anticipated for



(XXII) (XXIII)

exclusive migration of the *exo*-7-substituent in this mixture is 2.27/1.00/1.13, we were now confident that this C—H (C—D) bond cleavage was operating stereospecifically.

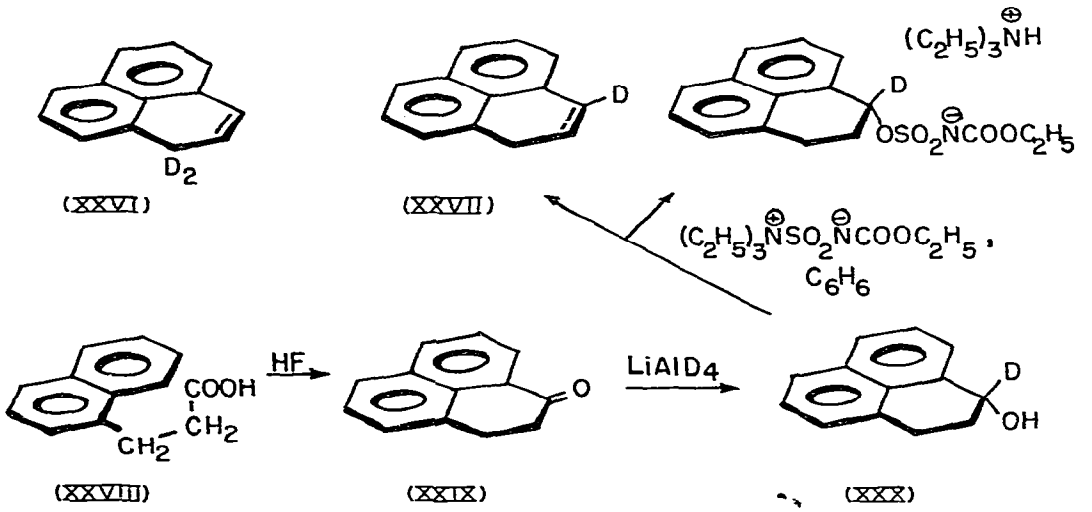
To evaluate the effect of added substituents, we next examined the susceptibility of XIII and XXIV to $[Rh(CO)_2Cl]_2$ and found them to be totally unreactive upon heating with the catalyst in C_6D_6 solution at 50°C for up to 5 days. In

(XXIV) (XXV)

contrast, the 8-methyl derivative did isomerize under these conditions, although at a rate somewhat slower than X (24 h for complete reaction). As expected from the earlier observations, a complex mixture of 1-, 3-, 4-, 6-, 7-, and 9-methylphenalenes was evidently produced in this case.

The deuterium scrambling which is observed during these rearrangements could occur within an organorhodium intermediate (see below), after production of the relevant phenalene, or under both circumstances. It therefore became desirable to prepare a specifically deuterated product such as XXVI or XXVII and to assess its stability to the reaction conditions. Initially, we examined the reduction of phenalenone with $LiAlD_4$ and $AlCl_3$ following the conditions employed by Pagni and Watson for the protio series [21]. However, the ^1H NMR

spectrum of the unpurified hydrocarbon product proved to be identical to that of XX. Since this type of reaction quite obviously involves hydride (deuteride) addition to the phenalenyl cation in the presence of a Lewis acid capable of hydride (deuteride) abstraction from phenalene, further exploration of this type of



(XXVI) (XXVII) (XXVIII) (XXIX) (XXX)

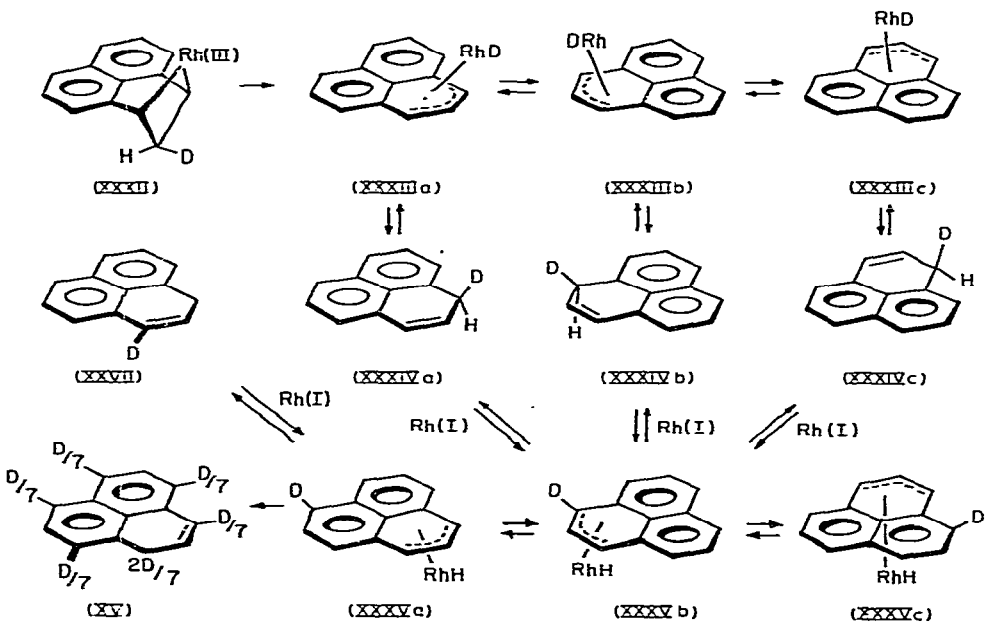
chemistry was not pursued. Rather, 3-(1-naphthyl)propionic acid (XXVIII) was cyclized in liquid HF [22] and the resulting phenalanone (XXIX) was transformed into deuterated alcohol XXX by $LiAlD_4$ reduction [23]. Subsequent dehydration of XXX with Burgess' reagent [24] gave the desired XXVII without detectable isotopic scrambling. Samples of unpurified phenalene prepared in this manner lacked the absorption at δ 6.4 ppm due to H(3). Unfortunately, attempts to purify XXVII by thin-layer chromatography on silica gel or simple high vacuum sublimation (10^{-4} torr) for that matter caused the signal at 6.4 ppm to increase rapidly in intensity. Accordingly, the crude hydrocarbon product (containing small amounts of XXXI) was treated directly with the rhodium catalyst. The pale yellow solution became deep red upon mixing; immediate ^1H NMR analysis gave a spectrum with the features of XV. Thus we see that rapid isotopic scrambling is also possible at the phenalene level.

Discussion

The results described above meet all the criteria for initial oxidative addition of rhodium into the C(8)—C(8′) central bond of the cycloprop[*a*]acenaphthylenes. This first step, which may be rate-determining, finds direct analogy with certain other transition metal isomerizations [2,25]. With a methyl group present at C(8) as in XXV, the overall rate of reaction is slowed, presumably as the direct result of steric factors which develop at the transition state of kinetic consequence. The formation of XXXII is believed to proceed solely from outside of the "flap" associated with the bicyclo[3.1.0]hexene part structure. This assumption receives strong support from the behavior of the various C(7)-deuterated substrates examined in this study which show the *exo*-7 deuterium (or proton) to migrate exclusively (within experimental error) to rhodium as η^3-

allyl complex XXXIIIa is produced. This transfer to rhodium(III) is fully expected to be intramolecular and therefore dependent upon proximity factors for its stereospecificity. The inability of XXIV to enter into isomerization at an observable rate if at all discloses the inability of intermediates such as XXXII to experience facile *endo*-H(7) (or D(7)) transfer.

The subsequent formation of allylrhodium hydride XXXIIIa serves concisely to account for the selective positional scrambling of deuterium over the entire phenalene framework. In line with the recognized chemistry of complexes of this general type [26] XXXIIIa probably decomposes to XXXIVa with regeneration of a catalytic rhodium(I) species. On the basis of the reactivity of XXVII, we would expect XXXIVa also to be susceptible to oxidative addition with insertion into either the C—D (→ XXXIIIa) or C—H (→ XXXVa) bond [27]. But this pair of reactions does not result in introduction of deuterium into the other two rings. Complete and rapid equilibration of XXXIIIa with XXXIIIb and XXXIIIc (as well as XXXVa with XXXVb and XXXVc), on the other hand,



conforms to the experimental data. An especially fascinating aspect of this isomerization is its degenerate nature. Seemingly, the stereoelectronic requirements of the η^3-allyl complex do not preclude migration of the metal center over the periphery of this planar ring system. The special stability of the phenalenyl radical and cation undoubtedly contribute to the facilitation of this interesting chemical process.

In summary, therefore, we have found that cycloprop[*a*]acenaphthylenes which are unsubstituted at C(7) rearrange at convenient rates when heated to 50°C in benzene solution with $[Rh(CO)_2Cl]_2$. The conversions to phenalene involve as a key step the stereospecific migration of a 7-*exo* deuterium or hydrogen to rhodium(III) in XXXII and proceed with statistical redistribution of the translocated group (D or H) over C(1), C(3), C(4), C(6), C(7), and C(9) of

the tricyclic product *. Accordingly, the increase in ring size relative to bicyclo-[2.1.0]pentane which is present in the bicyclo[3.1.0]hexene part structure of the title compound does not allow for kinetically competitive attack from the underside of the "flap" at a level which is spectroscopically detectable.

Experimental

The ^{1}H NMR spectra were determined with a Varian Associates HA-100 spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV.

General rearrangement procedure. A catalyst stock solution was prepared by dissolving 58.6 mg of $[Rh(CO)_2Cl]_2$ in 7.81 ml of C_6D_6 under argon. After dissolution, argon was bubbled through this solution for a brief time and the ampoule was sealed with a septum. The concentration of catalyst was 2.25 mg per 0.3 ml aliquot.

Into an NMR tube which was continuously being flushed with argon was placed 50 mg of the cycloprop[*a*]acenaphthylene and 0.3 ml of the catalyst solution. The tube was sealed with a rubber septum but maintained under argon at atmospheric pressure by connection through a syringe needle to an argon line. The tube was heated in a 50°C oil bath during 5 h or more, allowed to cool to room temperature, and examined by 100 MHz NMR spectroscopy. Multiple machine integrations were made in each case and a level of precision of ±3% (raw data) was achieved. This translates to ±0.07 in the quoted ratios.

Dichromate oxidation of II. The contents of a given NMR tube were transferred to a 10 ml flask and freed of C_6D_6 by vacuum evaporation. The residue was oxidized according to Wittig's procedure [16]. Yield of phenalenone: 59%.

Cycloprop[a]acenaphthylene-7,8-d_2 (XVIII). To a solution of XIV [16] (228 mg, 1.36 mmol) in absolute ether (10 ml) was added 3.1 ml of 2.2 *M* n-butyllithium in hexane (6.82 mmol) under argon. This solution was stirred for 4 days at room temperature and the anion quenched by slow addition of D_2O (3 ml) in dry tetrahydrofuran (9 ml). The reaction mixture was stirred for 90 min at room temperature prior to the addition of ether (50 ml) and separation of the aqueous phase. The organic layer was washed with water (3 × 15 ml), dried, and evaporated. The residue was sublimed at 60°C and 0.5 mmHg and recrystallized from ether to give 125 mg (55%) of XVIII. ^{1}H NMR analysis indicated the H(8)/H(7) *endo* ratio to be 1.14/1.00 which translates to 86% *d* at position 8. Because cycloprop[*a*]acenaphthylene gives no molecular ion, it was not convenient to confirm the NMR result by this technique.

Cycloprop[a]acenaphthylene-7,8,8'-d_3 (XIX). The above procedure was repeated four times starting with 250 mg (1.5 mmol) of XIV. On each pass, 3.4 ml of 2.2 *M* n-butyllithium in hexane (7.5 mmol) was employed. After the second exchange, the product was sublimed before use. After the first and third exchanges, the crude product was utilized directly. Finally, the residue was sublimed and recrystallized from ether to give 85 mg (33%) of XIX. Integra-

* Katz and Cerefice [28] have previously described an example of a stereospecific deuterium atom transfer to a new position within a distantly related cyclopropane system, but these workers did not establish whether the *exo*- or *endo*-cyclopropyl substituent was involved in the isomerization.

tion of the H(8) and $H(7)_{endo}$ absorptions showed the ratio to be 0.20/1.00 or 80% d_2.

Epimerization-deuteration of exo-7-lithiocycloprop[a]acenaphthylene (XXII). Bromide XIII [16] (122 mg, 0.5 mmol) was placed in a heavy-walled pyrolysis tube fitted with a vacuum stopcock. After five evacuation cycles intermittent with the bleeding-in of argon, 1 ml of dry, purified hexane, 0.45 ml of 2.2 *M* n-butyllithium in hexane (1.0 mmol), and finally an additional ml of hexane were introduced. The vessel was closed and heated at 100°C in an oil bath for 12.5—32.5 h (no significant change in epimerization noted over this time range). After being cooled to room temperature, the tube was opened and the contents were treated dropwise with a solution of D_2O (1 ml) in dry tetrahydrofuran (3 ml). The tube was shaken for 2 h, the reaction mixture transferred to a separatory funnel, and the tube rinsed with ether (3 × 10 ml). The separated organic layer was washed with water (2 × 5 ml), dried, and evaporated. The residue was sublimed (60°C, 0.5 mmHg) and recrystallized from ether to give 51 mg (61%) of mono-deuterated cycloprop[*a*]acenaphthylene. NMR integration showed the solid to consist of 46% *exo*-7-*d* (XIV) and 54% *endo*-7-*d* (XXIII). When these absorptions were related with that due to H(8) and H(8') the level of deuterium incorporation was seen to be 80%.

8-Methylcycloprop[a]acenaphthylene (XXV). To a solution of X [16] (750 mg, 4.5 mmol) in anhydrous ether (30 ml) was added dropwise under argon at 0°C a solution of n-butyllithium in hexane (10.2 ml of 2.2 *M*, 22.5 mmol). This mixture was stirred at room temperature for 4 days, freed of solvent in vacuo, and treated slowly with methyl iodide (10 ml) under an argon atmosphere. The methylation was allowed to proceed with magnetic stirring overnight at room temperature prior to the addition of ether (100 ml), extraction with water (2 × 30 ml), and drying. The residue obtained after evaporation of solvent was chromatographed on silica gel (pentane elution) to give 580 mg (72%) of XXV; δ (C_6D_6)(TMS) 7.60—7.08 (m, 6), 2.64 (dd, *J* 8 and 2 Hz), 1.76 (s, 3), 1.41 (dd, *J* 8 and 4 Hz), and 0.90 ppm (dd, *J* 4 and 2 Hz), found 180.0944; $C_{14}H_{12}$ calcd.: *m/e* 180.0939.

Isomerization of XXV. The customary procedure was followed: 37.8 mg of XXV (0.21 mmol) and 0.2 ml of the standard catalyst solution in C_6D_6 under argon. The progress of reaction was monitored by ^1H NMR and found to be complete after 24 h. Signals were seen at δ 3.6 and 4.0 ppm, as well as at 6.0 and 6.8—6.6 ppm, very close to those of phenalene itself. Thin layer chromatography on silica gel (pentane/ether 9/1) showed five products to be present. These were not separated on a preparative scale.

Phenalene-3-d (XXVII). A solution of XXIX [22] (600 mg, 3.3 mmol) in anhydrous ether (6 ml) was added dropwise to a stirred slurry of lithium aluminum deuteride (60 mg, 1.43 mmol) in ether (4.5 ml). The mixture was stirred for an additional 10 min at room temperature before decomposition with water and then 10% hydrochloric acid in the cold. The organic layer was washed with water (3 × 1 ml), dried, and evaporated. There was obtained 560 mg (92%) of colorless crystalline solid XXX (≥95% d_1 by ^1H NMR analysis) which was utilized without further purification.

To 100 mg (0.54 mmol) of XXX in dry benzene (2 ml) was added dropwise under an argon atmosphere a solution of Burgess' inner salt [24] (136 mg, 0.54

mmol) in benzene (2 ml). The solution was stirred at room temperature for 11 h and diluted with ether (10 ml) and water (2 ml). The organic layer was dried and evaporated. The ^{1}H NMR spectrum of the product showed XXVII (no absorption at δ 6.4 ppm) to be the major component, although small amounts of XXXI were also present. Key features of its ^{1}H NMR spectrum are: δ ($CDCl_3$) (TMS) 7.8—7.0 (m, 6), 5.0 (br t, 1), 3.15 (apparent q with fine coupling, J 6 Hz, 2), and 2.14 ppm (apparent t, J 6 Hz, 2).

Attempts to purify XXVII as described in the text caused isotopic scrambling.

Reaction of XXVII with $[Rh(CO)_2Cl]_2$. To unpurified dehydration product obtained from 61.7 mg of XXX and contained in an NMR tube was added under argon 0.2 ml of the catalyst stock solution. The pale yellow solution very quickly became deep red in color. Immediate recording of the ^{1}H NMR spectrum showed scrambling of the deuterium label, the spectral features become comparable to those of XV.

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