also some electronic contribution to the increase in barrier. The exact nature of bonding of such molecules as amides to the uranyl group is subject to discussion.[14] However, whatever the exact nature of the bond, there must be a shift in electron density toward the oxygen atom. This requires an increased double-bond character and greater stiffness in the amide bond. To a much smaller extent, the oxygen atom is "made larger," presumably by hydrogen bonding to $CHCl_2CHCl_2$. The small increase in barrier (0.2 kcal) with this solvent compared with *o*-dichlorobenzene is at least qualitatively real. Very careful experiments were performed in which samples of XI in the two solvents were alternated in the spectrometer at 110°. In the latter solvent, the signals were definitely more nearly coalesced.

Registry No.—I, 17372-54-2; II, 20678-83-5; III, 13936-76-0; IV, 13936-78-2; V, 13936-77-1; VI, 20643-10-1; VII, 20643-11-2; VIII, 20643-12-3; IX, 13936-74-8; X, 20643-14-5; XI, 17372-56-4; XII, 17372-55-3; XIII, 13936-79-3; XIV, 20643-18-9; XV, 20633-57-2; XVI, 20633-58-3; XVII, 20633-59-4; XVIII, 6840-46-6; XIX, 20633-61-8.

Acknowledgment.—We are indebted to J. E. Conner for operating and maintaining the A-60 spectrometer and for other valuable assistance.

A Study of the Photoaddition Reactions of Norbornadiene with 2-Cyclohexenones[1]

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To gain mechanistic information on photoaddition reactions of 2-cyclohexenones, the additions of 2- and 3-methyl-2-cyclohexenone and 2-cyclohexenone to bicyclo[2.2.1]heptadiene have been studied. The products are of the following types: (i) cyclobutane derivatives (*cis*- and *trans*-fused structures are formed); (ii) α- and β-nortricyclyl-2-cyclohexenones; and (iii) α- and β-(7-*anti*-norbornenyl)-2-cyclohexenones. The nortricyclyl compounds were prepared by independent routes, and one of the norbornene derivatives was degraded to 7-norbornanecarboxylic acid. Other structure assignments rest on infrared and nmr spectra. In the reaction of 3-methyl-2-cyclohexenone and norbornadiene a 16% yield of 9-methyl pentacyclo[$7.4.0.0^{2,7}.0^{3,5}.0^{4,8}$]tridecan-13-one (9) is obtained. It is proposed that this and the cyclohexenone derivatives are formed *via* biradical intermediates. Hydrogen shifts are involved in the formation of the latter products, and a deuterium-labeling experiment showed that one such shift is intramolecular and stereospecific. Naphthalene quenching experiments imply that the cyclohexenone derivatives are formed by a triplet-state reaction.

The chemistry of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) is rich in reactions, in which both double bonds of the diene are involved. Such reactions include ionic[3] and free-radical[4] additions, photoisomerization,[5] and the 2,6 cycloaddition known as the homo Diels–Alder reaction.[6] Nortricyclene derivatives and 7-substituted norbornenes are oft-encountered products of these reactions.

In this paper we describe some photoadditions of norbornadiene with simple[7] 2-cyclohexenones, which are of particular interest for the following reasons. First, although photoadditions of alicyclic enones and unsaturated esters have long been known[8,9a] and have been extensively studied,[9,10] attention has been focussed on dimerizations of the carbonyl compounds or cross additions with uncomplicated alkenes. No work prior to our communication[1] had been reported in which a homoconjugated diene was employed as the substrate in a cross addition. It was, therefore, of interest to see to what extent the spatial relationship of the double bonds in norbornadiene modified the course of enone photoadditions to this diene. Such modification might result, for example, if biradical species were discrete intermediates in the addition reaction.[9a]

A further interesting aspect of photoadditions with this diene was the question of whether the symmetry-forbidden 2,6 cycloaddition[6] would occur. This is symmetry allowed,[11] and well known,[6] in ground-state chemistry.

To determine whether homoconjugated dienes do differ from alkenes in their photoaddition behavior, a study of the photoreactions of 2-cyclohexenone,

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[1] For preliminary reports, see J. J. McCullough and J. M. Kelly, *J. Amer. Chem. Soc.*, **88**, 5935 (1966); J. J. McCullough and P. W. W. Rasnussen, *Chem. Commun.*, 387 (1969).

[2] Author to whom requests for reprints should be addressed.

[3] See J. A. Berson, "Molecular Rearrangements," Part I, Interscience, New York, N. Y., 1963, p 198.

[4] (a) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, **80**, 635 (1958); (b) D. J. Trecker and P. Henry, *ibid.*, **85**, 3204 (1963); (c) N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962); (d) S. J. Cristol and D. J. Davies, *ibid.*, **29**, 1282 (1964); (e) T. V. Van Auken and E. A. Rick, *Tetrahedron Lett.*, 2709 (1968).

[5] (a) S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.*, **76**, 5600 (1954); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron Lett.*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961).

[6] (a) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959); (b) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Lett.*, 615 (1962); (c) H. K. Hall, *J. Org. Chem.*, **42**, 215 (1960); (d) S. J. Cristol, E. L. Alfred and D. L. Wetzel, *ibid.*, **27**, 4058 (1962).

[7] "Simple" is taken here to mean derivatives whose π system is similar to 2-cyclohexenone—*i.e.*, alkyl derivatives.

[8] Early examples are W. Treibs, *Chem. Ber.*, **63**, 2738 (1930); *J. Prakt. Chem.*, **138**, 299 (1933). A. Butenandt, L. K. Poschmann, G. Failer, U. Siebert, and E. Biekert, *Ann.*, **575**, 123 (1952).

[9] (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); a summary of early examples is given here. (b) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966). (c) M. Brown, *ibid.*, 340 (1965). (d) R. A. Schneider and J. Meinwald. *J. Amer. Chem. Soc.*, **89**, 2023 (1967). (e) P. Yates, S. N. Eğe, G. Büchi, and D. Knutsen, *Can. J. Chem.*, **45**, 2927 (1967). (f) S. N. Eğe and P. Yates, *ibid.*, **45**, 2933 (1967). (g) R. L. Cargill, M. E. Beckham, A. E. Sibert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965).

[10] (a) O. L. Chapman, "Photocycloaddition Processes," Abstracts of the 20th National Organic Symposium, Burlington, Vt., June 1967, p 127; (b) P. E. Eaton, *Accounts Chem. Research*, **1**, 50 (1968); (c) A. Cox, P. de Mayo, and R. W. Yip, *J. Amer. Chem. Soc.*, **88**, 1043 (1966); (d) H. D. Scharf and F. Korte, *Ber.*, **99**, 1299 (1966); (e) R. L. Cargill and M. R. Willcott, III, *J. Org. Chem.*, **31**, 3938 (1966).

[11] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

Table I

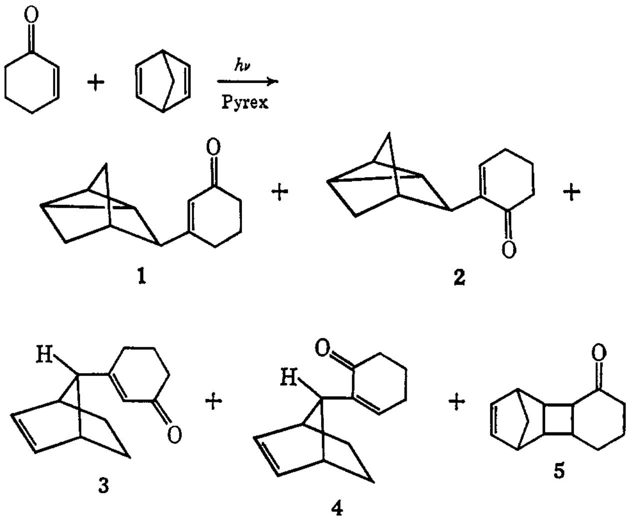
Effect of Solvent and Added Naphthalene on the Product Composition in 2-Cyclohexenone–Norbornadiene Additions

		Reactants, molar concn			Product composn, %[a]		
Run	Solvent	2-Cyclohexenone	Norbornadiene	Naphthalene	Cyclobutanes	α-Substituted cyclohexenones	β-Substituted cyclohexenones
1[b]	Hexane	0.025	0.25		55.0	13.3	31.7
2	Hexane	0.025	0.25		53.3	15.9	30.8
3	*t*-Butyl alcohol	0.025	0.25		52.5	15.4	32.1
4	*t*-Butyl alcohol	0.025	0.25		52.3	16.3	31.4
5[c]	Hexane	0.0248	0.28	0.0492	50.8	15.7	33.5
6	*t*-Butyl alcohol[d]	0.0246	0.28	0.0492	59	14	27

[a] All ratios were by vpc, column B. [b] Runs 1 and 3 had 70% residual 2-cyclohexenone; 2 and 4 had 30%. [c] No light was absorbed by naphthalene. Bismuth trichloride–cupric sulfate filter[23a] solution was used. [d] Contained 7.5% methanol.

2-methyl-2-cyclohexenone, and 3-methyl-2-cyclohexenone, with norbornadiene, was undertaken.

Chart I



Results

The light source used in all of the photolyses was a Hanovia, Type L, 450-W mercury lamp, contained in the usual water-cooled immersion apparatus. A Pyrex sleeve, 1 mm thick having 0% transmission at 280 $m\mu$, was used in all runs. The reactions were run in hexane, *t*-butyl alcohol, or *t*-butyl alcohol containing 10% methanol, and no solvent effect was observed (Table I). Typically, 400 ml of solution containing 4.0 g of cyclohexenone and 40.0 g of norbornadiene (tenfold molar excess of diene) were irradiated under nitrogen until monitoring of aliquots by gas or thin layer chromatography or infrared or nmr analysis showed that the reaction was complete (2–8 hr, depending on the cyclohexenone used and the conversion desired). The residue obtained after solvent distillation was chromatographed on silica gel, and the fractions eluted by benzene–ethyl acetate, which were enriched in the various product types, were subjected to preparative gas chromatography.[12] The pure products thus isolated were examined by spectroscopic methods, and the purity was checked by gas chromatography and elemental analysis.

The system **2-cyclohexenone** and **norbornadiene** was the first to be investigated and will be considered first. Photolysis of 2-cyclohexenone and norbornadiene as described in the Experimental Section, in *t*-butyl alcohol or in hexane, resulted in the formation of adducts, as shown by vpc, thin layer chromatography, and infrared monitoring. These compounds were all shown to be 1:1 adducts of cyclohexenone and norbornadiene by their mass spectra which had molecular ions of *m/e* 188. They were separated by silica gel column and gas chromatography, and have been assigned the structures shown in Chart I, which are 3-(3-tricyclo$[2.2.1.0^{2,6}]$-heptyl)-2-cyclohexenone (**1**, 20%), 2-(3-tricyclo$[2.2.1.0^{2,6}]$heptyl)-2-cyclohexenone (**2**, 8%), 3-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (**3**, 9%), 2-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (**4**, 8%), and a mixture of cyclobutanes (**5**, 55%).

The cyclobutanes, of which there are at least three stereoisomers, showed infrared peaks at 5.82 and 5.88 μ (*trans*- and *cis*-fused bicyclo[4.2.0]octan-2-ones, respectively).[9a] The compounds having absorption at 5.82 μ did not survive gas chromatography or treatment with alumina, but could be chromatographed without isomerization on silica gel. This behavior is as expected for *trans*-fused cyclobutanes (**5**) from the work of Corey, *et al.*[9a] These compounds also had infrared absorption at 14.2 μ (norbornene double bond[13]) and resonance at 6.00 ppm (2 H, vinyl protons) in the nmr. No attempts have been made to establish precisely the stereochemistry of any of these cyclobutanes.

The minor but more interesting products, the substituted cyclohexenones **1**–**4**, all had infrared bands at 5.99 μ (α,β-unsaturated ketone). The nortricyclyl products **1** and **2** had strong bands at 12.42 and 12.35 μ, typical of nortricyclene derivatives,[14] while norbornenes **3** and **4** had absorption at 14.20 μ.

3-Nortricyclylcyclohexenone (**1**) showed a resonance at 5.81 ppm (1 H, vinyl, α to carbonyl) in the nmr, and also a sharp signal at 1.16 ppm, attributed to the nortricyclene system. Structure **1** was confirmed by independent synthesis from 3-ethoxycyclohexenone and nortricyclylmagnesium bromide using the general procedure of Woods, *et al.*[15] 2-Nortricyclylcyclohexenone had a similar nmr spectrum to **1**, except that the vinyl resonance (1 H) was at 6.63 ppm showing that the cyclohexenone was α substituted.

Structure **3** for one of the norbornenyl cyclohexenones was derived by nmr spectroscopy. The low-field part of this spectrum showed signals at 5.70 (1 H, singlet, α to carbonyl) and at 6.11 ppm (2 H, triplet, norbornene

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[12] For details of gas chromatography, see Experimental Section.

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, p 48; (b) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **82**, 2341 (1960).

[14] G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962).

[15] G. F. Woods, P. H. Griswald, Jr., B. H. Armbrecht, D. I. Blumenthal, and R. Plapinger, *J. Amer. Chem. Soc.*, **71**, 2028 (1949).

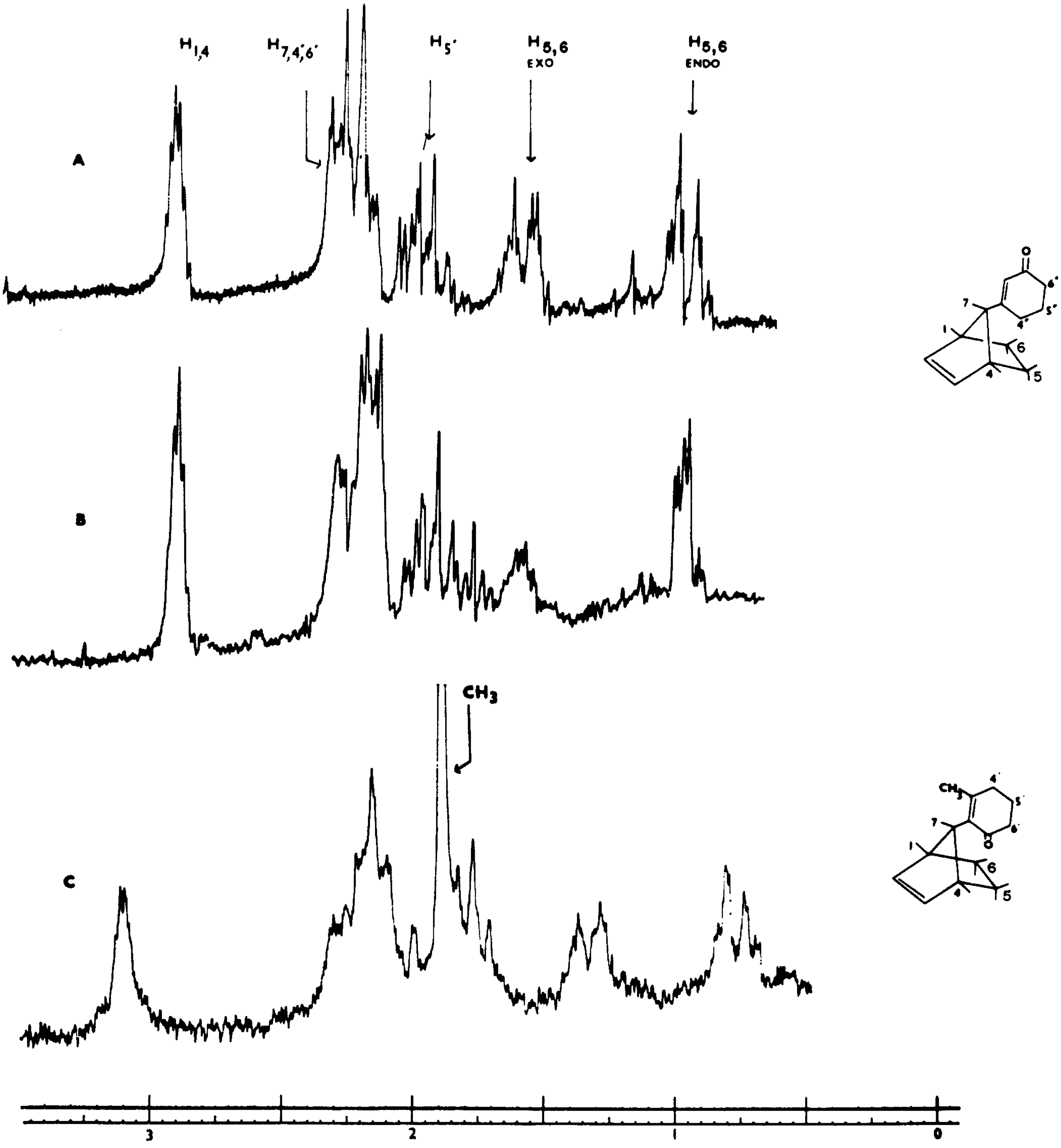

Figure 1.—100-Mcps nmr spectra: A, spectrum of **3**; B, spectrum of **3** showing one dueterium in the *exo* position; C, spectrum of **4**.

vinyl). The high-field region is shown in Figure 1A, and this is in accord with the substituent being at C_7 of the norbornene system. Thus, the *exo* and *endo* pairs of protons show as two pairs of multiplets of an AA′XX′ system, the *endo* multiplet being at higher field.[16] Irradiation of the multiplet at 2.21 ppm, which includes the resonance of the allylic C_7 proton, caused the *endo* multiplet to simplify to a quartet. This shows that H_7 is coupled to the *endo* protons and therefore must be *syn* to the norbornene double bond.[17] The assignments of the remaining protons are shown in Figure 1.

Compound **4** had a similar nmr spectrum to that of **3** except that a resonance appeared at 6.63 ppm (1 H, singlet, β to carbonyl) again showing that the norbornene substituent was at the α carbon of the cyclohexenone.

Since some of the products are conjugated enones, and consequently would absorb light in the reaction, it was important to check their photostability. It was noted that the product ratio did not change detectably as the reaction proceeded. Also, 3-nortricyclylcyclohexenone (**1**), the major enone product, was irradiated

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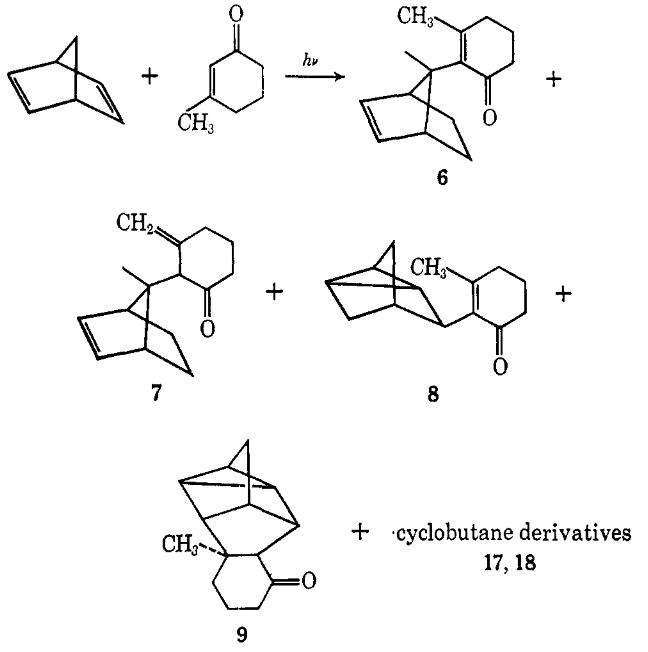
[16] R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962); R. G. Foster and M. C. McIvor, *Chem. Commun.*, 280 (1967).

[17] J. Meinwald and Y. C. Meinwald, *J. Amer. Chem. Soc.*, **85**, 2514 (1963).

separately and did not change on a 6-hr peroid of photolysis.

Photoaddition of **3-methyl-2-cyclohexenone** and **norbornadiene** in hexane or *t*-butyl alcohol gave rise to products to which the structures shown in Chart II

Chart II

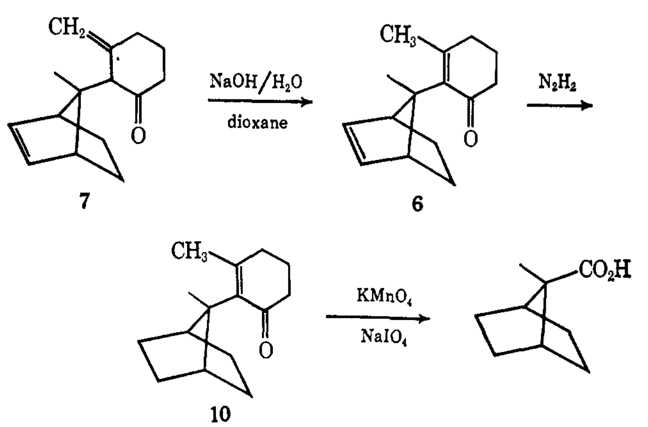


have been assigned. These structures are 3-methyl-2-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (**6**, 2%), 3-methylene-2-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)cyclohexanone (**7**, 15%), 3-methyl-2(3-tricyclo[2.2.1.0^{2,6}]-heptyl)-2-cyclohexenone (**8**, 8%), 9-methylpentacyclo-[7.4.0.0.^{2,7}0.^{3,5}0.^{4,8}]tridecan-13-one (**9**, 16%), and cyclobutane derivatives (59%).

This mixture was also resolved by silica gel column and gas chromatography, as detailed in the Experimental Section. The compounds all had molecular ions at *m/e* 202. The structures assigned to enones **6** and **7** are based on spectroscopic evidence and a chemical degradation. In the infrared, both compounds had bands at 14.2 μ (norbornene).[13] The carbonyl absorption was at 5.99 (α,β unsaturated) for **6**, and at 5.83 μ (cyclohexanone) for **7**; the latter also had a strong band at 11.2 μ (*exo*-methylene group). Enones **6** and **7** were shown to be tautomers, since mild treatment of **7** with base caused clean isomerization to **6**. Diimide reduction[18] of **6** gave the corresponding norbornane **10** in quantitative yield. Oxidation of the latter with aqueous permanganate–periodate[19a] gave 7-norbornanecarboxylic acid, mp 74–75° (lit.[19b] mp 75–76.5°), identified by comparison with an authentic sample.[20] The degradation scheme is shown in Chart III.

The detailed nmr analysis and the unambiguous degradation show that all of the norbornenyl derivatives are 7-substituted compounds. Therefore the structures assigned earlier[1] (5-substituted norbornenes) are incorrect; no 5-substituted norbornenes were isolated from these reactions.

Chart III



The nmr of **6** appears in Figure 1C, and its relationship with that of **3** is evident. Spin decoupling by irradiation of the multiplet centered at 2.30 ppm (which includes H_7) caused the resonance of the *endo* protons to simplify, showing that the 7 substituent is *anti* to the norbornene double bond (*cf.* nmr of **3**). The nmr of **7** is quite different in appearance from those of **3** and **6**. Resonances do appear at 4.60 and 4.70 ppm, which are attributed to the methylene group, and a triplet appears at 6.11 ppm due to the norbornene vinyl protons. The *endo* protons give rise to a multiplet (2 H) centered at 0.9 ppm; the remaining protons are all included in a wide multiplet bounded by 1.5 and 2.6 ppm.

Inspection of space-filling models[21] of **7** reveals that there is severe steric hindrance to rotation of the methylenecyclohexanone substituent, and this would create an anisotropic environment for the *exo* and the bridgehead protons, which may result in the unique nmr spectrum.

A further interesting type of product, isolated only from the reaction of 3-methyl-2-cyclohexenone and norbornadiene, is **9**, the product of formal homo Diels–Alder addition of these molecules. This product was always contaminated with unsaturated compounds whenever purification was by chromatography. The latter contaminants were removed by oxidation with permanganate/periodate reagent.[19a] This product had infrared absorption at 5.90 and at 12.37 μ (doublet, nortricyclene). The nmr showed no signals in the vinyl region, but had a methyl resonance at 1.02 ppm; structure **9** is assigned on the basis of these spectra and the resistance of the compound to oxidation. The stereochemistry shown for **9** in Chart II should be preferred if steric effects are important in the addition reaction.

Photolysis of **2-methylcyclohexenone** and **norbornadiene** gave a mixture of adducts which consisted of 2-methyl-3-(3-tricyclo[2.2.1.0^{2,6}]heptyl)-2-cyclohexenone (**11**, 14%), 2-methyl-3-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (**12**, 10%), and cyclobutane adducts (**13**, 76%) (Chart IV).

Separation of these was achieved by the usual chromatographic methods (see Experimental Section). The adducts had molecular ions of *m/e* 202. As in the first reactions described, the cyclobutanes were not thor-

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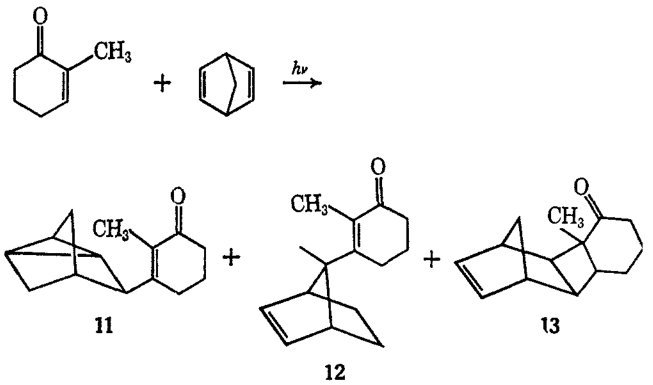
[18] W. C. Baird, B. Franzus and J. H. Surridge, *J. Amer. Chem. Soc.*, **89**, 410 (1967).

[19] (a) J. T. Edward, D. Holder, W. H. Lunn, and I. Puskas, *Can. J. Chem.*, **39**, 599 (1961). (b) P. Yates and R. J. Crawford, *J. Amer. Chem. Soc.*, **88**, 1562 (1966).

[20] Kindly supplied by Dr. J. Warkentin of this department.

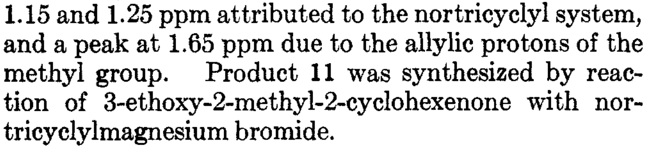
[21] Models used were Courtauld's Atomic Models, available from Griffin and George Ltd., Wembley, Middlesex, England.

CHART IV



oughly investigated. The presence of *cis*- and *trans*-fused bicyclo[4.2.0]octan-2-ones was inferred from the carbonyl region in the infrared, where bands appeared at 5.90 and 5.80 μ. It will be noted that enolization leading to isomerization is blocked by a methyl group in these adducts, and it was possible to isolate one of the *trans*-fused adducts by preparative gas chromatography, as described in the Experimental Section.

The substituted cyclohexenones **11** and **12** both had infrared bands at 5.98 μ (α,β-unsaturated carbonyl). The nortricyclene absorption[14] of **11** appeared at 12.37, and **12** had the band at 14.2 μ attributed to the norbornene double bond.[13] In the nmr, 2-methyl-3-nortricyclylcyclohenenone **11** showed signals consistent with the proposed structure, having narrow peaks at 1.15 and 1.25 ppm attributed to the nortricyclyl system, and a peak at 1.65 ppm due to the allylic protons of the methyl group. Product **11** was synthesized by reaction of 3-ethoxy-2-methyl-2-cyclohexenone with nortricyclylmagnesium bromide.



The structure of the norbornenylcyclohexenone **12** was assigned from its nmr spectrum, which is shown in Figure 2. The high-field region had the following signals: a multiplet at 0.97 (2 H, *endo* protons); a complex multiplet centered at 1.70 (7 H), which included resonances of the methyl group, the *exo* protons, and the pair of protons at C$_5$ of the cyclohexenone ring; a multiplet centered at 2.20 (4 H), assigned to the methylene groups at C$_4$ and C$_6$ of the cyclohexenone ring; and a broad peak (1 H) at 2.52 ppm assigned to the C$_7$ proton of the norbornene moiety. Also observed were resonances at 2.95 (2 H, bridgehead protons) and at 6.11 ppm (2 H, norbornene vinyl protons).

Irradiation of the single proton peak at 2.52 ppm resulted in simplification of the two-proton multiplet at 0.97 ppm (Figure 2) confirming the *anti* stereochemistry of this compound. This irradiation also revealed that the methyl protons are coupled to H$_7$, as the methyl resonance was also simplified by irradiation at 2.52 ppm.

To test the multiplicity of the cyclohexenone excited state which gives rise to these products, the photolysis of 2-cyclohexenone and norbornadiene was run with naphthalene (0.0492 *M*) present. The product ratio was examined by vpc (column B, 240°), and the results are given in Table I. Although this concentration of naphthalene caused a threefold retardation in reaction rate, the product distribution was not altered significantly from the reactions without naphthalene. The interpretation of this result is to be found in the Discussion.

A second experiment of mechanistic importance was the photoaddition of 3-deuterio-2-cyclohexenone[22] and norbornadiene, and examination of the 3-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (**3**) which was formed. The mass spectrum had a molecular ion of *m/e* 189 ($C_{13}H_{15}DO$). The nmr (100 Mcps) is shown in Figure 1. It can be seen that the deuterium label in this product is located in the *exo* position of the ethano bridge of the norbornene moiety, since the *exo* multiplet has area one-half of its value for the protio compound, whose nmr is also shown in Figure 1. The conclusions from this observation are also presented in the Discussion.

Discussion

The products of photoaddition of 2-cyclohexenone and 2- and 3-methyl-2-cyclohexenones with norbornadiene are shown in Charts I, II, and IV. It will be noted that three types of products are obtained in each case: (i) cyclobutane derivatives (*cis*- and *trans*-fused bicyclo[4.2.0]octan-2-ones are formed; these were expected products, and will not be considered in any detail); (ii) α-substituted 2-cyclohexenone (except from 2-methyl-2-cyclohexenone); (iii) β-substituted 2-cyclohexenones (except from 3-methyl-2-cyclohexenone). For mechanistic reasons which will become apparent later, products **7** and **9** in Chart II are considered with groups ii and iii, respectively.

Excepting the cyclobutane adducts (group i), all of these products arise by novel photochemical pathways. Our work on these structures is primarily of mechanistic interest, and this discussion will be concerned with the mechanisms of their formation.

We will deal first with the question of the multiplicity of the enone excited state which gives rise to the substituted cyclohexenones. Photochemical reactions of cyclic enones in solution, including rearrangements,[23] photoreduction,[23a] and cycloadditions[24] generally proceed *via* triplet states. Therefore, a quenching experiment was performed to determine whether all of the products in the reaction of 2-cyclohexenone and norbornadiene arise from a triplet state. This photoaddition was run in the presence of 0.0449 *M* naphthalene, a

[22] (a) The 3-deuterio-2-cyclohexenone was prepared by LiAlD$_4$ reduction of 3-ethoxy-2-cyclohexenone by the method of W. F. Gannon and H. O. House, *Org. Syn.*, **40**, 148 (1960); (b) *ibid.*, **40**, 41 (1960). (c) Deuterio **1** was also isolated. The nmr and mass spectra showed the presence of one deuterium atom in **1**, which appeared to be on a methylene bridge of the nortricyclyl moiety.

[23] (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelback, *J. Amer. Chem. Soc.*, **88**, 1965 (1966); (b) H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968).

[24] (a) P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966). (b) J. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5671 (1966); **89**, 4944 (1967). (c) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967). (d) P. de Mayo, J.-P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967). (e) P. de Mayo, J.-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968). (f) O. L. Chapman, J. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, **90**, 1657 (1968).

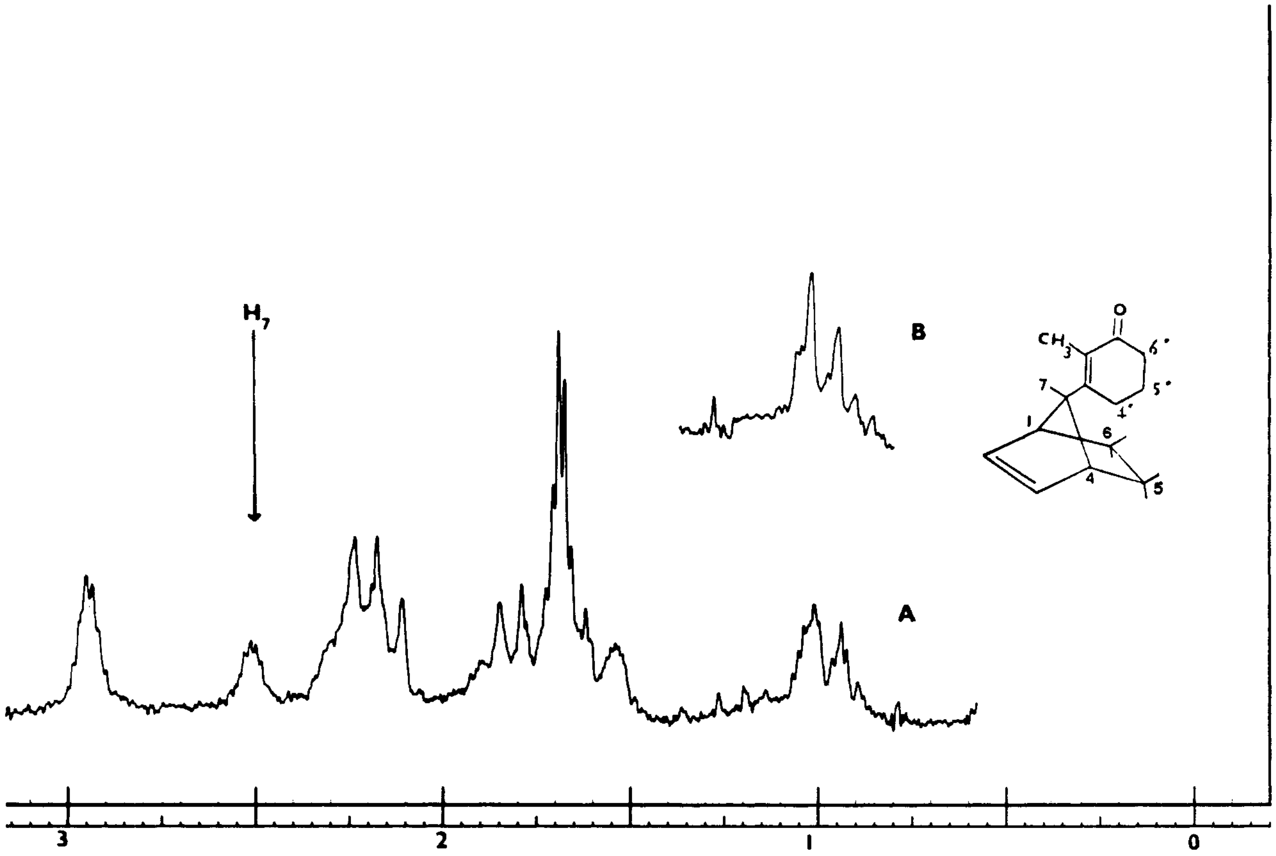


Figure 2.—Nmr spectrum of 2-methyl-3-(7-*anti*-norbornenyl)-2-cyclohexenone (12): A, normal spectrum; B, *endo*-proton multiplet when H_7 peak is irradiated.

quencher of 2-cyclohexenone triplets.[23,25] This naphthalene concentration caused a threefold retardation in rate, but no significant change in the product distribution, according to gas chromatography.[26] Since cycloadditions of 2-cyclohexenones and 2-cyclopentenone involve triplet states, our result[25] shows that the substituted cyclohexenones arise from a triplet[27] also. This might be the same species (or combination of species) which leads to the cyclobutane products, or two triplets could be involved which transfer energy to naphthalene at similar rates.

The second step in the formation of the 2-cyclohexenones and related products must involve bonding of norbornadiene to the α- and β-carbon atoms of the reacting cyclohexenone triplet. In the case of 2-cyclohexenone, which has the same substituent (hydrogen) at the α and β positions, the ratio of α- to β-substituted cyclohexenones in this addition is 4:9. It is tempting to try to correlate the predominance of β substitution with some property of the enone triplet. For example, the Hückel coefficients of π_3 (the lower antibonding MO) are -0.228 for the α and 0.657 for the β position of acroleinlike systems.[28] This orbital is singly occupied in the n–π^* and π–π^* triplets, and the larger coefficient of π_3 at the β position would give the higher odd-electron density there. If the triplet then reacts faster at the position of greater odd-electron density, the higher β coefficient is in accord with the higher amount of β-substituted products. Such interpretations are risky, however, on account of the large amount of cyclobutane adducts formed. Before the α/β ratios can be explained, it is necessary to know the relative amounts of cyclobutanes which arise from α and β bonding to the enone triplet, a figure which we cannot determine at present.

The structure of the substituent in the α- and β-substituted cyclohexenone products will now be discussed. The three addition reactions all give rise to compounds in which the substituent is either a nortricyclyl or a 7-

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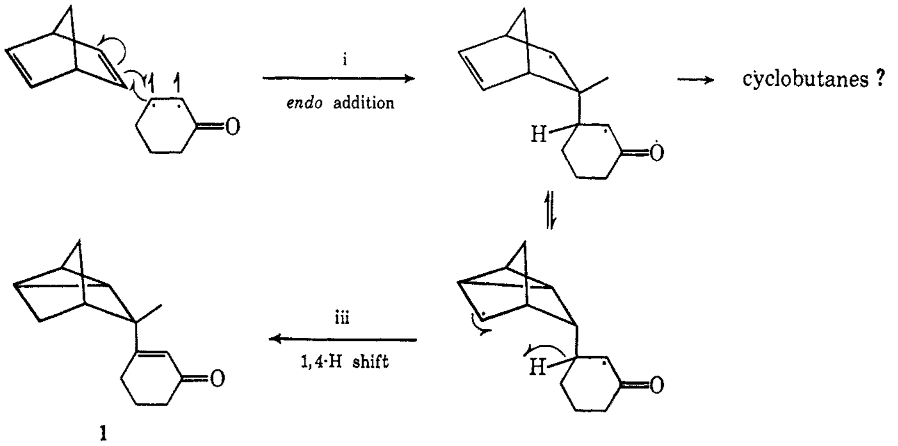
(25) Hammond, *et al.*,[24c] report that naphthalene *sensitizes* the dimerization of 2-cyclohexenone. This may be a result of singlet sensitization, since H. E. Zimmerman and J. S. Swenton [*J. Am. Chem. Soc.*, **89**, 906 (1967)] report quenching of naphthalene fluorescence by cyclohexenones.

(26) Although the product distribution was not significantly affected by naphthalene quenching according to vpc, infrared spectra showed that the *cis*- to *trans*-fused cyclobutane ratio was decreased in the quenched runs, in accord with the results of Chapman, *et al.*[24f] The change in the latter ratio on quenching may not be great enough to cause a significant difference in the enone/cyclobutane ratio, or the two proposed cyclohexenone triplets[24f] may both be involved in formation of the cyclohexenone derivatives.

(27) (a) The electronic configuration of the reacting triplet is not known at present. Excitation is to the n–π^* singlet, since a Pyrex filter was used in the reactions. Recenty reported work by H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman [*J. Amer. Chem. Soc.*, **89**, 6589 (1967)] has shown that, for ground-state geometry, the n–π^* triplet is the lowest lying excited state of conjugated enones, and should be the reactive species in solution. See, however, ref 24d–f. (b) Since it is well known that norbornadiene and quadricyclane interconvert on sensitization [see, *e.g.*, G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964)], the following possibilities for these reactions must be considered. (i) The adducts might arise by reaction of norbornadiene triplet with the enones. This seems unlikely, since the norbornadiene triplet would be required to react rapidly with the low concentration of enone, and not with the higher concentration of norbornadiene. The dimer of norbornadiene is not observed. We have quantitative results which suppport this conclusion, to be reported later. (ii) Some adducts might result from reaction of enone triplet with quadricyclane. Some of the latter is formed in the photolysis. However, when quadricyclane replaced norbornadiene in the photolysis, no adducts were formed.

(28) C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965, p 227.

CHART V



anti-norbornenyl group. Our thesis is that the nortricyclylcyclohexenones (*e.g.*, 1 and 2) are formed by initial attack of the cyclohexenone triplet from the *endo* side of the norbornadiene, while the 7-*anti*-norbornenyl derivatives (*e.g.*, 3 and 4) arise from corresponding *exo* attack. It is helpful to have structures representing the proposed intermediates before us to discuss the mechanisms. The formation of a nortricyclyl derivative is depicted in Chart V.

This proposed mechanism consists of the following steps: (i) *endo* addition of the cyclohexenone triplet, with formation of a diradical species; (ii) a bridging process, leading to the nortricyclyl system; and (iii) a hydrogen transfer, forming the product **1**.

It is obvious that initial *endo* attack of the enone triplet is necessary for intramolecular hydrogen transfer to occur in step iii. We are committed to say, then, that (at least) 26% of the addition of 2-cyclohexenone to norbornadiene occurs from the *endo* side. By analogy with free-radical additions to this diene, 26% *endo* attack is a perfectly reasonable fraction.[29]

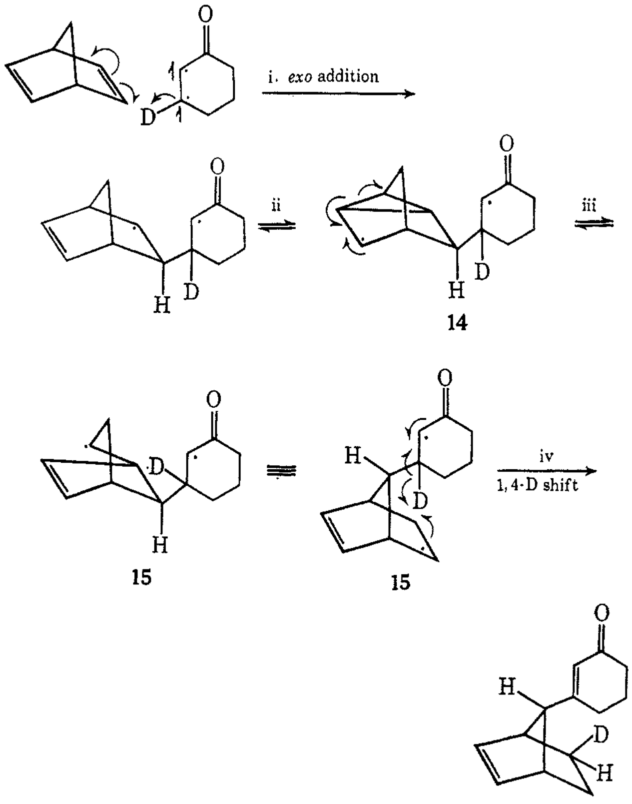
The first-formed intermediate is represented as a biradical species. An alternative zwitterionic intermediate seems unlikely since the product ratios in these additions are identical in hexane, cyclohexane, ethanol, and *t*-butyl alcohol (Table I). Also, work of Zimmerman and coworkers[30] using migratory aptitudes to probe the excited-state structure has shown that the β carbon is not electron deficient, making the zwitterion a less reasonable intermediate than the biradical species. This biradical may be analogous to the intermediates proposed by others[9a,d] as the species which cyclize to a four-membered ring.

Step ii has precedent in ground-state, free-radical chemistry in the norbornenyl–nortricyclyl radical equilibrium.[31] It is possible, however, that the bridging process, by which the nortricyclyl system is formed, and bonding to the enone triplet (*i.e.*, steps i and ii) are concerted.

The final step in the sequence leading to **1** is represented as a 1,4-hydrogen shift, which takes place from the biradical intermediate. While 1,2- and 1,3-hydrogen shifts do not occur readily in radical systems,[32] the corresponding 1,4[33] and 1,5[34] processes are known.

The proposed mechanism for the formation of a 7-*anti*-norbornenyl derivative (**3**) is shown in Chart VI.

CHART VI



exo addition of the enone triplet, followed (or accompanied) by bridging, gives an intermediate biradical (**14**) which cannot cyclize or migrate hydrogen to form a stable molecule. If, however, the three-membered ring opens as shown in step iii the intermediate **15** has a geometry which allows 1,4-hydrogen transfer with production of **3**. The effect of these transformations is to

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[29] T. V. van Auken and E. A. Rick[4e] report 17–20% *endo* attack of thiol radicals to norbornadiene. H. Kwart and J. L. Nyce [*J. Amer. Chem. Soc.*, **86**, 2601 (1964)] report 20% *endo* addition of bromine radicals to norbornene.

[30] H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967).

[31] C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966); D. I. Davies, J. N. Done, and D. H. Hey, *Chem. Commun.*, 725 (1966).

[32] For discussions, see (a) R. Kh. Freidlina in *Advan. Free Radical Chem.*, **1**, 211 (1965); (b) C. Walling in "Molecular Rearrangements," Vol. I, Interscience, New York, N. Y., 1963, p 407.

[33] H. A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, **31**, 853 (1959).

[34] D. Helmlinger and G. Ourisson, *Ann.*, **686**, 19 (1965).

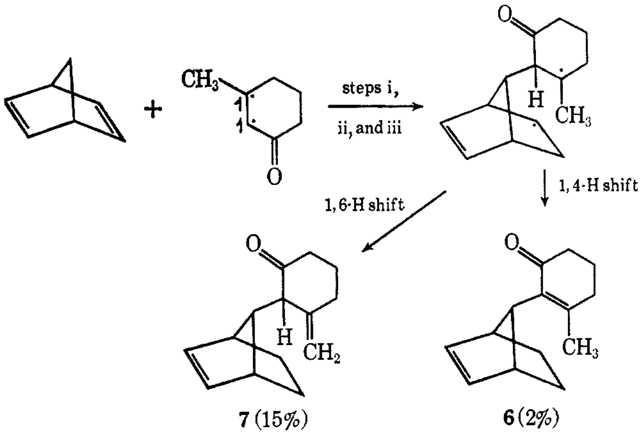
give a formal Wagner–Meerwein shift, affording the 7-*anti*-norbornenyl-2-cyclohexenones. These shifts are, of course, much better known in carbonium-ion chemistry, but at least one case of formation of 7-substituted norbornenes in a free-radical addition has been reported.[35]

The scheme of intramolecular processes shown in Chart VI predicts that the β hydrogen of reactant 2-cyclohexenone will be transferred to the *exo* side of the ethano bridge in **15**. To test this prediction, the photoaddition was carried out using 3-deuterio-2-cyclohexenone.[22a] The nmr (Figure 1) of deuterio **3** showed that the deuterium was exclusively in the *exo* position of the norbornene moiety, consistent with an intramolecular mechanism.[22c]

Sequences analogous to the mechanisms in Charts V and VI can, of course, be drawn to account for the α-nortricyclyl and α-norbornenylcyclohexenones. The reaction is initiated in these cases by attack with the α-carbon atom of the enone triplet.[36]

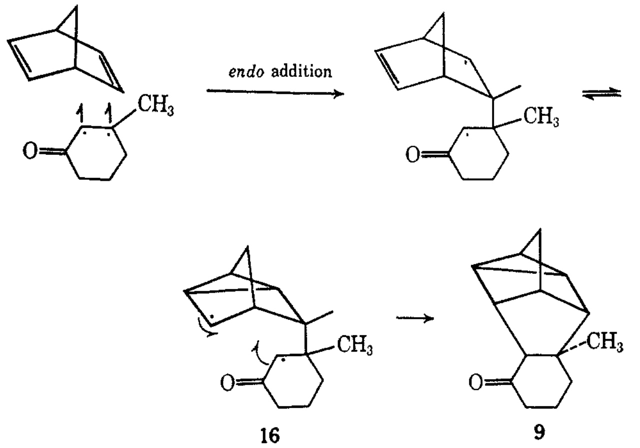
The unique products (**7** and **9**) (Chart II) which are formed in the addition of 3-methyl-2-cyclohexenone and norbornadiene are of interest. The methylenecyclohexanone (**7**) is a 7-*anti*-norbornene derivative and is almost certainly formed from the same intermediate as **6** (Chart VII). It is interesting that the 1,6 shift is apparently favored over the 1,4 process, although the transition state for the former appears less favorable in molecular models. In a control experiment, **6** was found to be quite stable to photolysis and certainly is not the precursor of **7** in the reaction.

Chart VII



Of considerable interest is the product of Diels–Alder-like addition[37] of 3-methyl-2-cyclohexenone and norbornadiene (**9**). This type of adduct was sought for but not found in the additions of 2-methyl-2-cyclohexenone and 2-cyclohexenone to norbornadiene. Its absence in the latter cases is also of interest. It probably arises in the reaction where formed by the route in Chart VIII.

Chart VIII



Attack of the enone triplet with the β-carbon atom from the *endo* side followed by bridging gives a diradical species **16** which cannot undergo the usual 1,4-hydrogen shift, but instead cyclizes to a five-membered ring.

The important question of whether or not the proposed initially formed 1,4 biradicals are intermediates[38] in the formation of the cyclobutane structures will now be considered. The possible processes which are available *a priori* to 1,4 and 1,5 biradicals are as shown in Chart IX.

Since nortricyclyl cyclohexenones are observed, and the product of cyclization to a five-membered ring is not (except in one special case), we must conclude that the 1,4-hydrogen shift is more rapid than this cyclization. In the reaction which does give rise to a cyclization product of the 1,5 biradical, formed from 3-methylcyclohexenone and norbornadiene, the 1,5 biradical is unable to undergo the 1,4-hydrogen shift (Chart VIII). If, then, 1,4 biradicals are precursors of the cyclobutane derivatives, clearly the cyclization reaction is sufficiently faster than a 1,3-hydrogen shift to exclude the latter completely; otherwise the formation of substituted 2-cyclohexenones would be common in many enone addition reactions, and 2-substituted norbornenes would be formed in the norbornadiene additions, neither of which is observed.[9]

Conclusions

The isolation of nortricyclyl- and 7-norbornenylcyclohexenones in the above addition reactions shows that the arrangement of double bonds in norbornadiene modifies the course of these reactions. The former products demand a mechanism in which one bond is formed between the reactants, followed by rearrangements and hydrogen shifts. The nortricyclyl and norbornenyl groups may be bonded to the α and β positions of the cyclohexenone. These products are best interpreted in terms of biradical-like intermediates, and the latter may be of the same type as gives rise to the well-known cyclobutane derivatives.

Experimental Section

Materials.—All solvents and reagents for photoaddition reactions were distilled before use. 2-Cyclohexenone (Aldrich

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[35] J. A. Claisse and D. I. Davies, *Chem. Commun.*, 209 (1965).

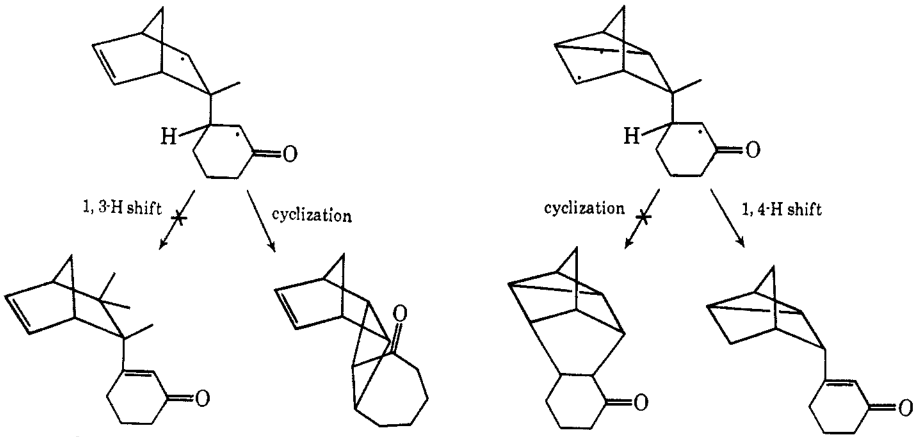
[36] The electronic structure drawn for the cyclohexenone triplet in Charts V and VI is not intended to imply that the excitation is localized in the carbon–carbon double bond; it is simply a convenient way of representing a species with "free valence" at the α- and β-carbon atoms, and has been used previously by Corey, *et al.*[9a]

[37] Orbital symmetry considerations[11] predict that a concerted photochemical addition of this type is forbidden. In view of the other structures isolated in our work, we favor a stepwise mechanism for the formation of **9**.

[38] Corey, *et al.*,[9a] and Schneider and Meinwald[9d] explained their results in terms of biradical intermediates.

CHART IX

POSSIBLE REACTIONS OF 1,4 AND 1,5 BIRADICALS



product not observed observed product product not observed observed product

reagent) had bp 61–62° (16 mm), and 3-methyl-2-cyclohexenone (Aldrich reagent) had bp 58° (10 mm). 2-Methyl-2-cyclohexenone was prepared according to "Organic Syntheses"[39] and had bp 60–66° (20 mm). Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) (Aldrich reagent) was distilled at atmospheric pressure, bp 89–90°, and was used immediately as it polymerized on standing. Hexane (Eastman practical grade) was purified by successive shaking with concentrated sulfuric acid, water, aqueous potassium permanganate, and finally water. It was then dried over calcium chloride, filtered through a 34 × 4 cm column of silica gel, and distilled, bp 66.5–67.5°. The solvent thus purified had negligible absorption above 250 mμ. *t*-Butyl alcohol was Baker Analyzed reagent, bp 82°.

All photolyses were run under nitrogen, Canadian Liquid Air, certified grade, further purified by successive passage through vanadous sulfate[40] solution and concentrated sulfuric acid and over potassium hydroxide pellets.

Column chromatography was on silica gel, Grace, grade 923 (100–200 mesh). Both analytical and preparative gas chromatography (vpc) were employed. Analytical vpc was performed on a Varian Aerograph Model 204-B, dual-column instrument, with flame-ionization detectors. The following columns were used, with helium carrier gas at 27 ml/min: column A—0.125 in. × 5 ft 10% FFAP on Chromosorb W (60–80 mesh); column B—0.125 in. × 10 ft 12% FS 1265 on Chromosorb W (60–80 mesh); column C—0.125 in. × 5 ft 10% Ucon 300X on Chromosorb W (60–70 mesh). Preparative vpc was conducted on a Varian Aerograph Model 200 instrument with thermal conductivity detector. Helium gas at 60 ml/min was used with the following columns: column D—0.375 in. × 9 ft 20% FS 1265 on Chromosorb W (60–80 mesh); column E—0.375 in. × 4 ft 25% FFAP on Chromosorb W (45–60 mesh); column F—0.375 in. × 10 ft 15% SE-30 on Chromosorb W (60–80 mesh).

Nuclear magnetic resonance (nmr) spectra were routinely run on a Varian A-60 instrument in CCl_4 or CS_2, using tetramethylsilane as internal standard, and chemical shifts are given in parts per million downfield from this standard. Spectra in which spin decoupling was required were run at 100 Mcps on a Varian HA-100 instrument.

Infrared spectra were recorded with a Beckman IR-5 instrument, and for precise measurements a Perkin-Elmer 521 spectrometer was used. Spectral grade CCl_4 or CS_2 were the solvents, depending on the region of interest in the spectrum. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer, usually Fisher "spectranalyzed *n*-hexane" was the solvent.

Mass spectra were obtained using a Hitachi Perkin-Elmer MRU 6 mass spectrometer.

Elemental analyses were by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Photoaddition of 2-Cyclohexenone and Bicyclo[2.2.1]hepta-2,5-diene.—Irradiation of 2-cyclohexenone (8.06 g, 0.84 mol) and norbornadiene (68.8 g, 0.745 mol) in hexane (400 ml), with a Hanovia type L450W lamp fitted with a Pyrex sleeve, in the usual quartz immersion apparatus, under purified nitrogen, resulted in the disappearance of 2-cyclohexenone and the appearance of reaction products.

Progress of the reaction was followed by gas chromatography (column B, 240°) and by thin layer chromatography (tlc) on Eastman Kodak T.L.C. Kit, silica gel coated sheet, K301R developed with 3% ethyl acetate–benzene, of aliquots taken at 15-min intervals. After 7 hr, gas chromatography showed that nearly all of the 2-cyclohexenone had reacted, and the solvent was removed under vacuum. Gas chromatography (column B, 240°) showed components of retention times 4.0 min (**2** and **4**, mixture according to nmr and infrared), 4.5 min (**5**), 7.2 min (**3**), and 8.2 min (**1**), as well as 2-cyclohexenone (1.3 min).

Chromatography of Photolysate.—Since several spots corresponding to the products were obtained on silica gel thin layer chromatography, 2.467 g of the above photolysis mixture were chromatographed on a 64.0 × 4.0 cm column of silica gel, slurry packed in 4% ethyl acetate–benzene; the column was eluted with 6 l. of this solvent, followed by 5 l. of 20% ethyl acetate–benzene, and 125-ml fractions were collected. Fractions 1–3 contained unidentified nonketonic material (53 mg); fractions 4–6 contained **2** and **4** (627 mg); fractions 7–16 contained components **5** (982 mg); **3** and **1** were found in fractions 17–45 (517 mg). Recovery was 2.279 g (92%).

Identification of 2 and 4.—Fractions 4–6 from the column were combined and subjected to preparative vpc (column F, 200°). Two α,β-unsaturated cyclohexenones (infrared band at 5.99 μ) were obtained. Both cyclohexenones had a proton at the β carbon (nmr signal at 6.63 ppm). One was identified as a nortricyclene derivative by the doublet at 12.40 μ in the infrared; the other had a band at 14.20 μ (norbornene double bond).[13]

Identification of Components 5.—Fractions 7–16 contained components **5**; the two carbonyl bands in the infrared (5.82 and 5.88 μ) are characteristic of *cis*- and *trans*-fused isomers[9a] of **5**. The 5.82-μ band attributed to the *trans*-fused system disappeared on attempted separation by preparative vpc at 200°, or on treatment with alumina (*cf.* ref 9a). Also consistent with structure **5** were the infrared absorption at 14.2 μ (double bond) and nmr resonance at 6.00 ppm (2 H, vinylic protons).

Identification of 3.—Components **3** and **1** were found in fractions 17–45 and were separated by vpc (column E, 240°). Compound **3** was a 2-cyclohexenone (infrared band 5.99 μ, carbonyl) and also showed a band at 14.20 μ (double bond).[13] The structure was elucidated by nmr spectroscopy (see Results and Figure 1), and **3** was thus identified as 3-(7-*anti*-bicyclo[2.2.1]-hept-2-enyl)-2-cyclohexenone.

Anal. A satisfactory analysis was obtained for the monodeuterated derivative of **3**; see below.

Identification of 1.—This compound was also purified by vpc of column fractions 17–45. The significant infrared bands were at 5.99 (carbonyl) and 12.35 μ (doublet, nortricyclene).[14] This with the nmr spectrum pointed to 3-(3-tricyclo[2.2.1.0^{2,6}]heptyl)-2-cyclohexenone, which was confirmed by synthesis as described below.

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[39] E. W. Warnhoff, D. G. Martin, and W. S. Johnson, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 162.

[40] L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

Synthesis of 1.—Nortricyclylmagnesium bromide from nortricyclyl bromide (Aldrich reagent) (5.26 g, 0.030 mol) and magnesium (0.742 g, 0.03 g-atom) in ether (20 ml) was treated with 3-ethoxy-2-cyclohexenone[22b] (4.17 g, 0.029 mol) in ether (10 ml) at 0°, according to the general procedure of Woods, *et al.*[15] Addition was complete in 10 min, and the mixture was stirred for a further 20 min and decomposed with 5% sulfuric acid. The product was isolated with ether and dried with calcium chloride. After solvent removal *in vacuo*, the product was chromatographed on a 34 × 3 cm column of silica gel to remove 3-ethoxy-2-cyclohexenone. The column was eluted with 6% ethyl acetate–benzene, and 125-ml fractions were collected. Fractions 9–12 contained the 3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone (1), 1.27 g, 23% based on nortricyclyl bromide. This material was identical with 1 from the photolysis, as shown by vpc behavior and infrared and nmr spectra.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.59. Found: C, 82.80; H, 8.72.

Photostability of 3-(3-Tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone (1).—A solution of 1 in cyclohexane (400 ml, 0.006 *M*) was photolyzed under reaction conditions for 14 hr, and the composition of the solution was monitored by vpc and infrared and ultraviolet spectroscopy. The absorption at 340 mμ had decreased slightly after this time, but no photolysis products appeared on vpc, and the infrared spectrum was unchanged.

Photoaddition of 3-Deuterio-2-cyclohexenone and Norbornadiene.—3-Deuterio-2-cyclohexenone[22a] (4.955 g, 0.0510 mol), judged 99% deuterated at the β position by nmr, and norbornadiene (36.72 g, 0.399 mol) in hexane (380 ml) were photolyzed for 5 hr through Pyrex with the Hanovia type L450W lamp. The photolysate (8.623 g) obtained on solvent evaporation was analyzed by vpc (column A, 228°) and showed the same products as the addition of 2-cyclohexenone and norbornadiene. 5-Deuterio-3-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone was isolated as described above for the protio compound. The mass spectrum had a molecular ion at *m/e* 189 ($C_{13}H_{15}DO$), and the nmr spectrum is shown in Figure 1.

Anal. Calcd for $C_{13}H_{15}DO$: C, 82.50; H + D, 9.05. Found: C, 82.53; H + D, 9.11.

Photoaddition of 3-Methyl-2-cyclohexenone and Norbornadiene.—Irradiation of 3-methyl-2-cyclohexenone (4.583 g, 0.0416 mol) and norbornadiene (50.0 g, 0.543 mol) in *t*-butyl alcohol (350 ml) and methanol (20 ml), for 3 hr as described for 2-cyclohexenone and norbornadiene, resulted in reaction of about 60% of the 3-methyl-2-cyclohexenone, estimated by infrared and vpc (column B, 231°) monitoring. After solvent distillation, the liquid residue (5.960 g) was chromatographed on a 36 × 4.0 cm column of silica gel, slurry packed in 3% ethyl acetate–benzene. The column was eluted with 5 l. of 3%, 6 l. of 5%, and 10 l. of 15% ethyl acetate–benzene, and 200-ml fractions were collected. The fractions were monitored by infrared and nmr spectra, and by vpc on the Ucon column C at 195°, on which all of the products of interest had different retention times. Fractions 10–12 contained a single product—7 (retention time 12.4 min) (688 mg); fractions 13–15 (1.045 g) contained five products—7 (12.4 min), 17 (18.0 min), 9 (19.6 min), 6 (21.4 min), and 8 (24.4 min). Fractions 16 and 17 were compound 18 (19.0 min, 474 mg). Fractions 18–60 were a mixture of *cis*- and *trans*-fused cyclobutanes (1.090 g) which were not investigated in detail, and 3-methyl-2-cyclohexenone (1.619 g) was eluted in the latter fractions). Recovery from the column was 4.916 g (84%). From the vpc analyses of these fractions, an estimate of the yields of products (6–9) could be made. These yields are given below for each component along with its characterization.

Isolation and Identification of 7.—The yield (15%) was also measured by vpc of the reaction mixture on column B at 230°. Preparative vpc of fractions 10–12 (column E, 245°) afforded pure 7, retention time 11 min. The spectral data showed that the compound was a cyclohexanone, and contained a vinyl methylene group and a norbornene double bond. The ultraviolet spectrum showed enhanced n-π* absorption, $\lambda_{\max}^{\text{hexane}}$ 300 mμ (ε 103), suggesting a β,γ-unsaturated ketone. The mass spectrum had a molecular ion of *m/e* 202, and all of the data pointed to 3-methylene-2-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)cyclohexanone.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.22; H, 8.86.

This structure was confirmed by the isomerization of 7 to 6, the conjugated isomer which was identified by degradation.

Base-Catalyzed Isomerization of 7 to 6.—The *exo*-methylene ketone 7 (0.786 g, 0.00388 mol) was stirred with sodium hydroxide (0.494 g, 0.0124 mol) in dioxane (150 ml) and water (60 ml) under nitrogen for 52 hr at 25°. The solution was ether extracted (four 50-ml portions); the extracts were washed with water (eight 50-ml portions) and dried ($MgSO_4$). Evaporation of the ether gave 0.500 g (64%) of a 2-cyclohexenone (infrared band at 5.99 μ), identified with component 6 of the photolysis by vpc on column C at 200°, retention time 19.6 min. The latter was not isolated from the photolysis, since it was only formed in 2% yield. The spectral data (see Results) were obtained on material from the isomerization of 7, and the structure assigned to 6 therefore that of is 3-methyl-2-(7-*anti*-bicyclo[2.2.1]hept-2-enyl-2-cyclohexenone.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.99; H, 8.97.

Photostability of 6.—The conjugated enone (6, 141 mg), from isomerization of the *exo*-methylene ketone 7 in hexane (54 ml), was irradiated with the Hanovia 450-W lamp for 5.5 hr. Gas chromatography (column C, 195°) did not show any peaks other than 6, retention time 23 min. Evaporation of the hexane afforded a quantitative recovery of 6, characterized by infrared and nmr spectroscopy.

Diimide Reduction[18] of 3-Methyl-2-(7-*anti*-bicyclo[2.2.1]hept-2-enyl-2-cyclohexenone (6).—Compound 6 (0.500 g, 0.00247 mol) and the dipotassium salt of azodicarboxylic acid (0.800 g, 0.00412 mol) in methanol (30 ml) were stirred under nitrogen while glacial acetic acid was added dropwise until all the solid salt had dissolved. Saturated $NaHCO_3$ solution (40 ml) was added, and the solution was extracted with ether (three 25-ml portions) and the extracts were dried ($MgSO_4$). Evaporation of the ether afforded 0.450 g (90%) of liquid which gave one peak on column B at 228°, was a cyclohexenone (infrared band at 5.99 μ), and had no vinylic protons (nmr spectrum). The mass spectrum had a molecular ion, *m/e* 204, consistent with the structure of 3-methyl-2-(7-bicyclo[2.2.1]heptyl)-2-cyclohexenone.

Oxidative Degradation of 3-Methyl-2-(7-bicyclo[2.2.1]heptyl)-2-cyclohexenone.—To a mixture of 7-norbornylcyclohexenone from the diimide reduction (0.450 g, 0.00221 mol), potassium carbonate (0.452 g, 0.00328 mol) dissolved in 13 ml of water, 48 ml of *t*-butyl alcohol–water azeotrope, 8 ml of a solution of sodium metaperiodate (3.23 g) in water (40 ml), and 8 ml of 0.8% aqueous potassium permanganate were added; then a further 33 ml of the above periodate solution was added at the rate of 1.8 ml/min for 10 min, then 0.5 ml/min for 30 min.

Sodium metabisulfite solution was then added, until the solution turned from red to brown, then a slight excess was added, and the solution was concentrated under reduced pressure to about 30 ml, cooled to 4°, and acidified with ice-cold 50% sulfuric acid (40 ml). The solution was ether extracted (four 25-ml portions); the extracts were washed with sodium metabisulfite, then with water, and dried ($MgSO_4$). The oily residue was subjected to liquid–liquid partition chromatography[41] on a column 3 × 55 cm slurry packed in pentane with 83.3 g of Mallinckrodt silicic acid and 16.7 g of Eagle–Picher Celatom, which had been coated with a mixture of 8.5 ml of water, 40 ml of methanol, 7.5 drops of 1 *N* ammonia, and 5 ml of bromocresol green solution (0.200 g/25 ml of methanol); 125-ml fractions were collected; and pentane eluted an acid, mp 56–64°, found in fractions 3 and 4. This was sublimed twice at atmospheric pressure to afford waxy white crystals, mp 74.0–75.0° (lit.[19b] mp 75–76.5°). The acid was identical with an authentic sample of 7-norbornanecarboxylic acid[20] by infrared, nmr, and mixture melting point.

Identification of 17.—Fraction 13 of the above column was subjected to vpc, column B at 245° (retention time 17 min). This infrared had bands at 5.90 and 14.20 μ (norbornene), consistent with a *cis*-fused cyclobutane adduct of norbornene and 3-methyl-2-cyclohexenone.

Identification of 9.—The infrared and nmr spectra of fractions 14 and 15 suggested that these might contain a nortricyclic adduct having a cyclohexanone carbonyl, which would correspond to structure 9, Chart II. The following oxidation procedure was employed to remove unsaturated compounds. A mixture containing 57% 9 (640 mg) in 30 ml of *t*-butyl alcohol–water azeotrope was added to K_2CO_3 (278 mg) in water (70 ml) with stirring. This was followed by the addition of 5 ml of a solution of sodium metaperiodate (2.0 g) in water (25 ml) and 2.0 ml of 0.8% aqueous potassium permanganate. A further 10 ml of periodate solution was added over 10 min, followed by 7.0 ml over 20 min.

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(41) W. A. Neville, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962).

Further additions of the permanganate solution were made—1 ml was added after 2 min, then six 0.5-ml portions were added at 5 min intervals. Stirring was continued for 3 hr, excess bisulphite solution was added, and the solution was concentrated to half-volume *in vacuo;* it was cooled in ice, neutralized with cold 50% H_2SO_4, and extracted with ether. The extracts were washed with $NaHCO_3$ solution and water, then with 5% NaOH solution and again with water, and dried ($CaSO_4$). Evaporation of the ether gave **9** (160 mg), retention time 21 min on column C at 195°. The infrared had peaks at 5.90 (cyclohexanone carbonyl) and at 12.35 μ (nortricyclene doublet). The nmr showed a methyl signal at 1.02 ppm and no absorption downfield of 2.50 ppm. The mass spectrum had a molecular ion of *m/e* 202, and an analytical sample was obtained by preparative vpc (column E, 227°). The yield of **9** is estimated at 16%, and the assigned structure is that of 9-methylpentacyclo[7.4.0.$0^{2,7}$.$0^{3,5}$.$0^{4,8}$]tridecan-13-one.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.10; H, 8.87.

Identification of 8.—Fraction 13 from chromatography of the photolysis mixture was subjected to preparative vpc (column E, 235°). A peak (**8**) of retention time 18 min was collected and had a methyl peak at 2.07 ppm in the nmr and no vinylic protons. The infrared bands were at 6.00 (conjugated carbonyl) and 12.37 μ (nortricyclene). Product **8** is thus identified as **3-methyl-2-(3-tricyclo[2.2.1.0^{36}]heptyl)-2-cyclohexenone** and was formed in 8% yield in the photolysis.

Identification of 18.—Fractions 16 and 17 of the chromatography had *cis*- and *trans*-fused cyclobutanes with carbonyl bands at 5.86 and 5.91 μ and one of these was purified by gas chromatography. A peak of retention time 18 min on column E at 235° was collected. From the latter part of this peak an adduct was isolated which gave a molecular ion of *m/e* 202 and had infrared absorption at 5.91 (carbonyl, *cis*-fused system) and at 14.12 μ (norbornene). The adduct is identified as a *cis*-fused cyclobutane adduct of 3-methylcyclohexenone and norbornadiene and further stereochemical details are unspecified.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.19; H, 8.95.

Photoaddition of 2-Methyl-2-cyclohexenone and Norbornadiene.—2-Methyl-2-cyclohexenone (2.327 g, 0.0211 mol) and norbornadiene (19.854 g, 0.2155 mol) in *t*-butyl alcohol (375 ml) and methanol (20 ml) were photolyzed for 8 hr under the usual conditions. Monitoring by gas chromatography (column B, 245°) showed peaks of retention times 2.8 min (**13**), 6.9 min (**12**), and 7.9 min (**11**). Also observed were several peaks of retention times between 3.8 and 4.6 min and these components were not investigated in detail. The vpc analysis also showed that 75% of starting enone had reacted. The infrared spectra of aliquots had carbonyl bands at 5.80, 5.90, and 5.99 μ. The mixture remaining after solvent evaporation was chromatographed on a 36 × 4.0 cm column of silica gel, slurry packed in 2% ethyl acetate–benzene. The column was eluted with 6 l. of 2%, 1.5 l. of 3%, 2.5 l. of 4%, and 2 l. of 15% ethyl acetate–benzene, 200-ml fractions being collected. Fractions 12–17 (1.145 g) contained the components with retention times of 3.8–4.6 min, and these had infrared absorption at 5.90 μ (*cis*-fused cyclobutanes) except for fraction 12 which was mainly the 2.8-min compound (**13**). Fractions 18–60 (688 mg) contained **12** and **11**. Recovery from the column was 1.833 g.

Identification of 13.—Fraction 12 of the above column was separated by preparative vpc (column E, 245°) to afford **13**, which had infrared carbonyl absorption at 5.80, typical of *trans*-fused cyclobutane adducts of 2-cyclohexenones and alkenes, and absorption at 14.2 μ (norbornene double bond). This product was formed in 5% yield in the photolysis.

Identification of 12.—Fractions 20–28 were resolved by preparative vpc (column E, 245°). Compound **12** was collected (retention time 36 min); this had infrared bands at 5.99 (conjugated carbonyl) and at 14.20 μ (norbornene). The nmr spectrum is discussed in Results and is shown in Figure 2. From these spectra the structure assigned to **12** is that of **2-methyl-3-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone.**

Identification of 11.—Fractions 36–44 contained **11**, which was purified by preparative vpc on column A at 245° (retention time 40 min). The infrared showed unsaturated carbonyl absorption at 5.99 and a nortricyclene band at 12.37 μ. The nmr was similar to that of other nortricyclenes which we have characterized in this work. The spectra suggested that this product (**11**), which constituted 14% of the photolysis products, was **2-methyl-3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone,** and this structure was confirmed by the synthesis outlined in Results.

2-Methyl-3-ethoxy-2-cyclohexenone.—This was prepared by a modification of the method of Gannon and House.[22b] A mixture of 2-methyl-1,3-cyclohexanedione (Aldrich) (24.82 g, 0.197 mol), *p*-toluenesulfonic acid monohydrate (1.035 g, 0.00544 mol), absolute ethanol (115 ml), and benzene (400 ml) were heated for 10 hr so that the benzene–water–ethanol azeotrope distilled at 67–70° during this time. The volume of the mixture was half of the original volume after 10 hr, and the mixture was extracted as described for 3-ethoxy-2-cyclohexenone.[22b] The dried ether solution was evaporated, and the following crystallization procedure was conducted in a drybox, under dry nitrogen. To the solid residue from the ether evaporation was added hexane (300 ml), and the solid was dissolved by warming. The solution deposited white crystals on cooling which were filtered, mp 58.5–59.5°, 11.75 g. A second and third crop (total 6.85 g) of yellow crystals were obtained from the filtrate; these had mp 56–59°. The total yield was 18.60 g (61%). The infrared showed two peaks in the carbonyl region at 6.05 and 6.18 μ, which are also shown by 3-ethoxy-cyclohexanone. The nmr spectrum was also consistent with the structure of **2-methyl-3-ethoxy-2-cyclohexenone.**

Anal. Calcd for $C_8H_{12}O_2$: C, 70.10; H, 9.15. Found: C, 70.26; H, 9.25.

The crystals were very hygroscopic and liquified rapidly in the air of the laboratory.

Synthesis of 11.—The Grignard reagent from nortricyclyl bromide (Aldrich) (8.572 g, 0.0495 mol) and magnesium (1.227 g, 0.0505 g-atom) in ether (30 ml) was prepared by the procedure of Woods, *et al.*,[15] but the reaction was run in a drybox under nitrogen. To the Grignard reagent cooled to 0° was added 2-methyl-3-ethoxy-2-cyclohexenone (7.735 g, 0.0502 mol) in ether (45 ml); the addition required 15 min; and the mixture was stirred. The stirring was continued for a further 30 min, and the solution was allowed to reach ambient temperature. After decomposition with 5% H_2SO_4, the ether solution was separated, washed with water, and dried ($CaSO_4$). The ether was evaporated to yield 7.62 g of oil, which was chromatographed on a 3 × 44 cm column of silica gel, slurry packed in 6% ethyl acetate–benzene, and eluted with this solvent, and 200-ml fractions were collected. Fractions 3–7 contained **11**, 1.10 g (11%), judged pure by vpc on column C at 195°, and identical with the photolytic product **11** by infrared and nmr spectra. Product **11** is therefore identified as 2-methyl-3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.21; H, 8.90.

Registry No.—Norbornadiene, 121-46-0; **3**, 20678-85-7; **4**, 20678-86-8; **5**, 14478-12-7; **6**, 20678-87-9; **7**, 20678-89-1; **12**, 20678-90-4; 5-deuterio-3-(7-*anti*-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexanone, 20678-88-0; 2-methyl-3-ethoxy-2-cyclohexenone, 20643-20-3.

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