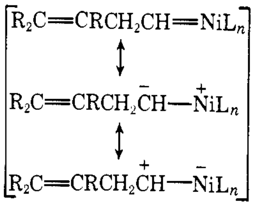
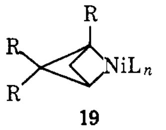
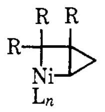


$$\left[\begin{array}{c} R_2C{=}CRCH_2CH{=}NiL_n \\ \updownarrow \\ R_2C{=}CRCH_2\overset{-}{C}H{-}\overset{+}{N}iL_n \\ \updownarrow \\ R_2C{=}CRCH_2\overset{+}{C}H{-}\overset{-}{N}iL_n \end{array}\right]$$

18



19



20

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]

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(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
Department of Chemistry, Nagoya University
Chikusa, Nagoya, Japan

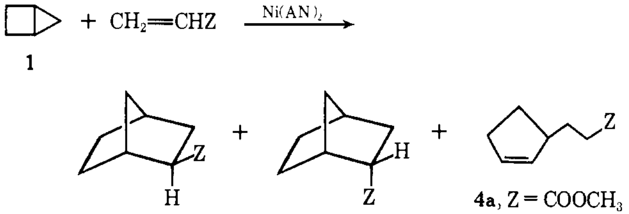
Received June 7, 1971

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 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 CH_3COOAg–$(C_2H_5)_3N$–CH_3OH at 70°



2a, Z = $COOCH_3$
2b, Z = CN

3a, Z = $COOCH_3$
3b, Z = CN

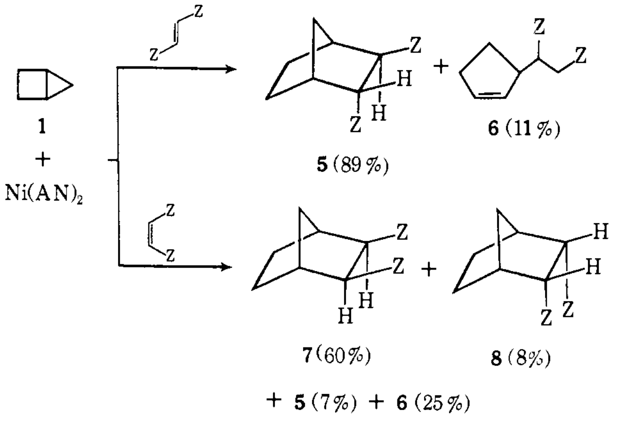
4a, Z = $COOCH_3$
4b, Z = CN

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–CH_3OH. 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



Z = $COOCH_3$

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(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).

(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 ($CHCl_3$) 1732 cm^{-1} (C=O); nmr (CCl_4, TMS) δ 1.2–2.8 (m, 9 H, $>CH_2$, $=CHCH_2$, $=CHCH$, and CH_2COOCH_3), 3.60 (s, 3 H, OCH_3), 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).

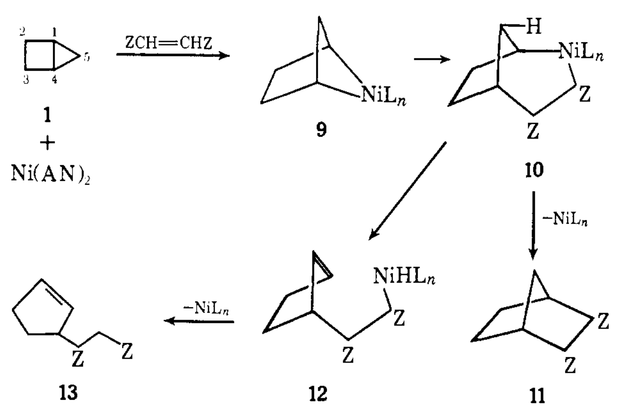
(10) Ir ($CHCl_3$) 2240 cm^{-1} (CN); nmr (CCl_4, TMS) δ 1.2–3.0 (m, 9 H, $>CH_2$, $=CHCH_2$, $=CHCH$, and CH_2CN), and 5.6–6.0 (m, 2 H, $=CH$).

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

results. When **1** (1.2 mmol) was allowed to react with dimethyl fumarate (3.7 mmol) in benzene (3 ml) containing Ni(AN)$_2$ (0.2 mmol) at 60° for 45 hr, a single cycloadduct **5** was obtained in 30% yield. A small amount of the monocyclic adduct **6** was also produced. Similarly, the reaction of **1** and dimethyl maleate afforded a mixture of coupling products, **5**, **6**, **7**, and **8** (46% total yield). The stereospecificity of the cycloaddition was at least 91%,[12] as determined by the ratio **7** + **8**/**5** + **7** + **8**. The identity of the adducts **5**, **7**, and **8** was established by comparison with respective authentic samples.[13,14]

Although the situation is oversimplified, the overall reaction producing bicyclo[2.2.1]heptanes and cyclopentene derivatives may be reasonably illustrated by Scheme II: (1) the initial oxidative addition of the strained C-1–C-4 bond of **1** onto the nickel(0) atom (formally d^{10} → d^8 conversion) forming the organonickel intermediates **9** (L = AN or ZCH=CHZ),[15,16] (2) the insertion of the coordinated olefin into the Ni–C σ bond[17] to produce the new organonickels **10**, and (3) the reductive elimination to give the bicyclic products **11**, and the regeneration of the nickel(0) catalyst (d^8 → d^{10}). Formation of the cyclopentene derivatives would tentatively be accounted for by assuming the nickel–hydride elimination at the stage of **10** followed by the ejection of the nickel(0) catalyst (**10** → **12** → **13**). Rigorously, however, the mechanistic possibility that the formation of the cycloadducts of type **11** is a transition-metal catalyzed concerted reaction[18] could not be excluded.

Scheme II



Attempted reaction of bicyclo[3.1.0]hexane or bicyclo[4.1.0]heptane with methyl acrylate in the presence of Ni(AN)$_2$ resulted in recovery of the starting materials. The lack of reactivity in these higher homologs could reasonably be attributed to the reduced strain energy of the *central* σ bonds.[19]

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(12) Unsaturated esters recovered from the reaction of **1** and dimethyl maleate consisted of maleate and fumarate (97:3). Dimethyl fumarate was not isomerized during the reaction.

(13) H. Bode, *Ber. Deut. Chem. Ges. B*, **70**, 1167 (1937).

(14) The spectral data of **6** are identical with those reported: P. de Mayo, S. T. Reid, and R. W. Yip, *Can. J. Chem.*, **42**, 2828 (1964). Compound **6** produced by the reaction of **1** and dimethyl fumarate is indistinguishable from that derived from **1** and dimethyl maleate (ir, nmr, glpc, and tlc), though the detailed stereochemistry is unknown.

(15) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

(16) For the oxidative addition of strained C–C single bonds, see: L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970); L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970); P. E. Eaton and S. A. Cerefice, *ibid.*, 1494 (1970); T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 2405, 6519 (1969); *Tetrahedron Lett.*, 2561 (1969).

(17) *Cf.* W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, **91**, 3661 (1969).

(18) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); J. Wristers, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970), and references cited therein.

(19) In the absence of the olefins, no isomerization of **1** was observed under identical reaction conditions.

R. Noyori,* T. Suzuki, H. Takaya
Department of Chemistry, Nagoya University
Chikusa, Nagoya, Japan

Received June 7, 1971

The Transition Metal Complex Induced Rearrangement of 1-Methyl-2,2-diphenylbicyclo[1.1.0]butane. A New Route to Azulenes[1]

Sir:

The intriguing nature of the transition metal induced rearrangement of derivatives of bicyclo[1.1.0]butane has been amply demonstrated by the plethora of publications in this area.[2] Although the role of the transition metal catalysts and the detailed mechanistic aspects of the rearrangements are of theoretical interest, it seems apparent that the published transformations of exotic derivatives of bicyclo[1.1.0]butane into simple dienes must be described as something less than an advance in organic synthesis. We now wish to report what we believe to be a synthetically useful new route to the azulene nucleus which has as the critical reaction the transition metal induced rearrangement of a phenyl-substituted bicyclo[1.1.0]butane.

When 1-methyl-2,2-diphenylbicyclo[1.1.0]butane[3] (**1**) was treated with 4 mol % of rhodium dicarbonyl chloride dimer in chloroform for 2 hr at room temperature, a mixture was formed which consisted of the three primary products, **2**, **3**, and **4**, and the two secondary products, **5** and **6**. The identity of **2** was established on the basis of its spectroscopic properties. The nmr absorptions occurred at τ 2.86 (10 H, broad singlet, aromatic protons), 3.40 (1 H, quartet, H$_X$), 4.76 (1 H, doublet of doublets, H$_B$), 5.00 (1 H, doublet of doublets, H$_A$), and 8.10 (3 H, singlet, methyl group). The coupling constants were J_{AB} = 1.5 Hz, J_{AX} = 10 Hz, and J_{BX} = 17 Hz, in good agreement with the constants previously reported for 3,4-dimethylpenta-1,3-diene.[4] The uv spectrum of **2** showed $\lambda_{max}^{pentane}$ 237 (ϵ 15,000) and 277 nm (ϵ 21,000). The ir spectrum of **2** was consistent with the proposed structure and the high-resolution mass spectrum showed a parent peak at *m/e* 220.1248 (calcd 220.1252).

The structures of **3** and **4** could not be unequivocally established due to spontaneous air oxidation[5] and our

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(1) Paper XXVI on the "Chemistry of Bent Bonds." For the previous paper in this series see P. G. Gassman, E. P. Williams, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 5199 (1971).

(2) For leading references see (a) P. G. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971); (b) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971); (c) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93**, 1288 (1971).

(3) The bicyclo[1.1.0]butane (**1**) can be prepared in greater than 70% yield from the dibromocarbene adduct of 1,1-diphenyl-2-methylpropene according to the excellent method of W. R. Moore and J. B. Hill, *Tetrahedron Lett.*, 4553 (1970).

(4) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970). See also L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p 85.

(5) Column chromatography of the crude reaction mixture gave a series of almost colorless fractions which were shown by vpc analysis to contain a mixture of **3**, **4**, and **6**. Exposure of these fractions to air resulted in the immediate formation of a dark blue-black solution due to the oxidation of **3** to **5**.