(0.432 g, 0.008 mole) was added to a solution of the tosylhydrazone (0.597 g, 0.00152 mole) in dry tetrahydrofuran (15 ml, distilled from lithium aluminum hydride) and the mixture was heated to reflux with an infrared bulb. The solution turned brick red and a copious amount of fluffy precipitate formed. The solvent was evaporated and the beige solid residue was kept under vacuum ($\leq$0.1 mm) at 25° for 3 hr. All operations were conducted in a nitrogen atmosphere. Nitrogen was bled back into the flask which was connected by means of a glass tube to a dry ice–isopropyl alcohol-cooled trap which was attached to a eudiometer tube. The dry tosylhydrazone salt was slowly (*ca.* 1 hr) heated with an oil bath to 160° at which time nitrogen ceased to evolve and the nitrogen volume produced represented 100% reaction. The dry reaction products were washed out with distilled water and extracted into ether to give an orange solution which was examined by infrared and nmr.

The reaction products could not be separated by vpc on Tide (9 ft, 30–60 mesh Chromosorb P); 5% SE-30 (5 ft, 60–80 mesh Chromosorb W; 10% diisodecylphthalate (10 ft, 70–80 mesh Chromosorb W; 5% Apiezon-L (5 ft); 10% Polar Ucon (8 ft, 60–80 mesh Chromosorb W; 15% tris(cyanoethoxy)propane (15 ft, 60–80 Chromosorb W); 6.5% E-600 (5 ft, 60–80 mesh Chromosorb P); 20% DEGS (20 ft, 60–80 mesh Chromosorb W); 20% Carbowax 20M (10 ft, 45–60 mesh Chromosorb P); 10% D. C. Silicone Grease; and activated cocoanut charcoal (4 ft, 6–14 mesh). Nmr analysis of the product mixture is described in the section on tosylhydrazone salt decomposition.

Decomposition of α-Phenylisobutyrophenone Tosylhydrazone (1a) in Ethylene Glycol.—A slurry of the tosylhydrazone (0.620 g, 0.00158 mole) in ethylene glycol (10 ml, redistilled) was stirred with sodium methoxide (0.432 g, 0.008 mole) and heated with an infrared lamp until the mixture became homogeneous. The solution was then heated in an oil bath at 161° until nitrogen evolution ceased, was cooled, then poured into 80 ml of distilled water, and extracted with ether.

The infrared spectrum from the yellow oil residue from the ether extract showed significant absorptions at 3580, 3400, 3100–2870, 1670 (w), 1600, 1490, 1450, 1370, 1100, 1050, and 1025 cm^{-1}.

The nmr spectrum showed an upfield singlet at 8.23 (product **2a**) but no absorption which corresponded to **3a** or **4a**.

Aprotic Decomposition of α-(*p*-Tolyl)isobutyrophenone Tosylhydrazone (1b).—The procedure previously described led to a mixture of compounds, the nmr analysis of which is described in the section on tosylhydrazone salt decomposition.

Decomposition of α-(*p*-Tolyl)isobutyrophenone Tosylhydrazone (1b) in Ethylene Glycol.—The solution of the salt was heated to a final temperature of 195°, cooled, and worked up in the manner previously indicated.

The infrared spectrum of the yellow oil showed absorptions at 3580, 3400, 3060–2860, 1670 (s), 1600 (w), 1580 (w), 1500, 1480, 1460, 1440, 1380, 1360, 1250, 1110, 1090, 1045, and 1018, 970, and 900 (w) cm^{-1}.

The nmr spectrum showed upfield singlets at 8.20 and 7.70 (product **2b**), but no absorptions characteristic of **3b** or **4b**.

Aprotic Decomposition of α-(*m*-Chlorophenyl)isobutyrophenone Tosylhydrazone (1c).—The dried sodium salt of the tosylhydrazone was heated to a final temperature of 195° as previously described. Analysis of the nmr spectrum is described in the section on tosylhydrazone salt decomposition.

Decomposition of α-(*m*-Chlorophenyl)isobutyrophenone Tosylhydrazone (1c) in Ethylene Glycol.—A solution of the salt was heated to a final temperature of 185° and worked up in the manner previously indicated.

The infrared spectrum of the yellow oil residue showed absorptions at 3400 (br), 3080–2870, 1670 (s), 1600, 1570, 1490 (sh), 1460, 1440, 1410, 1380, 1360, 1220, 1165, 1150, 1110, 1090, 1075, 1040, 1025 (sh), 1010 (w), 1000, 970 (s), 905, and 875 cm^{-1}. The nmr spectrum showed an upfield singlet at 8.22 (product **2c**), but no absorptions which corresponded to **3c** or **4c**.

Registry No.—**1a**, 14161-61-6; α-phenylisobutyrophenone, 13740-70-0; 4-methyldeoxybenzoin, 2430-99-1; **1b**, 14161-64-9; α-(*p*-tolyl)isobutyrophenone, 14271-33-1; **1c**, 14161-65-0; α-(*m*-chlorophenyl)isobutyrophenone, 14161-66-1; **2a**, 781-33-9; **2b**, 14161-67-2; **2c**, 14161-68-3; **3a**, 782-06-9; **3b** (*cis*), 14161-70-7; **3b** (*trans*), 14161-71-8; **3c** (*cis*), 14161-87-6; **3c** (*trans*), 14161-88-7; **4a** (*cis*), 14161-72-9; **4a** (*trans*), 14161-73-0; **4b** (*cis*), 14161-74-1; **4b** (*trans*), 14161-75-2; **5**, 14161-76-3; α-methylstilbene, 779-51-1; 1,3-diphenylbutane, 1520-44-1; 3,5-diphenyl-5-methyl-Δ^2-pyrazoline, 14161-79-6; α-phenylpropionitrile, 1823-91-2; α-phenylpropionic acid, 492-37-5; α-phenyl-*p*-methylpropiophenone, 14161-82-1; *p*-methyl-β-methylcinnamic acid, 14271-34-2; 1-benzoyl-2-(*p*-tolyl)propene, 14161-83-2; 3-phenyl-5-methyl-5-*p*-tolyl-Δ^2-pyrazoline, 14409-83-7; α-(*m*-chlorophenyl)propionitrile, 14271-35-3; α-(*m*-chlorophenyl)propionic acid, 14161-84-3; α-(*m*-chlorophenyl)propiophenone, 14161-85-4; 2-phenyl-3-(3-chlorophenyl)-1-butene, 14161-86-5.

Cycloadditions. XV. The Mercury-Sensitized Gas Phase Photodecarbonylation of Norcamphor[1,2]

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The mercury-sensitized gas phase photodecarbonylation of norcamphor gave as primary products 1,5-hexadiene and bicyclo[2.1.1]hexane. In important secondary photochemical reactions, 1,5-hexadiene was converted into bicyclo[2.1.1]hexane and allylcyclopropane. Concentration *vs.* time data for norcamphor, carbon monoxide, and these three hydrocarbons provided the distinctions between primary and secondary processes; the experimental curves were well-matched by plots generated by an analog computor programmed for an appropriate mechanistic scheme. Photolysis of bicyclo[2.1.1]hexane did not give substantial amounts of isomeric hydrocarbons. Photolysis of (2-cyclopentenyl)ethanal gave cyclohexene as the major product.

Although the direct, unsensitized photodecarbonylation of norcamphor in the gas phase gives 1,5-hexadiene and bicyclo[2.1.1]hexane,[5] the mercury-sensitized gas phase photodecarbonylation has been reported[6] to give at least three *primary* products, 1,5-hexadiene, bicyclo[2.1.1]hexane, and allylcyclopropane. The formation of allylcyclopropane from norcamphor in a primary process has been repeatedly cited in the re-

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[1] A preliminary account of this work has appeared: J. E. Baldwin and J. E. Gano, *Tetrahedron Letters*, 2099 (1967).

[2] Supported in part by the National Science Foundation (Grant No. 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.

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

[5] R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2590 (1961).

[6] R. Srinivasan, *ibid.*, **83**, 4923 (1961).

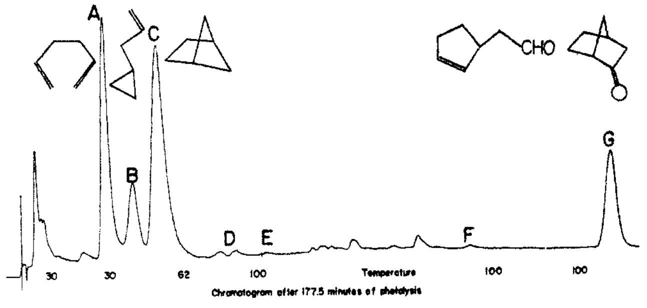

Figure 1.—A typical chromatogram of the norcamphor photolysate.

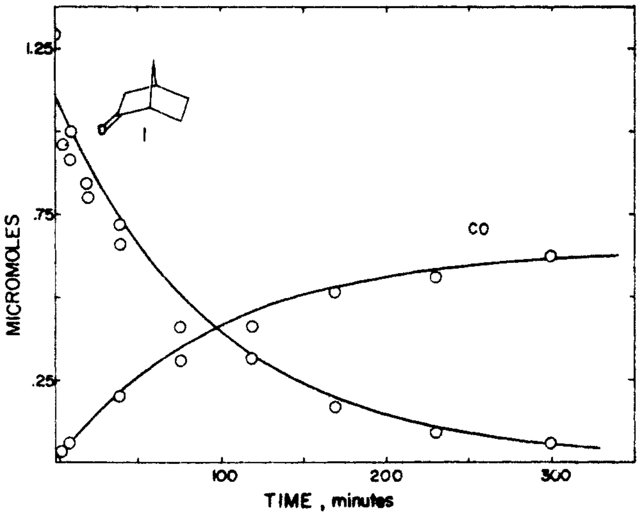

Figure 2.—Concentrations of norcamphor and carbon monoxide during the mercury-sensitized gas phase photolysis of norcamphor at 30°.

view literature as an interesting example of the mechanistic complexities which may be involved in mercury-sensitized photoreactions.[7-9]

We have followed the mercury-sensitized gas phase photolysis of norcamphor quantitatively; the experimental results indicate the only significant primary photochemical decarbonylation products are 1,5-hexadiene and bicyclo[2.1.1]hexane.

Results

The reported[6] identities and physical properties of the three major volatile hydrocarbon photoproducts from the mercury-sensitized gas phase photolysis of norcamphor were confirmed. Large-scale photolyses were carried out in 2-l. Vycor flasks; the products were purified by preparative glpc.

For the kinetic runs, small samples of purified norcamphor were quantitatively transferred on a vacuum line and sealed into Vycor tubes each containing 1 drop of mercury. The tubes were irradiated with 2537-A light and the entire contents were analyzed by glpc. A typical chromatogram of the norcamphor photolyzate is presented in Figure 1. The analytical results for a 15-tube run are shown in Figures 2–5.

After execution of a preliminary run and the first

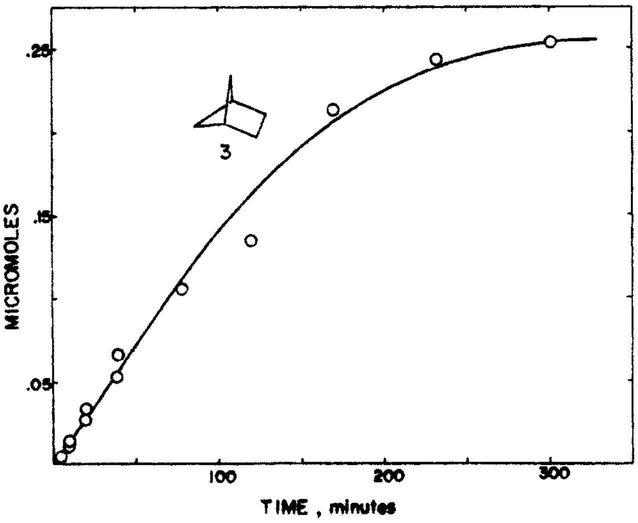

Figure 3.—Concentration of bicyclo[2.1.1]hexane during the photolyses shown in Figure 2.

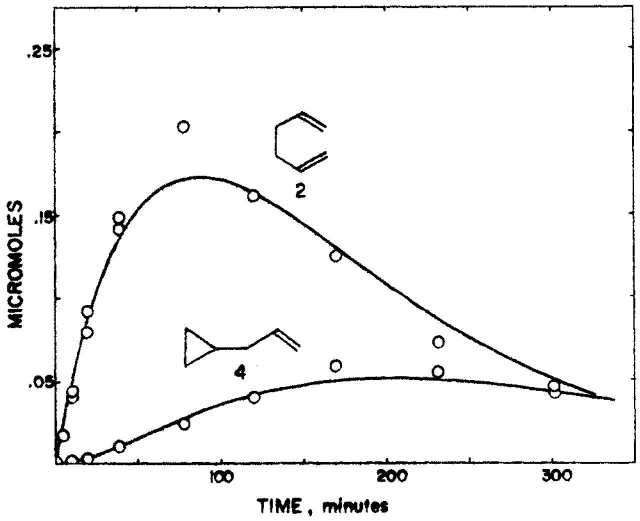

Figure 4.—Concentration of 1,5-hexadiene and allylcyclopropane during the photolyses shown in Figure 2.

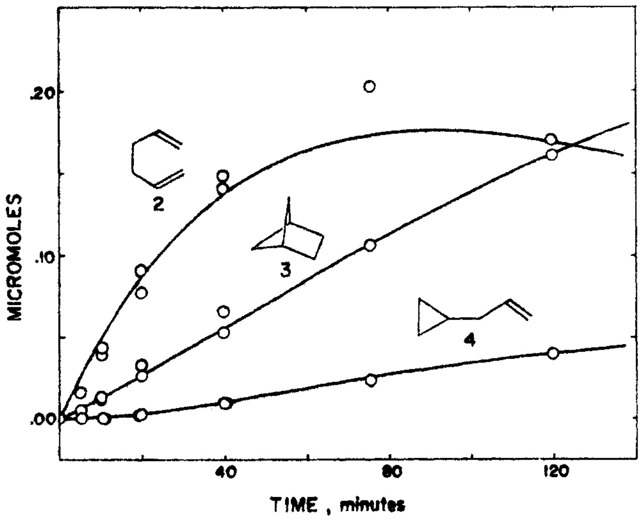

Figure 5.—Data from Figures 3 and 4 expanded about the origin.

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[7] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 108–109.

[8] R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., New York, N. Y., 1966, pp 76–77.

[9] R. Srinivasan, *Advan. Photochem.*, 1, 103 (1963).

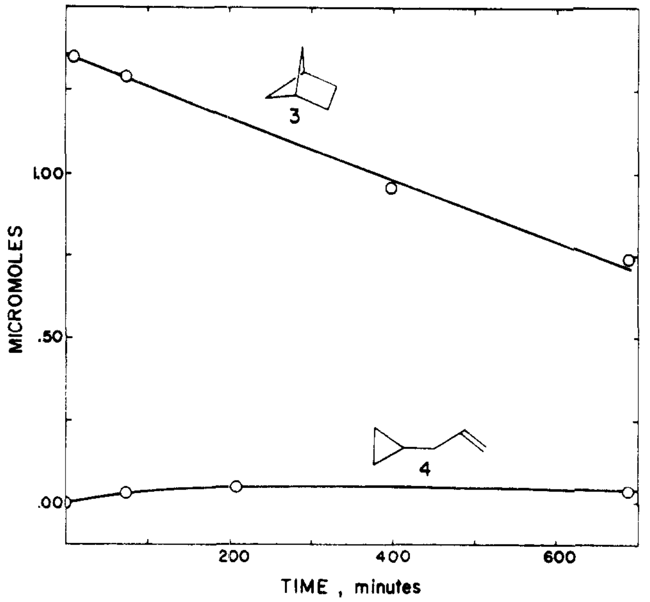
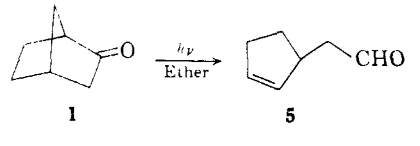


Figure 6.—Concentration of reactant and a product during the mercury-sensitized gas phase photolysis of bicyclo[2.1.1]-hexane at 30°. The allylcyclopropane was identified only by its retention time. Two other products in similar quantities were observed.

complete kinetic run, both of which gave similar results, the apparatus was totally dismantled and moved to a new location. A second kinetic run was carried out on the reassembled apparatus and the same results were obtained. The small quantitative deviations which were observed were shown on the analogue computer to be consistent with a slightly larger initial concentration of norcamphor and a slightly higher light intensity caused by a reorientation of the light source when the apparatus was reassembled.

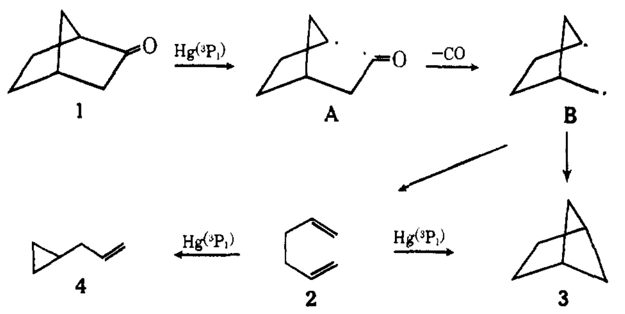
Figure 6 shows the change in concentration of reactants and a typical product during the mercury-sensitized gas phase photolysis of bicyclo[2.1.1]hexane under the same conditions. The preparative-scale photolysis of (2-cyclopentenyl)ethanal (**5**), the major product from the direct photolysis of norcamphor in ether and a minor product of the mercury-sensitized gas phase reaction, gave cyclohexene.[10]



Discussion

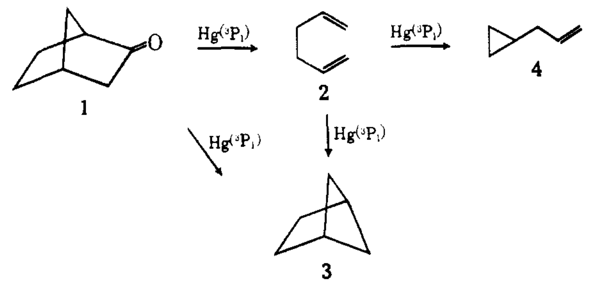
Currently available precedent and the new experimental data now reported for the photolysis of norcamphor are compatible with the following mechanistic schemes. Photoexcitation of ground-state mercury atoms [Hg ($^1S_0$)] by 2537-A light gives excited mercury atoms [Hg ($^3P_1$)] which can emit light or transfer energy to norcamphor. Next, either the excited norcamphor undergoes an α cleavage to produce the diradical A; decarbonylation of A gives a hydrocarbon diradical B which collapses to form bicyclo[2.1.1]hexane or opens to give 1,5-hexadiene (Scheme I); or

SCHEME I



bicyclo[2.1.1]hexane and 1,5-hexadiene are formed by two completely independent reactions of photoexcited norcamphor (Scheme II). Equations 1–11 correspond to these two schemes.

SCHEME II



$$\mathrm{Hg}\ (^1S_0) + h\nu(2537\ \mathrm{A}) \xrightarrow{I_a\Phi} \mathrm{Hg}\ (^3P_1) \qquad (1)$$

$$\mathrm{Hg}\ (^3P_1) \xrightarrow{k_2} \mathrm{Hg}\ (^1S_0) + h\nu(2537\ \mathrm{A}) \qquad (2)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{1} \xrightarrow{k_{2a}} \mathrm{Hg}\ (^1S_0) + \mathrm{CO} + \mathrm{B} \qquad (2a)$$

$$\mathrm{B} \xrightarrow{k_{2b}} \mathbf{2} \qquad (2b)$$

$$\mathrm{B} \xrightarrow{k_{2c}} \mathbf{3} \qquad (2c)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{1} \xrightarrow{k_3} \mathrm{Hg}\ (^1S_0) + \mathrm{CO} + \mathbf{2} \qquad (3)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{1} \xrightarrow{k_4} \mathrm{Hg}\ (^1S_0) + \mathrm{CO} + \mathbf{3} \qquad (4)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{1} \xrightarrow{k_5} \mathrm{Hg}\ (^1S_0) + \mathbf{NV} \qquad (5)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{2} \xrightarrow{k_6} \mathrm{Hg}\ (^1S_0) + \mathbf{3} \qquad (6)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{2} \xrightarrow{k_7} \mathrm{Hg}\ (^1S_0) + \mathbf{4} \qquad (7)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{2} \xrightarrow{k_8} \mathrm{Hg}\ (^1S_0) + \mathbf{NV} \qquad (8)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{3} \xrightarrow{k_9} \mathrm{Hg}\ (^1S_0) + \mathbf{NV} \qquad (9)$$

$$\mathrm{Hg}\ (^3P_1) + \mathbf{4} \xrightarrow{k_{10}} \mathrm{Hg}\ (^1S_0) + \mathbf{NV} \qquad (10)$$

$$\mathrm{Hg}\ (^3P_1) + \mathrm{CO} \xrightarrow{k_{11}} \mathrm{Hg}\ (^1S_0) + \mathrm{CO} \qquad (11)$$

In these schemes, I_a represents the intensity of the absorbed light and **NV** stands for minor or undetected nonvolatile products. Although the presence of carbon monoxide should promote the formation of Hg

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[10] The solution phase photochemical conversion of norcamphor to an isomeric aldehyde has been observed independently and first identified as (2-cyclopentenyl)ethanal by Professor O. L. Chapman and co-workers at Iowa State University. In our preliminary communication,[1] this aldehyde was mistakenly said to be (3-cyclopentenyl)ethanal. The photoproduct has since been oxidized with silver oxide to 2-cyclopentene-1-acetic acid, identical with an authentic sample obtained from Aldrich Chemical Co. The commercial acid has been transformed into the aldehyde through reduction of the corresponding acid chloride with lithium tri-*t*-butoxyaluminum hydride at −70°; the aldehyde so produced was spectroscopically identical with the photoaldehyde.

($^3P_0$) atoms,[11] nothing was observed which would require the inclusion of Hg ($^3P_0$) sensitized reactions.

By making the steady-state approximation with respect to Hg ($^3P_1$) atoms and the diradical B, differential equations corresponding to Schemes I and II (eq 1–11) were derived for the rate of change of the concentrations of norcamphor (**1**), carbon monoxide, 1,5-hexadiene (**2**), bicyclo[2.1.1]hexane (**3**), and allylcyclopropane (**4**) as a function of the time of irradiation. Both suggested schemes and a more complex treatment, including the steady-state approximations of the excited states of **1**, **2**, and **4**, gave equations having the same general form, $dX/dt = \Sigma_i a_i C_i/D$; the a_i are combinations of rate constants k, the C_i are concentrations of **1**, **2**, **3**, CO, and **4**, and D is a sum of concentration–rate constant products plus k_2. A modified Pace-31R analog computer, programmed for these differential equations, gave the curves drawn in Figures 2–5. As is required, the number of independent parameters used to fit the curves was eleven, equaling the number of independent rate constants plus the I_a term. The experimental data could be matched equally well by the computer-generated plots based on equations of the form $dX/dt = \Sigma_i a_i C_i$, appropriate to the assumption that the concentration of Hg ($^3P_1$) atoms was constant. The congruences between experimental and computer-generated concentration *vs.* time dependences shown in Figures 2–5 demonstrate the compatibility of the schemes developed with experimental fact. Other schemes, of course, could also be advanced that would fit the data; no unique aptness of the suggested mechanistic schemes may be claimed.

The rates of formation of 1,5-hexadiene, carbon monoxide, and bicyclo[2.1.1]hexane during the initial stages of reaction (Figures 2, 3, 4 and 5) show them to be primary products (eq 2a, 2b, and 2c, or 3 and 4). The data and computer generated plot for bicyclo[2.1.1]hexane show no significant decrease in rate of formation during the first 30 min, while the norcamphor concentration falls and the rate of formation of 1,5-hexadiene diminishes markedly; this behavior suggests a photoreaction converting the diene into bicyclo[2.1.1]hexane. Indeed, the sensitized excitation of 1,5-hexadiene has been shown to lead to bicyclo[2.1.1]hexane and some bicyclo[2.2.0]hexane.[12,13]

If allylcyclopropane arose directly from norcamphor, the rate of formation should be a maximum initially and decrease with time. The initial rate of formation of allylcyclopropane is zero at zero reaction time (Figure 5), and increases with the increase in the concentration of 1,5-hexadiene (Figure 4). Only minute amounts of allylcyclopropane accumulate during the mercury sensitized photolysis of bicyclo[2.1.1]hexane (Figure 6): therefore, the only major pathway for the formation of allylcyclopropane under the reaction conditions is through photoisomerization of 1,5-hexadiene (eq 7) in a secondary process.

Experimental results have just been reported which indicate an analogous situation exists in the photolysis of bicyclo[2.1.1]hexan-2-one.[14] The mercury-sensitized gas phase photodecarbonylation of this ketone gave bicyclo[1.1.1]pentane, 1,4-pentadiene, bicyclo[2.1.0]pentane, and vinylcyclopropane. It was suggested that the latter two compounds were not primary products but were instead formed in the mercury-sensitized photolysis of 1,4-pentadiene.

Carbon monoxide concentration plotted against the total concentration of hydrocarbons **2**, **3**, and **4** gives a straight line bisecting the first quadrant up to 68% conversion of the ketone, showing an excellent material balance for the decarbonylation products. Since the carbon monoxide only accounts for 50% of the photolyzed norcamphor, another main reaction pathway leading to oxygen-containing products must exist. Continued photolysis leads to the disappearance of all hydrocarbon products observable by our analytical method. This is consistent with the formation of nonvolatile materials, as observed in the preparative-scale photolysis.

Conclusions

The results from this investigation, providing quantitative concentration *vs.* time data for norcamphor and the products resulting from its mercury-sensitized photolysis in the gas phase, demonstrate that allylcyclopropane originates from a secondary photoisomerization of 1,5-hexadiene rather than from norcamphor directly; bicyclo[2.1.1]hexane is formed both from norcamphor and from a secondary isomerization of 1,5-hexadiene; bicyclo[2.1.1]hexane is not isomerized under the reaction conditions to significant amounts of other hydrocarbons.

The results also show that meaningful, reproducible, quantitative data can be obtained for mercury-sensitized photolyses with small samples at low pressures. While the methods utilized might be more arduous than alternate approaches based on gas-sampling techniques, they also offer certain advantages. Concentration and light intensity gradients in the reaction zone are minimized; no systematic errors arise when reaction products condense from the gas phase, and only small quantities of substrates and readily available equipment are required.

Applications of this technique now in progress in quantitative studies of the photolysis of other ketones may contribute to a more precise formulation of their photochemistry. The alternative Schemes I and II above and the discrepancies between the conclusions drawn here from the kinetic results and the reported[6] distributions of deuterium atoms in the hydrocarbon products derived from the mercury-sensitized gas phase photolysis of 3,3-dideuterionorcamphor are receiving further attention.

Experimental Section

Preparative-Scale Mercury-Sensitized Photolysis of Norcamphor.—Goldsmith Bros. triply distilled mercury (1–2 ml) was placed in a round-bottomed, 2-l. Vycor flask equipped with a Vycor–Pyrex graded seal, standard-tapered joint, and a side arm with a break seal and standard-tapered joint. The flask was attached to a vacuum line and 1–4 g of Aldrich norcamphor, redistilled and degassed through three freeze-pump-sublime cycles, was condensed within. The flask was sealed and heated for 20–30 min at 120°, then photolyzed for 5–15 hr

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[11] A. B. Callear and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A266**, 299 (1962).

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

[13] R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **89**, 407 (1967).

[14] J. Meinwald, W. Szerybalo, and D. R. Dimmel, *Tetrahedron Letters*, 731 (1967).

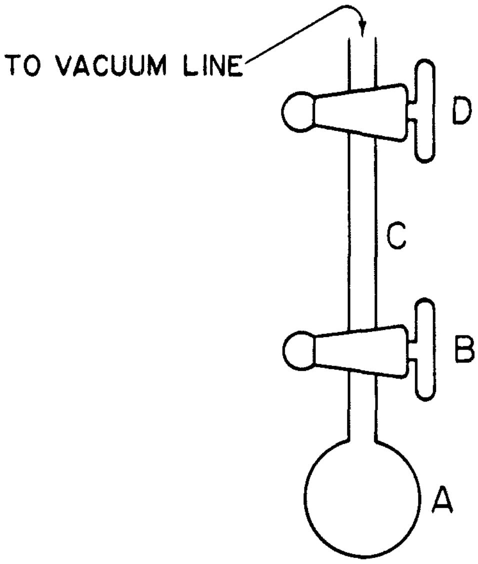

Figure 7.—Aliquoting apparatus.

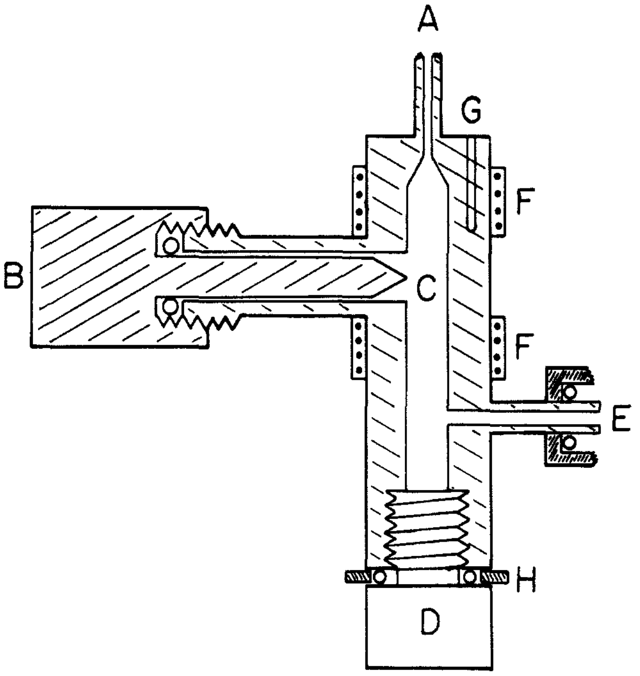

Figure 8.—Flash vaporizer injection system for the quantitative chromatographic analysis of samples sealed in glass tubes. A. Carrier gas inlet. B. Handle for crushing pin. C. Sample chamber. D. Access plug for sample chamber. E. Injection port of gas chromatograph. F. Heating coils. G. Thermocouple well. H. O-Ring retainer.

in a Rayonet photoreactor[15] preheated to 90–100° and equipped with 16 RPR-2537 low pressure mercury lamps. The side arm of the reaction vessel was attached to the vacuum line through three cold traps and a Teflon valve. After the vacuum system was evacuated, the valve was closed and the break seal was broken with a small magnet. The photolysate was allowed to pass slowly through the cold traps (−196°) by adjusting the Teflon valve. The valve was closed intermittently and the noncondensable gases were pumped away. When the pressure in the reaction vessel was a few millimeters, the system was pumped to 10^{-3} mm and left overnight to allow for complete transfer to the cold traps. The collected photolysate, 0.3–0.4 ml/g of norcamphor, was flash distilled and separated by preparative glpc (3 m by 0.94 cm o.d. column, 20% diisodecyl phthalate on Chromosorb W, 80–90°). The physical properties of the three major hydrocarbons obtained agreed in all respects with the literature values except the infrared spectra of bicyclo[2.1.1]hexane and allylcyclopropane. A direct comparison with a spectrum of an authentic sample of bicyclo[2.1.1]hexane,[16] however, confirmed the identification. The infrared spectra determined with 5% solutions in carbon tetrachloride showed bands for bicyclo[2.1.1]hexane at 2955(vs), 2865(s), 1280(m) and 1200(m) cm^{-1} and for allylcyclopropane at 3080(s), 3000(s), 2900(m), 1630(s), 1425(m), 1010(s), 990(s), and 905(vs) cm^{-1}.

Preparative-scale mercury-sensitized photolyses of (2-cyclopentenyl)ethanal were conducted as described above for the preparative scale photolyses of norcamphor. The photolysate obtained by photolyzing 1.34 g of (2-cyclopentenyl)ethanal for 310 min was shown by glpc to contain approximately 50% of the starting material and one other major component amounting to 70% of the low molecular weight material. This was identified as cyclohexene; it had a parent peak in the mass spectrum at *m/e* 82; the infrared and nmr spectra and the glpc retention time were identical with those of an authentic sample.

Photolysis of Norcamphor in Ether Solution.—Norcamphor (53 g, 0.48 moles) was dissolved in 300 ml of anhydrous ether contained in a Pyrex flask fitted with a fritted-glass gas inlet near the bottom, a reflux condenser, and a large ground-glass joint on top. A quartz water-cooled immersion well containing a Hanovia medium-pressure mercury lamp, Model L-679A-36, was fitted into the ground-glass joint. Nitrogen bubbling into the gas inlet and a magnetic stirrer agitated the solution. The photolysis was terminated after 38 hr when the infrared spectrum of the solution showed the two major carbonyl bands to be of equal intensity. The photolyzed solution was concentrated on a steam bath and fractionated on a 20-cm spinning-band column. The 17 ml of distillate having bp 66–69.5° (33–34 mm) was shown by glpc to be over 90% (2-cyclopentyl)ethanal. The aldehyde was purified by preparative glpc to give material having $n^{21}\mathrm{D}$ 1.4580; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 292 mμ (ε 27); infrared absorption (10% CCl_4) gave 3060(m), 2950(s), 2720(m), 1720(s), 1400(m), 1360(m), 1070(m) and 910(m) cm^{-1}; nmr peaks (10% CCl_4) at τ 0.24 (0.9 H), 4.28 (1.9 H), 6.92 (1.1 H) and 7.4–8.9 (6.0 H); parent peak in mass spectrum at *m/e* 110.

Anal. Calcd for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C, 76.64; H, 9.26.

Semicarbazone (mp 113.4–116.0°) and 2,4-dinitrophenylhydrazone (mp 98–102°) derivatives were prepared.

Anal. Calcd for $C_8H_{12}N_3O$: C, 57.45; H, 7.83; N, 25.13. Found: C, 57.57; H, 7.93; N, 25.41.

Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.81; H, 4.83; N, 19.31. Found: C, 53.99; H, 4.72; N, 19.03.

Kinetic Study of the Mercury-Sensitized Gas Phase Photodecarbonylation of Norcamphor.—Norcamphor was purified by preparative glpc and thereafter protected from exposure to sunlight. Analysis showed ≤0.04% (3-cyclopentenyl)ethanal as the major impurity. After degassing with four freeze-pump-sublime cycles at 10^{-4} mm, any traces of water were removed by passing the vapor twice through a calcium chloride drying tube on the vacuum line. The purified material was condensed in flask A (Figure 7) which was then suspended in a bath maintained below room temperature and constant to ±0.02°. The flask was allowed to equilibrate for at least 2 hr and then aliquots of norcamphor were sealed into 13 × 90 mm Vycor tubes having 1-mm walls, each containing 1 drop of mercury, as follows. Closing valve D and operating valve B for at least 5 min allowed tube C to fill with norcamphor vapor at the equilibrium pressure above solid norcamphor at the temperature of the bath. Valve B was then closed and D opened to allow the aliquot of norcamphor to transfer to the Vycor sample tube which was subsequently removed from the vacuum line with a hand torch. The volume of the tubes was found to be 8.3 ± 0.4 ml (standard deviation) by a water displacement method. The smaller volume (5.32 ± 0.02 ml) of tube C (Figure 7) and the relative temperatures of aliquoting and photolysis ensured that norcamphor would be in the gas phase during the photolysis.

The irradiation apparatus for the kinetic study consisted of a circular table with a series of vertical holes equidistant from the center for the sample tubes and a large hole in the center for the lamp. The table was positioned inside an air bath at 30 ± 1° and caused to rotate about its center on a vertical axis at 122 rpm. An air-cooled Pen-Ray low pressure mercury lamp

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[15] Available from the Southern N. E. Ultraviolet Co., Middletown, Conn.

[16] A sample of this hydrocarbon was generously provided by Professor R. Srinivasan.

Model 11SC-1[17] was positioned within a cylindrical 2-mm Vycor filter about which the table rotated. The filter was totally blackened except for eight, equally spaced, horizontal, 0.5-mm slits located at the level of the lamp. The 2537-A light passed through the slits and struck the vertical Vycor sample tubes positioned 8 cm from the lamp. The rotation of the table compensated for any slight nonuniformities in the lamp, slit size, filter thickness, or distance from the lamp.

The sample tubes were shaken to break up the mercury, wiped clean, and equilibrated in the photolysis apparatus for 9 hr at 40° to saturate the vapor with mercury. After reequilibration at 30° for 20 min, the tubes were rotated and photolyzed at 30° (pressure, 2.65 ± 0.35 mm throughout the reaction).

For the analysis of its contents, a Vycor sample tube was scratched on the neck, wiped clean with tissue, and placed inside the vacuum system. After evacuation to 10^{-4} mm, the tube was broken open near the scratch by turning a stopcock with an eccentric end.[18] The volatile contents were frozen into a 7 × 50 mm Pyrex tube which was sealed off with a hand torch leaving at least 95% of the mercury in the Vycor sample tube. The volatile photolyzate was quantatively analyzed by crushing the small Pyrex tube in the gas stream leading to the injection port of a Perkin-Elmer Model F-11 gas chromatograph using the flash vaporizer depicted in Figure 8. The tube remained about 30 sec in the flash vaporizer at 150–60° before it was crushed and analyzed on a 0.31-cm o.d. by 3-m column containing 10% diisodecyl phthalate on Anakrom (90/100) ABS at 30° for 14 min and then at temperatures increasing 4° per min to 100°. Peak areas were integrated with a polar planimeter. The response of the flame ionization detector was taken to be proportional to the number of carbon atoms present per molecule as suggested by Purnell.[19]

The peaks were identified by adding authentic material to a photolyzed sample and noting the peak enhancement. Carbon monoxide was determined as noncondensable gas. All sample tubes were found to transmit similar intensities of 2537 A light after the photolyses. Plots of the data obtained are presented in Figures 2–5.

Kinetic Study of the Mercury-Sensitized Gas Phase Photolysis of Bicyclo[2.1.1]hexane.—Bicyclo[2.1.1]hexane was obtained by glpc separation of the norcamphor photolyzate as described above. The amount of material in each tube was determined by standard pressure techniques. The data were corrected for the slight variation in initial concentration of hydrocarbon. The photolysis and analytical procedure were identical with those described above for the norcamphor work; the results obtained are given in Figure 6.

Registry No.—**1**, 14075-12-8; **2**, 592-42-7; **3**, 285-86-9; **4**, 4663-23-4; **1** semicarbazone, 2630-42-4; **1** 2,4-dinitrophenylhydrazone, 3281-03-6; (3-cyclopentenyl)-ethanal, 14055-37-9.

Acknowledgments.—We thank Professor R. F. Nystrom for suggestions concerning vacuum techniques and Professor R. J. Crawford for design information helpful in developing the flash vaporizer shown in Figure 8.

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[17] The manufacturer's specifications indicate over 90% 2537-A emission, and the remaining 10% would not be absorbed significantly by the norcamphor.

[18] An apparatus similar to the one used here has been described by R. J. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p 67.

[19] H. Purnell, "Gas Chromatography," John Wiley and Sons, Inc., New York, N. Y., 1962, p 302.

Cycloadditions. XVI. On the Relative Selectivity of Carbomethoxycarbene and Carbomethoxynitrene in Cycloadditions with Toluene and *t*-Butylbenzene[1,2]

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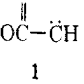
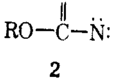
Carbomethoxynitrene generated thermally from methyl azidoformate adds to the aromatic nuclei of toluene and *t*-butylbenzene indiscriminately; all three possible isomeric alkyl-N-carbomethoxyazepines are formed in comparable amounts in both cases. The reactions of thermally generated carbomethoxycarbene with toluene and *t*-butylbenzene give rearrangement products from which isomer distributions of the initially formed alkyl-7-carbomethoxycycloheptatrienes could not be deduced.

Four intermolecular reactions common to carbalkoxycarbenes **1** and carbalkoxynitrenes **2** are insertions into carbon–hydrogen bonds, additions to olefinic and aromatic carbon–carbon bonds, and 1,3 cycloadditions. Through quantitative comparisons of the relative reactivity and selectivity of these short-lived chemical intermediates in all four types of processes, more complete understandings of their versatile behaviors may be gained.


$ROC(=O)\ddot{C}H$

1


$RO{-}C(=O){-}\ddot{N}{:}$

2

The relative reactivity of carbethoxycarbene and carbethoxynitrene in one of these reactions, cycloaditions with aromatics, has recently been established.[5] A log–log plot for the relative rate constants for the reactions of monosubstituted benzenes with carbethoxycarbene and -nitrene gave a linear correlation with a slope of 3.3. This linear free-energy relationship provided a quantitative measure of the greater reactivity and diminished discrimination between different monosubstituted benzenes characteristic of the carbethoxycarbene, relative to the -nitrene.

Carbalkoxynitrenes have been inferred to be more selective than carbalkoxycarbenes in insertions into aliphatic carbon–hydrogen bonds by a factor of about 10.[6-8] The selectivity of the two reactive intermediates in cycloadditions with olefinic double bonds[9-13]

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[1] Paper XV in this series: J. E. Baldwin and J. E. Gano, *J. Org. Chem.*, **32**, 3506 (1967).

[2] Supported in part by the National Science Foundation (Grant GP-522) 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.

[4] Archer Daniels Midland Co. Fellow, 1964–1965.

[5] J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, **89**, 1886 (1967).

[6] W. von E. Doering and L. H. Knox, *ibid.*, **83**, 1989 (1961).

[7] W. Lwowski and T. J. Maricich, *ibid.*, **86**, 3164 (1964).

[8] M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Letters*, 2945 (1964).

[9] I. A. Dyakonov, *Zh. Obshch. Khim.*, **19**, 1734 (1949).

[10] C. von der Heide, *Chem. Ber.*, **37**, 2101 (1904).

[11] P. S. Skell and R. M. Etter, *Proc. Chem. Soc.* (London), 443 (1961).

[12] I. A. Dyakonov and V. F. Myznikova, *Sbornik Statei Obshchei Khim., Akad. Nauk SSSR*, **1**, 489 (1954); *Chem. Abstr.*, **49**, 883 (1955).

[13] S. H. Harper and H. W. B. Reed, *J. Chem. Soc.*, 779 (1955).