Thermal and Photochemical Dimerization of Norbornadiene[1] Using Tetracarbonylnickel as a Catalyst[2]

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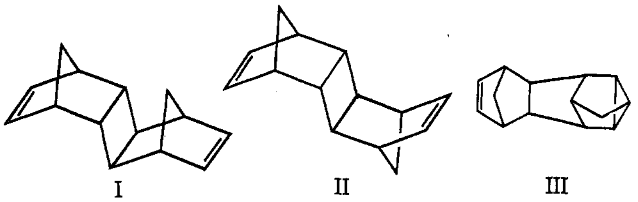
Thermal dimerization of olefins using transition metal complexes as catalysts have been investigated extensively,[3] but little attention has been focused on the analogous photochemical reactions.[4] As a result, few comparisons have been made between the two excitation processes. In this communication a comparison is made between thermal excitation and photochemical excitation on the $Ni(CO)_4$-catalyzed dimerization of norbornadiene. A structure is unambiguously established for one of the pseudo-Diels-Alder dimers from the photoreaction, and the effect of a cyclopropane ring on the nmr spectra of this pseudo Diels-Alder dimer is discussed.

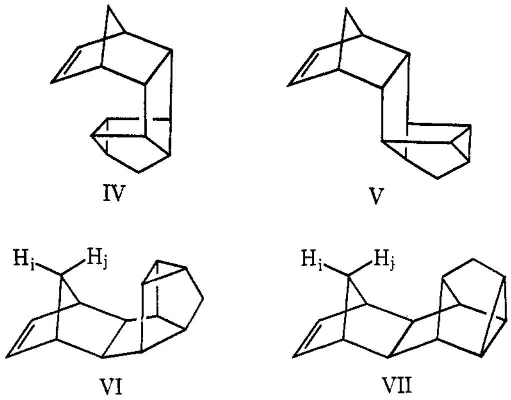
Previous investigators[3a–f] have shown that cyclobutane dimers I and II (Figure 1) are formed from the thermal reaction of $Ni(CO)_4$ and norbornadiene. Repetition of the thermal work in neat norbornadiene at 85° confirmed the above conclusions and we would simply add that the ratio of dimers I and II is 3:1, respectively.

Photochemical excitation using a Hanovia 450-W mercury lamp equipped with a Pyrex filter, cooling jacket, and "merry-go-round" sample holder gave two pseudo-Diels-Alder dimers having the general structure III (Figure 1). These two compounds were shown by gc and nmr to be identical with compounds previously prepared by Katz[3f,i] and Greco[5] through other processes. While Katz[3i] has suggested a structure for one of these dimers, we felt that a single-crystal X-ray structure analysis would accomplish two things. It would establish unambiguously the stereochemistry of one of the four possible dimer isomers which are discussed below. Furthermore, we could correlate the actual structure with its nmr spectrum which appeared to possess some useful information regarding cyclopropane interaction. We were able to show by nmr that no interconversion of cyclobutane and Diels-Alder dimers occurs under reaction conditions.



I II III

Figure 1.



IV V VI VII

Figure 2.

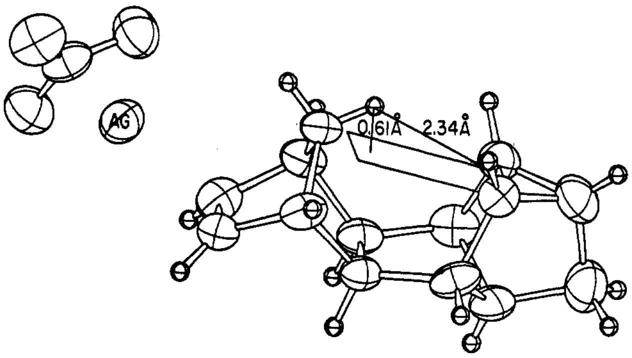


Figure 3.

The above observations suggest that $Ni(CO)_4$ has the unusual ability to produce cyclobutane dimers thermally and pseudo-Diels-Alder dimers photochemically with norbornadiene. It is our feeling that both processes are thermal, but in the photochemical reaction a different catalytic species is being generated. Another compound, $Co(CO)_3NO$, has been shown to yield cyclobutane and pseudo-Diels-Alder dimers[3h] under thermal excitation, only which suggests that the necessary element for Diels-Alder formation is the loss of three ligands. Perhaps in the $Ni(CO)_4$ reaction light is necessary to remove the third carbon monoxide moiety. Further mechanistic investigations are continuing.

Stereochemical Assignments.—There are four possible isomers of the general structure III (Figure 2). Prior to this investigation structures IV and V had been assigned their stereochemistry,[3f] but VI and VII which were obtained from the $Ni(CO)_4$ reaction had not been assigned unambiguously. To ascertain isomer identities, the silver nitrate complex of VI[6] was prepared and subjected to X-ray crystallographic analysis. The results are shown in Figure 3.

This evidence combined with previous work establishes the stereochemistry for three of the four possible

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[1] Bicyclo[2.2.1]hepta-2,5-diene.

[2] For the first paper in this area, see W. Jennings and B. Hill, *J. Amer. Chem. Soc.*, **92**, 3199 (1970).

[3] (a) R. Pettit, *ibid.*, **81**, 1266 (1959); (b) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, **No. 11**, 373 (1961); (c) D. M. Lemal and K. S. Shim, *ibid.*, 368 (1961); (d) L. G. Cannell, *ibid.*, 5967 (1966); (e) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965); (f) T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, **32**, 1301 (1967); (g) F. W. Hoover and R. V. Lindsey, Jr., *ibid.*, **34**, 3051 (1969); (h) P. W. Jolly and F. G. A. Stone, *J. Chem. Soc.*, 6416 (1965); (i) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967).

[4] (a) An excellent review article on the subject was written by G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968); (b) D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKean, *J. Amer. Chem. Soc.*, **88**, 3021 (1966); (c) D. J. Trecker, *et al.*, *ibid.*, **87**, 3261 (1965).

[5] A. Greco, *et al.*, *J. Org. Chem.*, **35**, 271 (1970).

[6] This major product isomer is the one labeled "predominant isomer" by Mrowca and Katz.[3i]

Figure 4.—Nmr spectra of isomer VI: (a) nondecoupled spectra; (b) the H_y proton decoupled from the H_j proton which is now observed as a resolved triplet;[9,10] (c) the H_j proton is decoupled from the H_i proton.

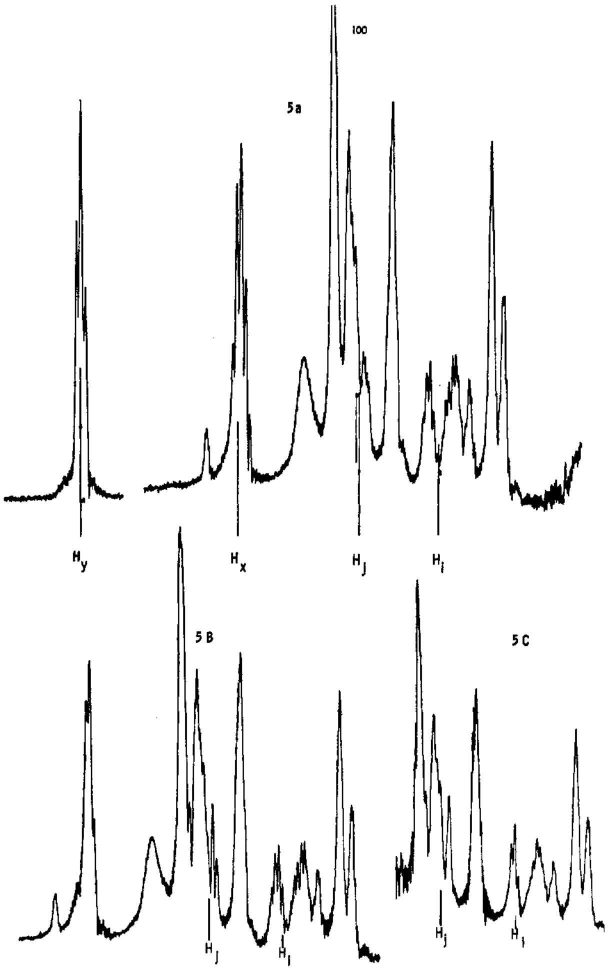

Figure 5.—Nmr spectra of isomer VII: (a) nondecoupled spectra; (b) the H_y protons are decoupled from the H_j proton which now shows only part of its triplet;[9,10] (c) the H_x protons are decoupled from the H_i and H_j protons which are collapsing toward doublets.

isomers of III. Since the fourth isomer[7] has similar ir and nmr spectra (Figure 4a and 5a) it is quite reasonably assigned to isomer VII.

Nmr Correlation.—While the X-ray analysis leaves little doubt as to the nature of isomer VI, it affords a unique opportunity for comparison between the structure and nmr spectrum. One distinct difference between isomers VI and VII (Figure 2) is the relative positions of the H_j protons with respect to the cyclopropane ring in the other nortricyclene moiety. We reasoned that either the H_i or H_j proton would be affected by the adjacent cyclopropane ring in VI, but unaffected in isomer VII. Furthermore, the effect might add evidence as to the nature of a ring current in cyclopropanes. The H_i and H_j bridge protons (Figure 6) can be characterized as an AX quartet with a coupling constant of ≈ 10 cps. By decoupling the H_X from H_i protons, we were able to determine signals belonging to H_i and H_j. Furthermore, the H_y protons are long range coupled to the H_j ones[8-10] and, thus, decoupling further facilitated the peak assignments for H_j and H_i (Table I). The doublets of the quartet are sufficiently separated for individual proton assignment. Portions of the decoupled spectra of isomers VI and VII are shown in Figures 4 and 5.

Table I

Isomer	Nmr ($DCCl_3$), ppm H_j	H_i	Difference
VI	2.43	1.15	1.28
VII	1.80	1.17	0.63

As suspected from the structures, the cyclopropyl ring is apparently deshielding the H_j proton in isomer VI and not in isomer VII. One cannot attribute these differences in chemical shift for the H_j proton in VI and VII to ring strain variation because the H_i proton would also be altered. A closer look at the crystal structure of VI (Figure 3) reveals that H_j lies 2.34 ± 0.04 Å from the cyclopropyl carbon–carbon bond and 0.61 Å above the projected equatorial plane of the cyclopropyl ring. Thus, it is clear that a proton in the equatorial plane of a cyclopropyl ring will experience a downfield shift suggestive of a ring current. These conclusions on cyclopropyl ring effects are in agreement with those proposed by Roberts.[11] The nmr assign-

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(7) This minor product isomer is identical with that of Figure 1e of Greco.[5]

(8) (a) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964); (b) Franzus, et. al., *ibid.*, **90**, 3721 (1968); (c) A. P. Marchaid and J. E. Rose, *ibid.*, **90**, 3724 (1968).

(9) This proton is coupled only weakly to the H_y one but exists as a triplet on decoupling because it is coupled to the two bridgehead protons (H_x).

(10) When the H_y protons are irradiated, the upfield H_i proton is unaffected.

(11) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963).

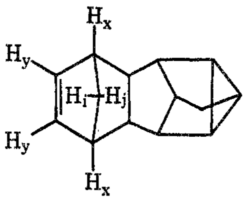

Figure 6.

ments are analogous to the work of Franzus[8] whose studies characterized this type of ring system.

We may conclude that $Ni(CO)_4$ is a unique catalyst having the ability to produce different types of norbornadiene dimers as a function of the type of excitation. Furthermore, all four Diels–Alder dimers structures are now firmly assigned and nmr interpretation of these types of structures is somewhat facilitated. Ring current effects in cyclopropane are implicated in deshielding an equatorial proton.

Experimental Section

General.—The nmr spectra were obtained from a Varian A-60 spectrometer while all the spin decoupling was done on a Varian HA-60 spectrometer. Gas chromatography information was determined by a Varian Aerograph Model 1740, and preparative separations were done on an Aerograph Autoprep Model A-700. A Varian CH-5 mass spectrometer with a gas chromatograph attached was used for mass spectral data. Norbornadiene was purchased from Frinton, purified (according to gc analysis) by recrystallizing the $AgNO_3$ complex of it in ethanol, and recovered by thermal decomposition under vacuum. The $Ni(CO)_4$ (toxic), obtained from Matheson, was distilled once prior to use.

Thermal Reaction.—To 8.5 ml of norbornadiene (7.73 g, 83.9 mmol) under oxygen-scrubbed N_2 in a flask fitted with reflux condenser and Hg bubbler was added $Ni(CO)_4$ (0.145 g, 0.849 mmol). The solution was brought to reflux (85–87°) and held there for 6.5 hr. Analysis by gc (6-ft column, 5% SE-30 on Gas-Chrom Z, 100–120 mesh) showed two dimer peaks in the ratio (peak heights) of 3:1. The dimers (3.17 g, 17.2 mmol) constituting a 41% conversion of norbornadiene [2030% yield based on $Ni(CO)_4$] were removed from solution by distillation under vacuum. Comparison of the nmr spectrum of the mixture with those of dimers I and II reported in the literature[3e] proved their identity. The integration of the olefin proton peaks in the nmr spectrum also showed a relative ratio of 3:1 I:II.

Photochemical Reaction.—Under vacuum (<0.015 mm) purified norbornadiene was transferred into a calibrated flask and 8.5 ml (7.73 g, 83.9 mmol) was transferred into a Vycor tube (10-mm i.d., 20-cm length). $Ni(CO)_4$ (0.145 g, 0.849 mmol) was added to the norbornadiene *via* syringe through a septum above the tube which was then sealed under vacuum and irradiated for 4.5 days in a "merry-go-round" tube holder by a Hanovia 450-W Hg lamp in a quartz, water-cooled jacket. From gc analysis (6-ft column, 5% SE-30 on Gas-Chrom Z, 100–120 mesh; 6-ft column, 20% Carbowax 20M on Chromosorb W, 80–100 mesh) the contents of the tube were found to contain dimers, 90% of which were the two pseudo-Diels–Alder dimers (peak height ratio of 2:1). Also detected were a trace of CO insertion product (parent peak in mass spectrum at m/e 212) and some trimer (parent peak at m/e 276). Separation of the products by vacuum distillation produced 0.876 g (4.75 mmol) of dimers [11% conversion of norbornadiene or 559% yield based on $Ni(CO)_4$] and 43 mg (0.156 mmol) of trimer. The dimers were separated on a 20-ft column, 20% Carbowax 20M on Chromosorb W, 80–100 mesh, 190°. The nmr spectrum of the original mixture of dimers (ratio of olefin proton integrations was 2:1 VI:VII) was the same as the combination of the nmr spectrum of each of the components. When Pyrex and quartz tubes were used rather than Vycor, both ratios and amounts as well as number of products were essentially the same from gc information.

Investigation of Interconversion of Dimers.—A mixture of pseudo-Diels–Alder dimers (5.15 g), the predominant one being VI, and $Ni(CO)_4$ (91 mg) were heated at 92° for 26 hr under nitrogen. An nmr spectrum showed the dimer mixture to be unchanged. Likewise, a mixture of dimers I and II (6.33 g) and $Ni(CO)_4$ (104 mg) were sealed under vacuum and irradiated as above for 1 week. The nmr analysis showed no change in dimer contents.

Silver Nitrate–Dimer Complex for Crystal Structure.—To dimer VI a saturated aqueous $AgNO_3$ solution was added and the resulting white precipitate collected. After being washed with water the precipitate was recrystallized from absolute ethanol and crystals were used for structure determination.

X-Ray Data.—This compound crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 17.554(9)$ Å, $b = 6.908(4)$ Å, $c = 11.031(5)$ Å, and $\beta = 103.10(3)°$.

A unique data set was collected by the θ–2θ scan technique on a GE XRD-5 diffractometer using zirconium-filtered Mo K_α radiation. Two crystals were used to collect 1181 pieces of data, of which 841 were found to be more than twice the standard deviation of the intensity and were thus considered observed. The data were reduced and corrected for absorption.

The structure was solved by the conventional heavy atom method. Hydrogens were located from the difference map. The structure was refined using full matrix least squares, treating hydrogen atoms isotropically and nonhydrogen atoms anisotropically, to an R value of 3.3%.[12]

Registry No.—I, 2957-68-8; II, 1624-13-1; IV, 17926-98-6; V, 17926-99-7; VI, 18067-61-3; VII, 33780-58-4; norbornadiene, 121-46-0; tetracarbonylnickel, 13463-39-3.

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[12] The complete X-ray data will be published in an appropriate journal.

The Photochemistry of 1-Keto-2-carbomethoxymethylenebenzocyclobutene

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We wish to report our results on the photochemical decomposition of 1-keto-2-carbomethoxymethylenebenzocyclobutene (**1a**). This keto ester is of interest because of its relation to the recently studied 2-methylenecyclobutanones,[2] benzocyclobutenones,[3] and benzocyclobutadienequinone.[4]

Ultraviolet irradiation of a dilute methanol solution of **1a** gave, upon preparative tlc, a 15% yield of an 85:15 mixture of cis and trans methyl *o*-carbomethoxycinnamate (**3** and **4**, Scheme I), as the major reaction products. Several additional unidentified minor components were also obtained in a combined yield of 6%. The remainder of the material remained at the origin of the tlc plate as a brown gum. Esters **3** and **4** were separated by preparative gas chromatography.

Methyl *o*-carbomethoxy-*cis*-cinnamate (**3**) showed the following spectral properties: nmr δ 3.51 (s, 3 H), 3.80

[1] NDEA Predoctoral Trainee, 1967–1970.

[2] D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

[3] M. P. Cava and R. J. Spangler, *ibid.*, **89**, 4550 (1967).

[4] H. A. Staab and J. Ipaktschi, *Chem. Ber.*, **101**, 1457 (1968).