$$E + I + H^+ \rightleftharpoons EI + H^+$$

$$EH + I \rightleftharpoons EHI \rightleftharpoons (EHI)' \qquad (A\text{-}8)$$

$$E + I + H^+ \rightleftharpoons EI + H^+$$

$$EH + I \rightleftharpoons (EHI)' \rightleftharpoons EHI \qquad (A\text{-}9)$$

$$A_bH + I + H^+ \xrightarrow{K_{12}} A_bHI + H^+$$

$$A_bH_2 + I \xrightarrow{K_{34}} A_bH_2I \xrightarrow{K_{45}} A_eH_2I \qquad (A\text{-}8a)$$

with K_{13} and K_{24} vertical equilibria.

$$A_bH + I + H^+ \rightleftharpoons A_bHI + H^+$$

$$A_bH_2 + I \rightleftharpoons A_eH_2I \rightleftharpoons A_bH_2I \qquad (A\text{-}9a)$$

$[A_bH_2I]/[A_bH_2][I]$, $K_{24} = [A_bH_2I]/[A_bHI]a_H$, and $K_{45} = [A_eH_2I]/[A_bH_2I]$. The expression for the overall binding constant for the mechanism A-8a is eq A-8b. Since

$$K_b = \frac{[A_bHI] + [A_bH_2I] + [A_eH_2I]}{([A_bH] + [A_bH_2])[I]} =$$

$$\frac{\dfrac{[A_bHI]}{[A_bH][I]} + \dfrac{[A_bH_2I]}{[A_bH][I]} + \dfrac{[A_eH_2I]}{[A_bH][I]}}{1 + \dfrac{[A_bH_2]}{[A_bH]}}$$

$$K_b = \frac{K_{12} + K_{13}K_{34}a_H + K_{13}K_{34}K_{45}a_H}{1 + K_{13}a_H} =$$

$$\frac{K_{12} + K_{13}K_{34}(1 + K_{45})a_H}{1 + K_{13}a_H} \qquad (A\text{-}8b)$$

that equation contains a number of equilibrium parameters whose values are unknown, it is useful to examine some limiting cases

$$\lim_{a_H \to \infty} K_b = K_{34}(1 + K_{45}) \text{ at low pH}$$

$$\lim_{a_H \to 0} K_b = K_{12} \text{ at high pH}$$

As an approximation we assume that $K_{34} \simeq K_{12}$. Since $K_{45} > 0$, we find that K_b (at low pH) > K_b (at high pH).

The expression for the enthalpy change in the overall binding process can be obtained from eq A-8b by differentiating $\ln K_b$ with respect to $1/T$.

$$\Delta H_b^\circ = \frac{K_{12}\Delta H^\circ_{12} + K_{13}K_{34}(1 + K_{45}) \times (\Delta H^\circ_{34} + \Delta H^\circ_{13})a_H + K_{13}K_{34}K_{45}\Delta H^\circ_{45}a_H}{K_{12} + K_{13}K_{34}(1 + K_{45})a_H} -$$

$$\frac{K_{13}a_H}{1 + K_{13}a_H}\Delta H^\circ_{13} \qquad (A\text{-}8c)$$

Similar mathematical manipulations may be performed for the mechanism A-9a. The expressions for the binding constant and the binding enthalpy derived according to this scheme look very similar to those obtained for the mechanism A-8a.

Communications to the Editor

Nickel(0)-Catalyzed Reaction of Bicyclo[1.1.0]butanes with Olefins[1]

Sir:

As the chemical consequence of the extraordinarily high strain energy of bicyclo[n.1.0]alkanes ($n = 1$ and 2), a variety of reactions characteristic of the bicyclic systems are expected.[2] This paper describes a novel reaction of bicyclo[1.1.0]butanes and olefins with the aid of transition-metal catalysis.

When a mixture of bicyclo[1.1.0]butane (**1a**)[3] (5.2 mmol) and methyl acrylate (50 mmol) containing a catalytic amount of bis(acrylonitrile)nickel(0) (Ni-(AN)₂)[4] (0.15 mmol) was heated at 60° for 36 hr under a nitrogen atmosphere, two isomeric adducts, *cis*- and *trans*-1-allyl-2-carbomethoxycyclopropanes (**2a** and **3a**, 65:35 ratio),[5] were obtained in almost quantitative

(1) Nickel-Catalyzed Reactions Involving Strained σ Bonds. II. Part I: R. Noyori, T. Odagi, and H. Takaya, *J. Amer. Chem. Soc.*, **92**, 5780 (1970).

(2) Review: K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 185 (1968).

(3) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(4) G. N. Schrauzer, *Chem. Ber.*, **94**, 642 (1961).

(5) All new compounds gave correct elemental analyses and/or molecular peaks in exact mass spectra. We thank Professor A. Tatematsu, Meijo University, for measurement of the spectra. Ir and nmr spectra were consistent with the structures assigned.

yield. The spectral data were in accord with the assigned structures: **2a**, ir (CCl₄) 1735 (C=O), 1645,


1a, R = H
1b, R = CH₃

2a, R = H
2b, R = CH₃

3a, R = H
3b, R = CH₃

4

5

6
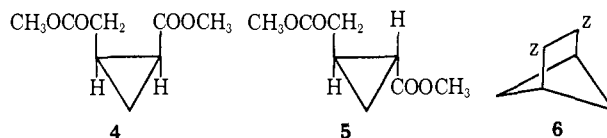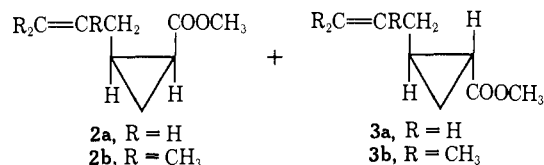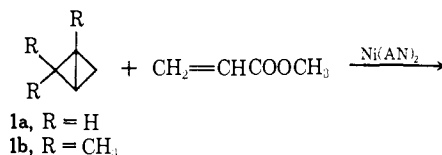
994, and 915 cm⁻¹ (CH₂=CH); nmr (CCl₄, TMS) δ 0.7–1.9 (m, 4 H, >CH, >CH₂, and CHCOOCH₃), 2.1–2.4 (m, 2 H, =CHCH₂), 3.59 (s, 3 H, OCH₃), 4.7–5.2 (m, 2 H, CH₂=CH), and 5.4–6.1 (m, 1 H, CH₂=CH);

3a, ir (CCl₄) 1735 (C=O), 1645, 994, and 915 cm⁻¹ (CH₂=CH); nmr (CCl₄) δ 0.5–1.6 (m, 4 H, >CH, >CH₂, and C*H*COOCH₃), 1.9–2.3 (m, 2 H, =CHC*H*₂), 3.60 (s, 3 H, OCH₃), 4.8–5.2 (m, 2 H, C*H*₂=CH), and 5.4–6.1 (m, 1 H, CH₂=C*H*). The products **2a** and **3a**, upon standard oxidative modification,[6] were converted into the corresponding dimethyl esters **4** and **5**, respectively.[7] In a similar manner, the reaction of 1,2,2-trimethylbicyclo[1.1.0]butane (**1b**)[8] and methyl acrylate under the influence of Ni(AN)₂ (60°, 36 hr) gave the cycloadducts **2b** and **3b** (65:35 ratio) in 70% combined yield.[5]

Noteworthy is the fact that the mode of the present reaction is in strong contrast to that of the corresponding uncatalyzed, thermal reaction which affords the cycloadducts of type **6** (Z = H, CN, CH₂=CH, etc.) along with considerable amounts of by-products.[2] The catalytic cyclopropane formation is formally viewed as the cycloaddition of allylcarbene across carbon–carbon double bonds. It is reminiscent of the recently reported Rh(I)-catalyzed isomerization of **1b** into 3,4-dimethyl-1,3-pentadiene which may be viewed as a retrocarbene addition followed by a hydride transfer.[9]

The mode of the cycloaddition was elucidated by control experiments using deuterium-labeled substrates. First, the lack of hydrogen scrambling, at least in the olefinic component, was confirmed by the reaction of **1a** and methyl acrylate-α,β-d₂[10] which resulted in the formation of **2a**-*2,3-d₂* and **3a**-*2,3-d₂*. The location of the deuterium atoms was determined by nmr analyses. The splitting patterns due to CH₂=CHC*H*₂–, compared with those of **2a** and **3a**, remained unchanged. Secondly, the specific bond cleavage at C-1–C-3 and C-2–C-3 of **1** was demonstrated as shown in Scheme I.

Scheme I

Z = COOCH₃; R = C(CH₃)=C(CH₃)₂
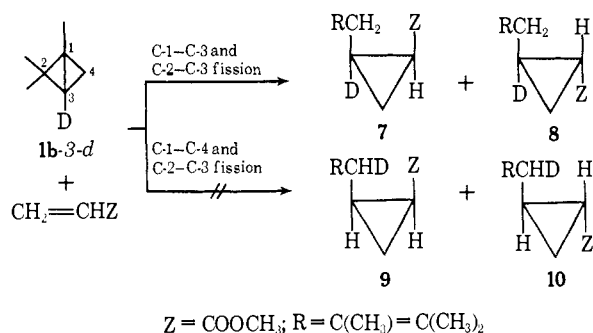
Reaction of **1b**-*3-d*[8] and methyl acrylate afforded a mixture of **7** and **8**, the structural assignment being readily established by nmr. The absence of the adducts **9** and **10** dismissed the possibility of the alternative pathway which involves a bond rupture at C-1–C-4 and C-2–C-3 followed by a hydrogen shift.

In order to examine the stereochemistry of the catalytic reaction, the reactions were carried out employing as the olefinic substrates the geometrically isomeric esters, dimethyl fumarate and dimethyl maleate (Scheme II). When a mixture of **1a** (1.8 mmol), dimethyl

Scheme II

Z = COOCH₃

fumarate (3.5 mmol), and Ni(AN)₂ (0.15 mmol) in benzene (5 ml) was heated at 40° for 60 hr, the 1:1 adducts **11** and **12**[5,11] were produced in 35% combined yield. The reaction of **1a** and dimethyl maleate afforded a mixture of the adducts (31% yield) consisting of **13** and **14** as well as a small amount of the stereochemical impurity **11**.[12] Only a negligible amount of **12** was formed. The unsaturated dimethyl esters **11**, **13**, and **14** were oxidatively converted to the trimethyl esters **15–17**,[6] respectively, the authentic materials being produced by independent syntheses.[13] Thus, these olefinic esters were shown to enter into the catalyzed cycloaddition with bicyclobutane in a highly stereospecific manner with retention of configuration.

At present the mechanism of the cycloaddition has not been elucidated. A possible pathway would be the attack of the nickel(0) complex on the C-1–C-3 bond (or at C-3) of **1** followed by bond isomerization

(6) The procedure consists of ozonolysis in CH₃OH at −70°, oxidative work-up with alkaline H₂O₂, acidification, and esterification with diazomethane.

(7) Authentic **4** was prepared from bicyclo[3.1.0]hex-2-ene,[6] whereas **5** was obtained by the reaction of methyl diazoacetate with methyl allylacetate in the presence of CuSO₄.
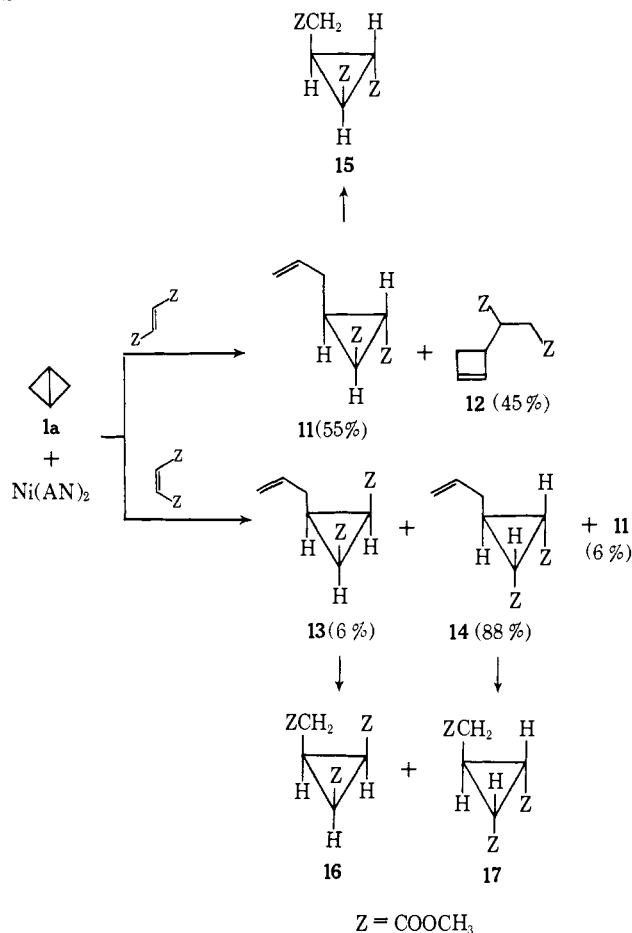
(8) L. Skattebøl, *Tetrahedron Lett.*, 2361 (1970); W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970).

(9) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970); P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 1042 (1971); P. G. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971); M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971).

(10) T. Yoshino, J. Komiyama, and M. Shinomiya, *J. Amer. Chem. Soc.* **86**, 4482 (1964).

(11) The stereochemistry (threo or erythro) of **12** was not determined.

(12) During the catalytic reaction, dimethyl maleate was slightly isomerized, and the recovered unsaturated esters contained 1% of dimethyl fumarate.

(13) **15** was derived by the oxidation of 6-*exo*-carbomethoxybicyclo-[3.1.0]hex-2-ene,[6] while **16** was obtained similarly starting from the endo isomer. Reaction of methyl (dimethylsulfuranylidene)acetate[14] and dimethyl glutaconate gave a mixture of **15** and **17** (64:36 ratio). Treatment of a mixture of **16** and **17** with *tert*-C₄H₉OK in dimethyl sulfoxide (25°, 3 hr) gave **15** (95% stereochemically pure).

(14) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967).

18
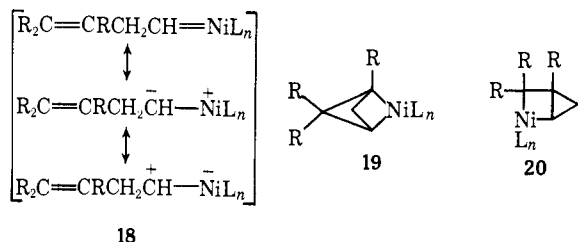
to give a nickel–allylcarbene complex of type **18**.[15] Alternatively, the cyclopropane formation would be achieved sequentially by way of an organonickel complex of type **19** or **20**,[16] rather than *via* the carbene transfer mechanism. Studies on the exact nature of the reactive intermediates are in progress.[17]

(15) The phenylmethoxycarbene–Cr(CO)₅ complex reacts with methyl crotonate to give the isomeric cycloadducts: E. O. Fisher and K. H. Dötz, *Chem. Ber.*, 103, 1273 (1970).

(16) *Cf.* R. Noyori, T. Suzuki, and H. Takaya, *J. Amer. Chem. Soc.*, 93, 5896 (1971).

(17) The efficiency of the catalyst is markedly influenced by the nature of the coordinated ligands [*cf.* P. G. Gassman, G. R. Meyer, and F. J. Williams, *Chem. Commun.*, 842 (1971)]. In the absence of olefins, no two-bond cleavages of **1b** were observed. The only product was 1-isopropenyl-1-methylcyclopropane (*ca.* 30% yield after heating at 60° for 36 hr in benzene).
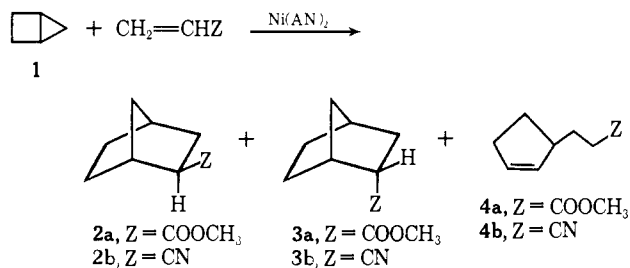
R. Noyori,* T. Suzuki, Y. Kumagai, H. Takaya

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Chikusa, Nagoya, Japan
Received June 7, 1971

Nickel(0)-Catalyzed Reaction of Bicyclo[2.1.0]pentane with Olefins[1]

Sir:

The behavior of bicyclo[*n*.1.0]alkanes in the nickel(0)-catalyzed transformations depends markedly on the number *n*. Bicyclo[2.1.0]pentane (**1**), whose *central* bond has the highest strain energy (47.4 kcal/mol) hitherto reported,[2] readily undergoes a cycloaddition across carbon–carbon double bonds under the influence of bis(acrylonitrile)nickel(0) (Ni(AN)₂). The mode is formally analyzed as a thermally forbidden [$_\sigma 2_s$ + $_\pi 2_s$] process,[3] and is strikingly contrasted to that of the lower homolog, bicyclo[1.1.0]butane, which suffers from a *two-bond* cleavage and exhibits a formal allylcarbene addition.[1]

When a solution of **1**[4] (2.4 mmol) and Ni(AN)₂[5] (0.3 mmol) in excess methyl acrylate (70 mmol) was

1

2a, Z = COOCH₃ 3a, Z = COOCH₃ 4a, Z = COOCH₃
2b, Z = CN   3b, Z = CN   4b, Z = CN

(1) Nickel-Catalyzed Reactions Involving Strained σ Bonds. III. Part II: R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *J. Amer. Chem. Soc.*, 93, 5894 (1971).

(2) R. B. Turner, *Theor. Org. Chem.*, Pap. Kekulé Symp., *1958*, 67 (1959); R. K. Bohn and Y.-H. Tai, *J. Amer. Chem. Soc.*, 92, 6447 (1970).

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969).

(4) P. G. Gassman and K. T. Mansfield, *Org. Syn.*, 49, 1 (1969).

(5) G. N. Schrauzer, *Chem. Ber.*, 94, 642 (1961).

heated at 40° for 36 hr under a nitrogen atmosphere, the stereoisomeric cycloadducts *exo*- and *endo*-2-carbomethoxybicyclo[2.2.1]heptane (**2a** and **3a**, 50:50 ratio) were produced in 66% combined yield. In addition, the monocyclic product methyl 3-(cyclopent-2-enyl)-propionate (**4a**) was obtained in 22% yield.[6,7] The identity of the adducts **2a** and **3a** was established by comparison with authentic samples.[8] The product **4a** was independently prepared by treatment of known α-(cyclopent-2-enyl)-α'-diazoacetone[9] with CH₃-COOAg–(C₂H₅)₃N–CH₃OH at 70°

The reaction of **1** with acrylonitrile under similar conditions (70°, 36 hr) afforded the corresponding coupling products, **2b**, **3b** (62:38 ratio, 75% combined yield), and **4b** (16%).[10] The cycloadducts **2b** and **3b** were identified by comparison with authentic specimens,[8] while the cyclopentene derivative **4b** was converted into the methyl ester **4a** by treating with HCl–CH₃OH. The reaction of **1** with either methyl acrylate or acrylonitrile under comparable thermal conditions was observed only in the presence of the nickel catalyst. Addition of triphenylphosphine (2 equiv per Ni(AN)₂) to the reaction system retarded the catalytic transformations.

It is worthwhile pointing out that the thermal, uncatalyzed reaction between **1** and olefins, rationalized as a multistep, diradical reaction, gives rise to complicated reaction mixtures, primarily monocyclic coupling products, the bicycloheptane derivatives being formed only as the minor components.[11]

In contrast to the purely thermal cycloaddition which occurs in a nonstereospecific manner,[11] the present catalysis leads to a nearly stereospecific cycloaddition as demonstrated by the reactions employing the isomeric unsaturated esters, dimethyl fumarate and dimethyl maleate, as the substrates. Scheme I summarizes the

Scheme I

5 (89%)   6 (11%)

7 (60%)   8 (8%)

+ 5 (7%) + 6 (25%)

Z = COOCH₃
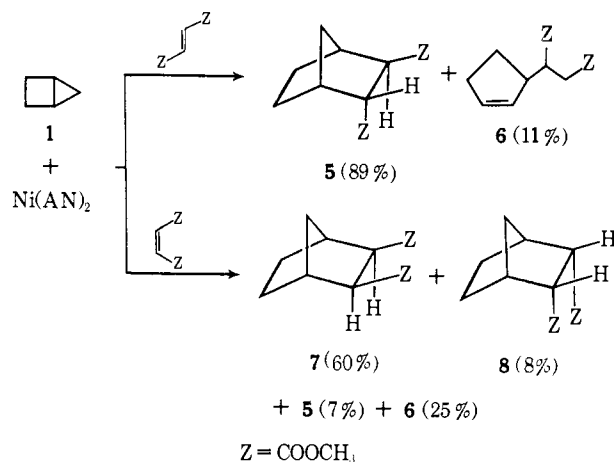
(6) All new compounds gave correct elemental analyses and/or molecular peaks in exact mass spectra. We are grateful to Professor A. Tatematsu, Meijo University, for measurement of the spectra.

(7) Ir (CHCl₃) 1732 cm⁻¹ (C=O); nmr (CCl₄, TMS) δ 1.2–2.8 (m, 9 H, >CH₂, =CHC*H*₂, =CHC*H*, and C*H*₂COOCH₃), 3.60 (s, 3 H, OCH₃), and 5.70 (narrow m, 2 H, =CH).

(8) K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, 91, 1516 (1958).

(9) C. R. Noller and R. Adams, *J. Amer. Chem. Soc.*, 48, 2444 (1926).

(10) Ir (CHCl₃) 2240 cm⁻¹ (CN); nmr (CCl₄, TMS) δ 1.2–3.0 (m, 9 H, >CH₂, =CHC*H*₂, =CHC*H*, and CH₂CN), and 5.6–6.0 (m, 2 H, =CH).

(11) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, 91, 1684 (1969), and references cited therein.