Cyclohexane.—A solution of ethyl propiolate (2.10 g, 20.5 mmol) and recrystallized dibenzoyl peroxide (485 mg, 2.0 mmol) in cyclohexane (30 ml) was refluxed under a slight positive pressure of nitrogen for 24 hr in a glass apparatus which had been dried under nitrogen at 110° prior to use. At the end of this time the solution gave a negative test for peroxides. The cyclohexane and ethyl propiolate were removed by evaporation at reduced pressure and left a residue (705 mg) which comprised 55% **2** and 45% **3** according to gas chromatographic analysis.

A reaction run under the same conditions containing only 0.1 mmol of peroxide for 12 hr gave less than 1% yield of products. A blank reaction, with no peroxide, gave no products.

Irradiation of 1-Hexyne in 2-Propanol.—A solution of 1-hexyne (20.8 g, 0.254 mol) in 2-propanol (460 ml) was irradiated for 3 days at an average bath temperature of 14°. The unreacted starting materials were removed by distillation at 100-mm pressure and the residue was distilled at 30-mm pressure to yield 5.9 g of a colorless liquid boiling at 80–85°. Gas chromatographic analysis of the product showed four components in a ratio 17:27:35:21, later identified as **18**, **19**, **16**, and **17**, respectively. The original distillate was redistilled at atmospheric pressure and yielded 13.3 g of 1-hexyne. Compounds **18** and **19** were readily separated from **16** and **17** by gas chromatography. Compounds **18** and **19** were, however, inseparable and were investigated as a mixture. Alcohol **16** was obtained pure by gas chromatography but the best separation left **17** containing approximately 10% **16**.

Alcohol **16** had a gas chromatographic retention time and an infrared spectrum identical with those of 2-hydroxy-2-methyl-*trans*-3-octene[30] which was prepared from 2-hydroxy-2-methyl-3-octyne[31] in a single step. Compound **17** had a gas chromatographic retention time and an infrared spectrum identical with those of 2-hydroxy-2-methyl-*cis*-3-octene, prepared by hydrogenation of the corresponding alkyne[31] over a Lindlar catalyst.

The mixture of ethers **18** and **19** had infrared absorption maxima at 1670, 1455, 1445 (shoulder), 1370, 1355, 1160 (shoulder), 1150, 1120, 1095, 1035, 1010, 990, 975, 950, 880 and 850 cm^{-1}. The nmr spectrum of the mixture was analyzed carefully considering the relative percentages of the two compounds present, and was fully assignable on this basis.

Cleavage of Ethers 18 and 19.—Following the procedure of Underwood, *et al.*,[20] a 3,5-dinitrobenzoate was isolated which had mp 121.5–122.5° and a mixture melting point with an authentic sample of the 3,5-dinitrobenzoate of 2-propanol of 121–122.5°.

Hydrogenolysis of Ethers 18 and 19.—A solution of the mixture of ethers (0.51 g, 2.8 mmol) in ether (25 ml) was hydrogenated over Pd-C catalyst (50 mg) at 0° and atmospheric pressure. When hydrogen uptake was complete (35 min) the solution was filtered free of catalyst and concentrated to a volume of *ca.* 2 ml by careful distillation. Gas chromatogaphic analysis indicated the presence of two products with retention times corresponding to those of 2-propanol and 2-methyloctane. The latter (0.16 g) was isolated by gas chromatography and shown to be identical with an authentic sample prepared from 2-hydroxy-2-methyl-3-octene[31] by dehydration and hydrogenation.

Registry No.—**1**, 623-47-2; **2**, 17343-88-3; **3**, 18521-02-3; **4**, 18559-89-2; **6**, 591-11-7; **7**, 539-88-8; **8**, 10150-92-2; **9**, 10150-93-3; **11**, 18521-05-6; **16**, 18521-06-7; **17**, 18521-07-8; **18**, 18521-08-9; **19**, 18542-61-5.

Acknowledgments.—The authors are indebted to the National Institutes of Health for financial support and to Dr. I. D. Rae for his help with the preparation of the manuscript.

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[30] K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **63**, 216 (1941).

[31] K. N. Campbell, B. K. Campbell, and L. T. Eby, *ibid.*, **60**, 2882 (1938).

Cycloadditions. XXIII. The Mercury-Sensitized Gas Phase Photodecarbonylation of 3,3-Dideuterio- and *exo*- and *endo*-3-Deuterionorcamphor[1,2]

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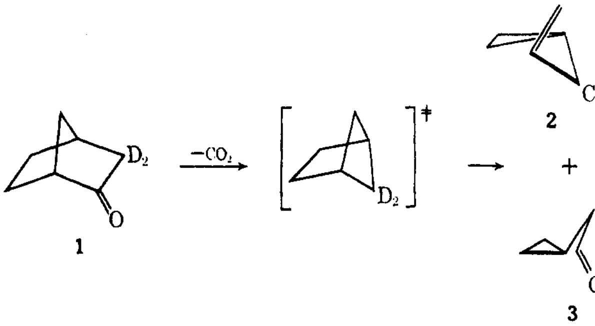
The mercury-sensitized gas phase photodecarbonylation of 3,3-dideuterionorcamphor gave 1,1- and 3,3-dideuteriohexa-1,5-diene in a 90:10 ratio; (3,3-dideuterioallyl)- and (1,1-dideuterioallyl)cyclopropane and allyldideuteriocyclopropane in a 45:45:10 ratio; and 5,5-dideuterio- and 2,2-dideuteriobicyclo[2.1.1]hexane in a 93:7 ratio. Photodecarbonylation of *exo*- and *endo*-3-deuterionorcamphor gave quantitatively analogous data; equal portions of *exo*- and *endo*-5-deuteriobicyclo[2.1.1]hexane and the same ratio of *cis*- and *trans*-1-deuteriohexa-1,5-diene were formed from either labeled ketone. These results are interpreted in terms of the known kinetics of the decarbonylation, diradical intermediates as precursors of the hydrocarbon products, and a Cope rearrangement that competes with collisional deactivation of the 1,5-hexadiene produced through the decarbonylation process.

The mercury-sensitized gas phase photolysis of 3,3-dideuterionorcamphor (**1**) has been reported[5] to give a 1:1 mixture of (3,3-dideuterioallyl)cyclopropane (**3**) and (1,1-dideuterioallyl)cyclopropane (**2**) (Scheme I). This result was taken as necessitating a symmetrical intermediate and was rationalized by postulating the production of allylcyclopropane through decomposition of a vibrationally excited, photochemically generated bicyclo[2.1.1]hexane. The other hydrocarbons reported were 1,1-dideuteriohexa-1,5-diene and 5,5-dideuteriobicyclo[2.1.1]hexane.[5]

SCHEME I



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[1] Papers XXI and XXII in this series: J. A. Kapecki and J. E. Baldwin, *J. Amer. Chem. Soc.*, **91**, 1120 (1969); J. E. Baldwin and S. Y. Hong, *J. Heterocycl. Chem.*, **5**, 565 (1968).

[2] Supported in part by National Science Foundation, Grant GP-5226, and a Du Pont Grant-in-Aid to the Department of Chemistry and Chemical Engineering of the University of Illinois.

[3] Alfred P. Sloan Research Fellow. To whom inquiries should be addressed: Department of Chemistry, University of Oregon, Eugene, Ore. 97403.

[4] Eli Lilly and Co. Fellow, 1964–1965; Allied Chemical Fellow, 1965–1966; Standard Oil of California Fellow, 1966–1967.

[5] R. Srinivasan, *J. Amer. Chem. Soc.*, **83**, 4923 (1961).

More recent kinetic evidence has established that allylcyclopropane stems from a secondary mercury-sensitized reaction of 1,5-hexadiene and is not a primary photoproduct.[6]

To resolve the possible ambiguity between the isotopic labeling results and their interpretation, and the kinetic facts, the labeling work has been confirmed and extended. Both types of evidence lead to a compatible description of the photocarbonylation process and secondary reactions.

Results

3,3-Dideuterionorcamphor was prepared from norcamphor through exchange with deuterium oxide in the presence of deuteriotrifluoroacetic acid at 130° for 8.5 days. When the same reaction was carried out at 23° for 22 hr, only one proton was exchanged. Previous work has indicated that the 3-*exo* proton in such ketones is preferentially exchanged;[7-10] the monodeuterio product obtained was accordingly formulated as *exo*-3-deuterionorcamphor. Partial exchange of the dideuterated ketone gave *endo*-3-deuterionorcamphor. Mass spectrometric data for the three ketones are given in Table I.

TABLE I
MASS SPECTROMETRIC DEUTERIUM ANALYSES FOR LABELED NORCAMPHOR

Label	Isotopic Distribution, %				Hydrogens per molecule
	d_0	d_1	d_2	d_3	
3,3-Dideuterio	0.1	9.8	90.1		8.10
endo-3-Deuterio	7.3	89.8	3.1	1.1	9.01
exo-3-Deuterio	8.9	82.4	8.0	0.6	9.01

The labeled norcamphor derivatives were photolyzed in the presence of mercury vapor and the products were isolated. Microanalytical analyses (Table II) for 3,3-dideuterionorcamphor and the three major photodecarbonylation products were in good agreement, indicating that no significant amount of intermolecular hydrogen or deuterium exchange accompanied the reaction.[11] The values for total deuterium in 3,3-dideuterionorcamphor obtained by mass spectrometry (Table I) and microanalysis (Table II), 8.10 and 8.01 hydrogens per molecule, corresponded within the combined experimental uncertainties of the two analytical methods.

TABLE II
MICROANALYTICAL DEUTERIUM ANALYSES FOR 3,3-DIDEUTERIONORCAMPHOR AND ITS DECARBONYLATION PRODUCTS

Dideuterated compd	Excess atom % deuterium	Hydrogens per molecule
Norcamphor	19.85	8.01
1,5-Hexadiene	19.55	8.05
Allylcyclopropane	19.50	8.05
Bicyclo[2.1.1]hexane	19.75	8.03

Proton nmr spectroscopic analyses for the hydrocarbons derived from 3,3-dideuterionorcamphor and for the undeuterated analogs are given in Table III. The integrated intensities for the hydrocarbons were scaled to 8.05 hydrogens per molecule (*cf.* Table II). The ═CH— absorption band, a broad complex multiplet, proved difficult to integrate reproducibly; the assumption that no deuterium label migrated to this location in the 1,5-hexadiene or allylcyclopropane was made and later verified through deuterium nmr spectroscopy.

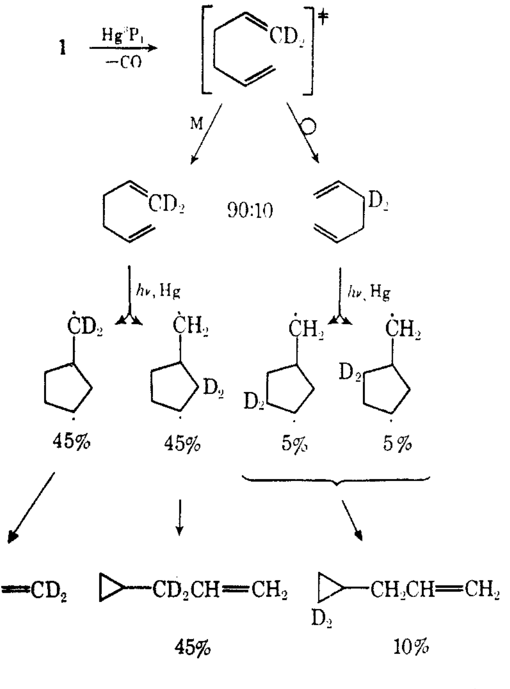
The three major hydrocarbon products from the photolysis of *exo*- and *endo*-3-deuterionorcamphor were isolated by preparative glpc and analyzed by deuterium nmr spectroscopy at 100 MHz; the results are summarized in Table IV. The deuterium nmr spectra of the bicyclo[2.1.1]hexane products and the protium nmr spectra of the olefinic region of the 1,5-hexadiene products are presented in Figures 1 and 2, respectively.

Discussion

The data of Table III from the photolysis of dideuterated norcamphor are in qualitative agreement with the results reported earlier.[5] The major products are 1,1-dideuterio-1,5-hexadiene, 5,5-dideuteriobicyclo[2.1.1]hexane, and a 1:1 mixture of (3,3-dideuterioallyl)- and (1,1-dideuterioallyl)cyclopropane. The quantitative agreement between experimental observations and relative integrated absorption intensities calculated by assuming that these are the only labeled products is, however, not satisfactory.

The results seem to require and may be easily accommodated through the rationale shown in Scheme II. Since the photoreactions are initiated by the 113-kcal mercury triplet and a molecule of carbon monoxide is evolved in the process, the decarbonylation products must initially possess considerable vibrational energy. At the low pressures of these experiments, a thermal

SCHEME II



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(6) (a) J. E. Baldwin and J. E. Gano, *Tetrahedron Lett.*, 2099 (1967); (b) *J. Org. Chem.*, **32**, 3506 (1967).

(7) A. F. Thomas and B. Willhalm, *Tetrahedron Lett.*, 1309 (1965).

(8) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

(9) H. C. Brown, *Chem. Brit.*, 199 (1966), and references cited therein.

(10) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 68 (1967).

(11) The norcamphor recovered from the decarbonylation reaction showed some loss of label (8.17 hydrogens per molecule by mass spectrometry); presumably, adventitious exchange occurred during the work-up and isolation of the ketone.

Table III
Relative Areas of Proton Nmr Resonance Absorptions in Hydrocarbons from Decarbonylation of 3,3-Dideuterionorcamphor

Compd	Type	Type of hydrogen				
		CH_2=	$-CH_2-$	$-CH_2-$ and *exo*-**H** on one-carbon bridge[a]	*endo*-**H** on one-carbon bridge	Cyclopropyl
1,5-Hexadiene	Unlabeled					
	Theory	4.00	4.00			
	Observed	4.00	4.00			
	Labeled					
	Theory I[b]	2.05	4.00			
	Theory II[c]	2.24	3.81			
	Observed	2.24	3.81			
Bicyclo[2.1.1]hexane	Unlabeled					
	Theory			6.00	2.00	
	Observed			6.01	1.99	
	Labeled					
	Theory I[a]			5.02	1.02	
	Theory II[c]			4.92	1.12	
	Observed			4.96	1.09	
Allylcyclopropane	Unlabeled					
	Theory	2.00	2.00			5.00
	Observed	1.99	2.00			5.01
	Labeled					
	Theory I[b]	1.02	1.02			5.00
	Theory II[c]	1.12	1.12			4.81
	Observed	1.11	1.11			4.83

[a] The *exo*-proton absorption is known to be superimposed upon the two-carbon bridge absorption [J. Meinwald and Y. C. Meinwald, *Advan. Alicyclic Chem.*, 1, 15 (1966)]. [b] Theory I is based on Scheme I from ref 5. [c] Theory II is given in Scheme II and the text.

Table IV
Relative Intensities of Deuterium Nmr Absorptions in Hydrocarbons from Decarbonylation of *exo*- and *endo*-3-Deuterionorcamphor[a]

Compd	Type	Type of deuterium				
		DCH=	-CHD-	-CHD- and *exo*-D on one-carbon bridge[b]	*endo*-D on one-carbon bridge	Cyclopropyl
1,5-Hexadiene	Observed					
	From *exo*	0.91	0.09			
	From *endo*	0.91	0.09			
	Calculated[c]	0.90	0.10			
Bicyclo[2.1.1]hexane	Observed					
	From *exo*			0.50	0.50	
	From *endo*			0.51	0.49	
	Calculated[c]			0.50	0.50	
Allylcyclopropane	Observed					
	From *exo*	0.42	0.47			0.12
	From *endo*	0.46	0.46			0.08
	Calculated[c]	0.45	0.45			0.10

[a] Taken with solutions in carbon tetrachloride at 15.381 MHz. [b] The *exo*-proton absorption is known to be superimposed upon the two-carbon bridge absorption (*cf.* footnote *a* of Table III). [c] According to the assumptions incorporated into Scheme II.

Cope rearrangement of vibrationally excited 1,1-dideuterio-1,5-hexadiene may compete successfully 10% of the time with collisional deactivation, giving 1,1-dideuterio- and 3,3-dideuterio-1,5-hexadiene in a 90:10 ratio (Scheme II).

Kinetic investigation of the mercury-sensitized photodecarbonylation of norcamphor demonstrated[6] that bicyclo[2.1.1]hexane was a primary product and also formed in a secondary process through isomerization of 1,5-hexadiene. An independent study of the mercury-sensitized photolysis of 1,5-hexadiene showed bicyclo[2.1.1]hexane to be a major volatile product.[12] The observed distribution of deuterium atoms in the bicyclo[2.1.1]hexane derived from 3,3-dideuterionorcamphor (Table III) reflects the two routes by which it is formed: more than 0% but less than 10% of the deuterium label resides on C-2 and C-3, since part of the hydrocarbon stems from norcamphor directly and part from the 90:10 mixture of 1,1- and 3,3-dideuterio-1,5-hexadiene.

Allylcyclopropane, which is now known to form exclusively from the secondary photolysis of 1,5-hexadiene,[7,12] is labeled with the two deuterium atoms at the CH_2=, $-CH_2-$, and cyclopropyl **H** positions in a 45:45:10 ratio. That allylcyclopropane does not form from vibrationally excited bicyclo[2.1.1]hexane is supported by the fact that the thermolysis of bicyclo[2.1.1]hexane gives 1,5-hexadiene exclusively.[13] Instead, the precursor for allylcyclopropane is probably the 3-cyclopentylmethyl diradical derived from the

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[12] R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).

[13] R. Srinivasan and A. A. Levi, *J. Amer. Chem. Soc.*, **85**, 3363 (1963).

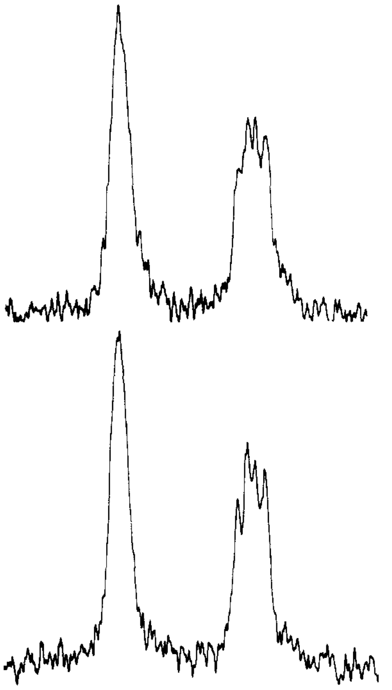


Figure 1.—Deuterium nmr spectra of monodeuteriobicyclo-[2.1.1]hexanes from *endo*-3-deuterio- (top) and *exo*-3-deuterionorcamphor (bottom) at 15.381 MHz. The magnetic field increases from left to right. The downfield absorption is the *exo*-deuterium superimposed on the absorption of any deuteriums on the two-carbon bridge. The upfield absorption is the *endo*-deuterium.

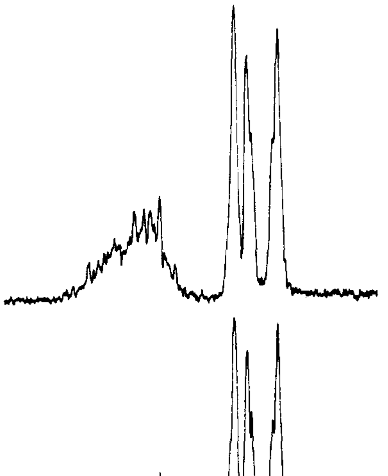


Figure 2.—Proton nmr spectra of the monodeuteriohexa-1,5-dienes from *endo*-3-deuterio- (top) and *exo*-3-deuterionorcamphor (bottom) in the olefinic region at 60 MHz. The magnetic field increases from left to right.

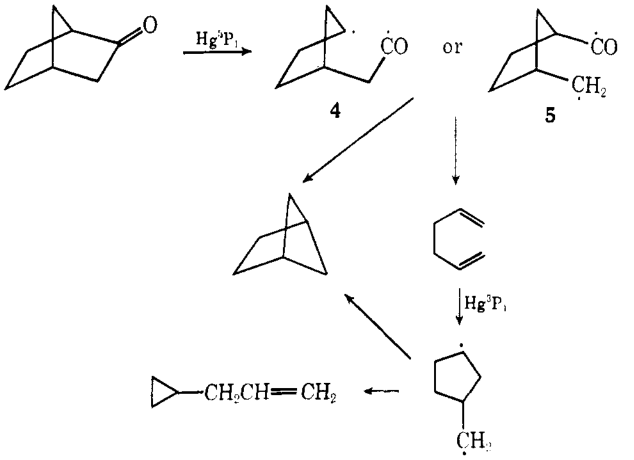
secondary photoisomerization of 1,5-hexadiene. This intermediate has been suggested before[14] and, in addition, analogous intermediates have been implicated in similar cases.[15]

The mercury-sensitized photolysis of *exo*- and *endo*-3-deuterionorcamphor provided a quantitative confirmation of the results obtained with 3,3-dideuterionorcamphor and rationalized through the sequence of events outlined in Scheme II. No absorptions for =CD– deuterions were detected in the hexadiene or allylcyclopropane samples, thus confirming that the photodecarbonylation and secondary photoreactions do not involve hydrogen or deuterium migrations.

The nmr spectra of the hydrocarbons derived from the two monodeuterated norcamphors also demonstrated that the primary photoproducts, 1,5-hexadiene and bicyclo[2.1.1]hexane, are formed with complete loss of stereochemical integrity: both *exo*- and *endo*-3-deuterionorcamphor gave identical mixtures of *cis*- and *trans*-1-deuterio-1,5-hexadiene and *exo*- and *endo*-5-deuteriobicyclo[2.1.1]hexane (Figures 1 and 2).

These results and kinetic data for the mercury-sensitized decarbonylation of norcamphor may be dovetailed neatly through mechanistic Scheme III.

Scheme III



Initial cleavage of a single bond gives an acylalkyl diradical (**4** or **5**) which produces bicyclo[2.1.1]hexane and 1,5-hexadiene as carbon monoxide is lost. Mercury-sensitized photoisomerization of 1,5-hexadiene leads through the 3-cyclopentylmethyl diradical to the formation of bicyclo[2.1.1]hexane and allylcyclopropane. (Scheme III does not reillustrate the Cope rearrangement of vibrationally excited 1,5-hexadiene covered in Scheme II.)

This interpretation corresponds with the second of the two mechanistic schemes outlined in less detailed form earlier and shown to be consistent with the observed kinetics of the decarbonylation.[6b]

Either (or both) diradical **4** or **5** would be consistent with available evidence. The high energy of the system following excitation by the mercury triplet could be held responsible for the totally nonstereoselective collapse of **4** as carbon monoxide is expelled, while a lifetime for **5** comparable with or longer than characteristic times for molecular vibrations ($\sim 10^{-14}$ sec) would allow it to obliterate stereochemical memory for the *exo* and *endo* protons (or deuterons).

The lack of stereochemical specificity observed in this work and in other nonsensitized gas phase photodecarbonylations of saturated ketones[16-18] contrasts strikingly with the great stereoselectivity observed for

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[14] G. J. Fonken, *Org. Photochem.*, **1**, 210 (1967).

[15] (a) M. Brown, *J. Org. Chem.*, **33**, 162 (1968); (b) R. Srinivasan, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P89.

[16] B. Rickborn, R. L. Alumbaugh, and G. O. Pritchard, *Chem. Ind.* (London), 1951 (1964).

[17] R. L. Alumbaugh, G. O. Pritchard, and B. J. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

[18] H. M. Frey, *Chem. Ind.* (London), 947 (1966).

photoisomerizations of such ketones in solution. Norcamphor gives (2-cyclopentenyl)ethanal but not (3-cyclopentenyl)ethanal,[19,20] formally through a selective abstraction of the *syn*-7-H from diradical **4** in preference to the *endo*-6-H. Carvonecamphor is photoisomerized in methanol to an aldoketene intermediate which in turn is converted into the corresponding ester. Only the α-*exo*-H is abstracted intramolecularly as the ketene forms.[21] Photolysis of bicyclo[5.2.1]decan-10-one in pentane gives products derived from octamethyleneketene but no unsaturated aldehyde.[22] The reported facile and stereoselective conversions in solution of *l*-thujone and other ketones having special structural features[23] may be considered as exceptional cases.[24]

Experimental Section

Mass spectra were secured by Mr. J. A. Wrona with an Atlas CH-4 instrument. Preparative-scale chromatographic separations were carried out on Aerograph 90-P and 90-P3 instruments. Deuterium analyses were determined by Mr. J. Nemeth, Urbana, Ill. Analytical, mass spectral, and nmr data for the deuterium-labeled compounds are summarized in the tables.

3,3-Dideuterionorcamphor.—Deuterium oxide (34.6 g, 1.98 mol) was cautiously transferred to a 1.6-cm i.d. by 50-cm combustion tube containing 3.95 g (0.036 mol) of redistilled norcamphor and 41.6 g (0.198 mol) of trifluoroacetic anhydride. The tube was sealed, heated at 130° for 8.5 days, cooled, and opened; its contents were cautiously neutralized with anhydrous potassium carbonate and extracted with pentane. The combined extracts were dried over magnesium sulfate, filtered, and carefully concentrated by slow distillation. Sublimation of the residue at 90° gave 2.62 g (65%) of material. Analysis of the two major sublimation fractions by glpc showed them to be 98+% norcamphor.

***exo*-3-Deuterionorcamphor.**—A solution containing 1.73 g of redistilled norcamphor, 2.83 ml of deuterium oxide, and 11.9 ml of deuteriotrifluoroacetic acid was sealed in a dry combustion tube, heated at 83 ± 1° for 22 hr, cooled, and transferred to a separatory funnel. The reaction mixture was saturated with potassium bicarbonate and extracted four times with pentane. The combined extracts were dried over sodium sulfate, filtered, and concentrated cautiously. The solid residue was sublimed to give 0.93 g (53%) of colorless product.

***endo*-3-Deuterionorcamphor.**—A solution containing 1.16 g of 3,3-dideuterionorcamphor, 1.99 ml of water, and 8.97 ml of trifluoroacetic acid was subjected to the reaction conditions (83 ± 1° for 20 hr) and work-up as described directly above. The colorless sublimed product weighed 0.62 g (54%).

Gas Phase Photolysis of 3,3-Dideuterionorcamphor.—The mercury-sensitized gas phase photolysis of 1.34 g of 3,3-dideuterionorcamphor in a reaction vessel previously dried for 3 hr at 10^{-4} mm was carried out as described in detail for the unlabeled ketone.[6b] Flash distillation of the photolyzate gave 0.282 g of clear colorless liquid from which samples of deuterium-labeled 1,5-hexadiene, bicyclo[2.1.1]hexane, and allylcyclopropane were obtained through preparative glpc. Control experiments showed no deuterium exchange occurred during chromatography of the hydrocarbons. The recovered norcamphor was purified by sublimation.

Solutions of 0.045 ml of hydrocarbon in 0.20 ml of carbon tetrachloride were used in determining nmr and infrared spectra for these three products.[6b] The spectral solutions were rechromatographed to provide pure samples of the hydrocarbons for microanalytical deuterium determinations.

Gas Phase Photolysis of *exo*- and *endo*-3-Deuterionorcamphor.—*exo*- and *endo*-3-deuterionorcamphor (458 and 525 mg, respectively) were separately photolyzed and the three major hydrocarbons were isolated as previously described.[6b]

Registry No.—**1**, 18153-61-2; *exo*-3-deuterionorcamphor, 18139-04-3; *endo*-3-deuterionorcamphor, 18139-05-4.

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(19) Reference 6b, note 10.

(20) But camphor does give the *endo*-6-H abstraction product, α-campholenic aldehyde; G. Ciamician and P. Silber, *Ber.*, **43**, 1340 (1910); R. Srinivasan, *J. Amer. Chem. Soc.*, **81**, 2604 (1959); see also W. C. Agosta and D. K. Herron, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P164.

(21) J. Meinwald, R. A. Schneider, and A. F. Thomas, *J. Amer. Chem. Soc.*, **89**, 70 (1967).

(22) C. D. Gutsche and J. W. Baum, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P163; *J. Amer. Chem. Soc.*, **90**, 5862 (1968). We thank Professor Gutsche for making available to us a preprint of the full paper on this work.

(23) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966), and references therein.

(24) *Cf.* J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966).

The *cis–exo* Addition of Isothiocyanic Acid to Norbornenes. Synthesis and Isomeric Configuration of the Herbicide Norea

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Isothiocyanic acid (HNCS) adds predominantly *cis* and *exo* to six norbornenes studied, producing norbornyl isothiocyanates in good to excellent yields. This *cis–exo* addition of HNCS to *endo*-dicyclopentadiene is utilized to prepare *exo*-5-isothiocyano-5,6-dihydro-*endo*-dicyclopentadiene, an intermediate used in the synthesis of the herbicide norea. Norea, which is predominantly *exo*-5-(3,3-dimethylureido)tetrahydro-*endo*-dicyclopentadiene, is prepared from the isothiocyanate in three steps: (1) the isothiocyanate is allowed to react with dimethylamine; (2) the resulting thiourea is converted into the corresponding urea by phosgenolysis and hydrolysis; and (3) the urea is catalytically hydrogenated to norea. Nonpolar media and moderate temperatures favor the *cis–exo* addition of isothiocyanic acid to *endo*-dicyclopentadiene.

The mode of addition of isothiocyanic acid (HNCS) to norbornenes was determined as part of our research on norea, a selective agricultural herbicide, and some of its analogs.[1] Under favorable reaction conditions, HNCS adds to six norbornenes *cis* and *exo* predominantly, producing norbornyl isothiocyanates in good to excellent yields without rearrangement of the norbornane ring structure.

Although the additions of many acidic reagents to norbornenes have been investigated, the addition of isothiocyanic acid has received relatively little attention. Moreover, those results reported on the additions of HNCS to norbornenes are not in agreement. Bruson and Riener, first to report an addition of this

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(1) (a) Norea is the common name and Herban is the registered trademark for 3-(hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylurea. (b) G. A. Buntin and W. R. Diveley (to Hercules, Inc.), U. S. Patent 3,304,167 (Feb 14, 1967).