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RHODIUM CATALYZED REACTIONS OF BICYCLIC HYDROCARBONS. SUBSTITUENT, STEREOCHEMICAL AND RING SIZE EFFECTS *

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Summary

Tris(triphenylphosphine)rhodium(I) chloride in the presence of oxygen catalyzes the rearrangement of bicyclo[3.1.0]hex-2-enes, producing cyclohexadienes. Rearrangement rates are increased by introduction of methyl or carboxymethyl substituents at C_6, the effects being maximized when the methyl group is *exo* and/or the carboxymethyl group is *endo*. Bicyclo[4.1.0]hept-2-enes are less reactive but yield analogous products. Bicyclo[6.1.0]non-2-enes are unreactive under the reaction conditions even after two years.

Introduction

Studies of metal catalyzed reactions of strained hydrocarbons have been devoted in large measure to bicyclo[*n*.1.0]alkanes and alkenes. The simplest of these, bicyclo[1.1.0]butane, has been the most intensively studied for two reasons. The molecule's simplicity has attracted theoreticians, and its extreme stability (it does not rearrange at temperatures below 150°C) in spite of a high strain energy (64 kcal/mol [3]) has attracted experimentalists [4]. Thermal rearrangement occurs exclusively by cleavage of two of the nonbridging carbon—carbon σ bonds to yield 1,3-butadienes [5]. In the presence of transition metal catalysts, however, methylated bicyclobutanes have produced vinylcyclopropane derivatives as well [5—7].

Bicyclo[2.1.0]pentane, whose bridging carbon—carbon bond has the highest reported strain energy on record [8] (47.4 kcal/mol) [9], rearranges quantitatively to cyclopentene in the presence of an appropriate catalyst such as $[Rh(CO)_2Cl]_2$ [10]. The bicyclobutane [5—8] and bicyclopentane [10,11] reactions are known to be dramatically effected by the nature and orientation of substituents.

* A preliminary report of portions of this work has appeared [1]. Abstracted from the thesis by D.L. Beach [2].

In the preceding paper [12] we described the results of studies of *endo*-6 carbomethoxy bicyclo[3.1.0]-hexane and -hex-2-ene in the presence of a variety of soluble metal catalysts. Herein we report the effects of ring size and substituent stereochemistry on these processes using "oxidized" $Rh(PPh_3)_3Cl$ as catalyst.

Experimental

General procedures for carrying out the catalytic processes and analyzing products were the same as those described in the preceding paper [12].

1,3- and 1,4-Cyclohexadiene were purchased from Aldrich Chemical Co. and 1-methyl-1,4-cyclohexadiene from K and K Chemicals and stored at 0°C until used. Epimeric 6-carbomethoxybicyclo[3.1.0]hex-2-enes II [12] and III [13] were prepared in pure form by the literature methods cited. The epimeric mixtures XI—XII and XIII—XIV were similarly prepared from cyclohexene and cyclooctene, respectively. They were kindly supplied by Professor D.L. Garin.

Preparation of bicyclo[3.1.0]hex-2-ene (I). 2,3-Diazabicyclo[3.3.0]octa-2,7-diene [14] was heated at 160°C in a sealed pyrex tube for 10 half-lives, as reported in the literature [14] to give I as a colorless liquid, which was purified by in vacuo distillation.

Preparation of endo- and exo-6-methylbicyclo[3.1.0]hex-2-ene (IV and V). Pyrolysis of *exo*-4-methyl-2,3-diazabicyclo[3.3.0]octa-2,7-diene [14] (4.0 g, 0.033 mol) (evacuated 150 ml pyrex tube, 145°C, 30 min) afforded 2.6 g (84%) of a 40 : 60 mixture of IV and V.

The epimers were separated and purified further by preparative VPC. IV and V exhibited retention times of 5.2 min and 6.8 min, respectively, on a 12 ft. × 3/8 in. 7% β,β'-oxydipropionitrile on Chromosorb G column (injector temperature 115°C, column temperature 60°C, detector temperature 120°C, filament current 175 mA, carrier gas (He) flow rate 100 ml/min).

Preparation of endo-6-carbomethoxy-exo-6-methylbicyclo[3.1.0]hex-2-ene (VI). This material was prepared in 97% yield by the semibenzilic acid rearrangement of the *exo*-methyl—*endo*-chloro cycloaddition adduct of chloromethylketene and cyclopentadiene [15]. NMR, δ ($CDCl_3$): 1.30 (s, CH_3); 1.50—1.70(m), 1.82—2.07(m, cyclopropane); 2.37—2.97 (m, CH_2); 3.55 (s, CO_2Me); 5.30—6.72 (m, olefin). Molecular weight: *m/e* calculated for $C_9H_{12}O_2$, 152; *m/e* found, 152.

Preparation of endo-6-methyl-exo-6-carbomethoxybicyclo[3.1.0]hex-2-ene (VII). Into a 50 ml flask containing *endo*-6-methylbicyclo[3.1.0]hex-2-ene-*exo*-6-carboxylic acid (0.29 g, 2.14 mmol) in 10 ml ether was added an excess of diazomethane in ether. The solution was allowed to stand for 0.5 h, anhydrous $MgSO_4$ was added, and the solution was filtered. Ether was removed from the filtrate by rotary evaporation to yield 0.25 g (76%) of VII. NMR, δ ($CDCl_3$): 0.83 (s, CH_3); 1.50—2.07 (m, cyclopropane); 2.09—2.97 (m, CH_2); 3.65 (s, CO_2Me); 5.53 (broad s, olefin). Molecular weight: *m/e* calculated for $C_9H_{12}O_2$, 152; *m/e* found, 152.

Results and discussion

Early in our investigations of the rhodium catalyzed ring-opening reactions of bicyclo[3.1.0]hex-2-nes [1,12] we noted that the orientation of the carbo-

methoxy substituent at C_6 dramatically affected both the rate and product distribution for this system. In an effort to determine the origin of these effects and to further elucidate the mechanism previously proposed [12] for the ring-opening reaction, substituent effects at C_6 were examined for all possible substituent permutations of —H, $-CH_3$, and $-CO_2CH_3$. Table 1 summarizes the reactants, ring-opening products, and qualitative half-lives. As discussed previously [12] the $t_{1/2}$ values reported here represent the time necessary for 50% of the starting material to react, based on integration of appropriate resonances in the proton-NMR spectra.

The parent compound bicyclo[3.1.0]hex-2-ene (I) undergoes ring-opening in the presence of $(PPh_3)_3RhCl$ and O_2 [1,12] to give a mixture of 1,3- and 1,4-cyclohexadiene. Reaction progress was conveniently monitored by the disappearance of the signal at δ —0.19 ppm from the *endo*-hydrogen at C_6. The products were unambiguously identified by comparison of their NMR spectra with those of authentic samples. Additionally, VPC analysis of the products revealed only two peaks, whose retention times were unaffected by doping injected samples of the product mixture with pure 1,3- and 1,4-cyclohexadiene, respectively.

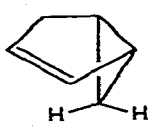
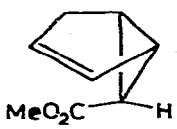
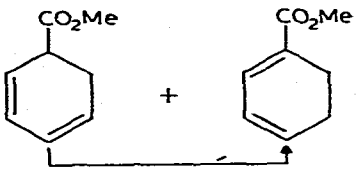
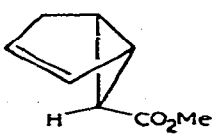
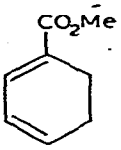
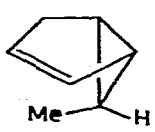
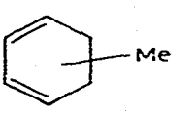
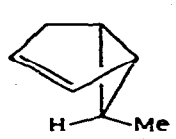
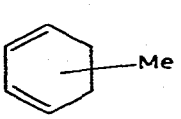
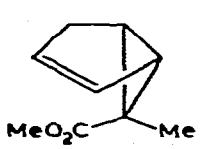
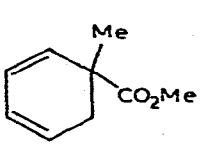
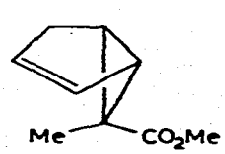
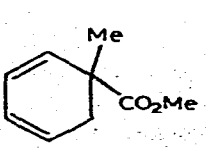
The half-life of ring-opening of I was measured to be 384 h, giving an initial 2 : 1 ratio of 1,3- to 1,4-cyclohexadiene, which remained unchanged throughout the ring-opening reaction. This result was unexpected, since in the *endo*-6-carbomethoxybicyclo[3.1.0]hex-2-ene system, all non-conjugated carbomethoxycyclohexadiene isomers were converted to the fully conjugated isomer 1-carbomethoxy-1,3-cyclohexadiene [12] (Table 1). To further explore this result, pure samples of 1,3- and 1,4-cyclohexadiene were subjected, in separate experiments, to ring-opening conditions. In both cases a 2 : 1 ratio of conjugated to non-conjugated cyclohexadiene was obtained, identical to the equilibrium established in the ring-opening of I. Since the cyclohexadiene equilibrium is established rapidly relative to ring-opening, it is not possible to determine whether both cyclohexadienes are formed simultaneously from I. The lack of a substituent, e.g. carbomethoxy [12], apparently lowers the activation energy for cyclohexadiene interconversions in the presence of the rhodium catalyst and a rapid equilibrium is reached. (The interconversions of the five isomeric cyclohexadiene products from II and III have been discussed previously [12]). The presence of the carbomethoxy substituent in compounds II and III also increases the rate of ring-opening (Table 1) relative to that observed for I.

The orientation of the methyl group in IV and V affected the rate of ring-opening under catalytic conditions, with half-lives,measured at 240 and 48 h respectively. It is interesting to note that the stereochemistry at C_6 for IV and V affects the rate in the opposite sense as for the carbomethoxy substituent. That is, when the carbomethoxy group is *endo*, a faster rate of rearrangement is observed, relative to carbomethoxy *exo*, whereas a methyl functionality *exo* gives a faster rearrangement rate, relative to methyl *endo*. In both sets of compounds, regardless of the orientation of the substituent at C_6, a faster ring-opening is observed than with bicyclo[3.1.0]hex-2-ene itself (Table 1).

Identifiifcation of the ring-opening products from IV and V based on proton-NMR spectra was difficult because of overlapping resonances [16]. However, for both epimeric methyl bicyclic starting materials, the eventual major product is 1-methyl-1,3-cyclohexadiene, based on the appearance of a singlet in the

TABLE 1

HALF-LIVES AND PRODUCTS FROM RING-OPENING REACTIONS OF BICYCLO[3.1.0]HEX-2-ENES

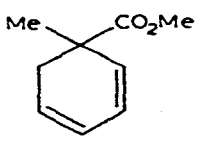
Compound		$t_{1/2}$ (h) [a, b]	Product(s)
	(I)	384	
	(II)	48	
	(III)	216	
	(IV)	240	
	(V)	48	
	(VI)	12	
	(VII)	2160	

[a] See text for definition. [b] Reproducable t ±5%.

methyl region at δ 1.64 (cf. δ 0.75 for IV and δ 1.03 for V), and the simplified alkyl proton region which changes from a broad multiplet (IV and V) to a singlet at δ 2.06. Other new resonances were also observed and presumably arise from other methylcyclohexadiene isomers, although these constitute only minor products (<5%).

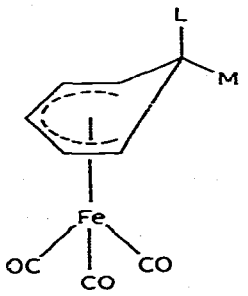
The appearance of non-conjugated methylcyclohexadiene isomers, if formed, would not be detectable by proton-NMR spectroscopy, as deduced from experiments with 1-methyl-1,4-cyclohexadiene. This compound, under ring-opening conditions, was rapidly isomerized to the conjugated 1-methyl-1,3-cyclohexadiene and, in this respect, closely parallels the behaviour of the non-conjugated carbomethoxy-1,4-cyclohexadienes, discussed previously [12].

The effects of the methyl and carbomethoxy substituents on the rate of ring-opening are not merely additive, as shown by experiments with the disubstituted derivatives VI (carbomethoxy *endo*, methyl *exo*) and VII (carbomethoxy *exo*, methyl *endo*). Compound VI was reproducibly measured to have a half-life, in the presence of $(PPh_3)_3RhCl$ and O_2, of 12 h, the fastest of any compound studied. VII exhibited a ring-opening half-life of about 2200 h, the slowest of any compound studied. When both substituents are present at C_6, they apparently synergistically affect the tendency of the internal cyclopropane bond to cleave. VI shows sharp singlets for the methyl and carbomethoxy protons at δ 1.30 and δ 3.55, respectively, Under ring-opening conditions new singlets appear at δ 1.27 and δ 3.68. In addition the complex multiplet at δ 5.53 from the olefin protons of VI disappears and a new olefin multiplet appears at δ 5.82. That only a single product is being produced was confirmed by VPC analysis, which showed only a single peak in addition to a small amount of remaining starting material. Purification of the product by preparative VPC yielded a colorless liquid whose infrared and UV spectra agreed with data reported in the literature [17] for 1-methyl-1-carbomethoxy-2,4-cyclohexadiene (VIII). In addition, the proton-NMR data are consistent with the formulation of the product as VIII.

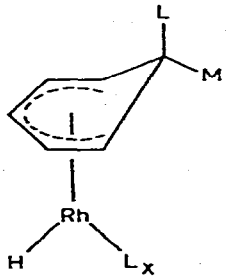


(VIII)

The substituent effects, although difficult to interpret mechanistically, are internally self-consistent and demonstrate that substitution at C_6 affects the tendency of the C_4—C_5 carbon—carbon bond to break. The results may be explained, at least partially, in terms of the perturbation by the substituent(s) at C_6 on the geometry of the proposed cyclohexadienylrhodium hydride intermediate [12]. Extended Hückel calculations have been recently used [18] to show that in structurally similar cationic substituted cyclohexadienyliron tricarbonyl complexes, the electronegativities of the groups at the saturated carbon site affect the degree of bending of the saturated carbon away from the plane of the pentadienyl ribbon. As shown in IX, the preferred orientation is with L *exo* and M *endo*, based on the degree of bending associated with each orientation of substituents.



(IX)



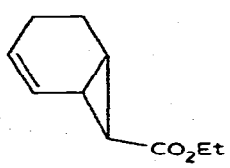
(X)

For the proposed cyclohexadienylrhodium complex [12] X, L (the less electronegative substituent) = H and M (the more electronegative substituent) = CO_2Me. According to the calculations performed for IX, a greater degree of bending is associated with CO_2Me *endo* than with CO_2Me *exo*. (It should be pointed out that the *endo*—*exo* nomenclature is somewhat confusing in this context, since a group which is *endo* in the bicyclo[3.1.0]hex-2-ene starting material produces an *exo*-cyclohexadienylrhodium complex.) It seems reasonable to conclude that the greater the degree of bonding involved in formation of X, then the slower the rate of ring-opening. Hence, when $-CO_2Me$ is *endo* in the bicyclohexene II a faster rate of ring-opening is observed than with $-CO_2Me$ *exo*, III. (Table 1.)

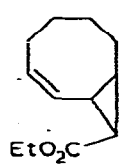
A similar argument may be applied in the case of a methyl substituent. Here, L = CH_3 and M = H and the preferred orientation on the cyclohexadienyl ligand is with CH_3 *exo* (*endo* in the bicyclohexene IV). More bending is associated with this orientation than with CH_3 *endo* (*exo* in the bicyclohexene V), and thus V ring opens at a faster rate than IV.

This rationale is also capable of explaining the dramatic differences in reactivity toward ring opening of the disubstituted bicyclo[3.1.0]hex-2-enes VI (CO_2Me *endo*, CH_3 *exo*) and VII (CO_2Me *exo*, CH_3 *endo*). The explanation is

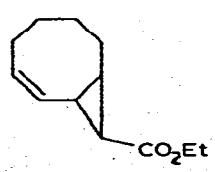
(XI)



(XII)



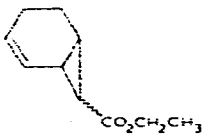
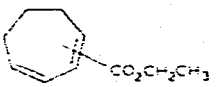
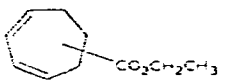
(XIII)



(XIV)

TABLE 2

SELECTED PROTON RATIOS FOR *endo*- AND *exo*-7-CARBOETHOXYBICYCLO[4.1.0]HEPT-2-ENE AND THEIR RING-OPENING PRODUCTS

Compound	Proton ratios	
	Olefin/—$OC_2\underline{CH_2}CH_3$	Olefin/—$CO_2CH_2\underline{CH_3}$
	1.0	0.67
	1.5	1.0
	2.0	1.3
Products observed	1.5	0.9

based on the difference in electronegativities of the groups L and M. With —CO_2Me and —Me, the difference is greater than with —CO_2Me vs. —H or —Me vs. —H, and hence a greater difference in the relative degrees of bending should exist, producing a greater difference in rates of ring-opening, as observed (Table 1) *.

A mixture of XI and XII in chloroform, under identical conditions used for I—VII, undergoes ring-opening, but at a slower rate than that observed for II and III. Although product identification was not as rigorous, proton-NMR evidence supports the formulation of products as carboethoxycycloheptadienes. The cyclopropyl protons of XI and XII are not resolved from the methylene protons of the larger ring and it was therefore not possible to observe an attenuation of cyclopropyl resonances. However, distinct line shape changes were evident for the alkyl and olefin regions of the spectrum. The most compelling evidence for the formulation of products as fully conjugated carboethoxycycloheptadienes was obtained from the ratio of olefin to methylene or methyl protons from the —$CO_2CH_2CH_3$ substituent. Except for the relative orientation of the double bonds, two types of isomers are possible, depending on whether the carboethoxy substituent is attached to an sp^2 or sp^3 carbon atom. As can be seen from Table 2, the indicated proton ratios differ significantly. The fact that the olefin/—$CO_2\underline{CH_2}CH_3$ or olefin/—$CO_2CH_2\underline{CH_3}$ ratios more closely fit a cycloheptadiene isomer with a —$CO_2CH_2CH_3$ substituent on an sp^2-hybrizided carbon implies

* π-Acceptor groups such as —CO_2Me could weaken the bond being broken, by analogy with studies of norcaradiene—cycloheptatriene interconversions [19,20]. Such an effect may be operative in the conversions described here, but we are unable to account for the large observed rate differences on this basis.

a ring-opening process similar to that of the 6-carbomethoxybicyclo[3.1.0]hex-2-enes, II and III [12].

In compounds XIII and XIV no reaction was detected, even after two years. These results indicate that the size of the ring fused to the cyclopropane entity is important, with the limiting ring size being reached or exceeded in the [6.1.0] system. This is not surprising in view of previous experiments demonstrating the necessity for both the presence of a double bond and ring strain [12]. In the [4.1.0] and [6.1.0] systems, the additional conformations of the six and eight membered rings, respectively, and the subsequent decrease in strain of the internal cyclopropane bond result in a decrease in reactivity of the bicyclic compound toward ring-opening. Recent work by Rettig and coworkers has shown that bicyclo[6.1.0]non-4-ene [19] and bicyclo[5.1.0]oct-3-ene [20] undergo internal cyclopropane bond cleavage in the presence of dichlorobis(benzonitrile)palladium(II). Thus the position of the double bond in these larger ring and the nature of the catalyst may also be controlling factors. We are currently investigating the reactions of XI—XIV and related substrates with soluble palladium and nickel-based catalysts to clarify the basic structural and mechanistic features of these processes.

Acknowledgements

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