least-squares method, yielding values for $(k_f + k_r)$. In general, $K_e = k_f/k_r$, where K_e is the isotopic equilibrium constant. Ordinarily, as in the present case, if isotope effects are neglected, these equilibrium constants involve only statistical factors. Thus, at equilibrium, for 3,3-dimethyl-2-butanone-1-^{14}C, K_e = **1b**/**1a** = 3 and $(k_f + k_r) = \frac{4}{3}k_f$. The experimental rate constant, $^{\alpha}k$, is equal to k_f, and is obtained by dividing the least squares slope by $\frac{4}{3}$. Similarly, for 3,3-dimethyl-2-butanone-2-^{14}C, $K_e = 1$, and $^{*}k$ is obtained by dividing the least squares slope by 2. The values for $^{\alpha}k$ and $^{*}k$ calculated in this manner are tabulated in Table I. Sample calculations, assuming 2% errors in activity measurements, give values for $^{\alpha}k$ and $^{*}k$ which fall within the circles or triangles in Figure 1, or which are specifically indicated by the vertical lines on the points in Figure 1. The usual activity measurement error is more like 0.5–1.0%. These calculations reflect only errors resulting from variations in counting data, which is probably the largest source of error, but other errors such as in the determination of the sulfuric acid concentration, the time of reaction, errors in the work-up procedure, etc., might cause some additional uncertainties in the rate constant values. These are probably not very important since the points in Table II fall very nicely on straight line kinetic plots.

Registry No.—Sulfuric acid, 7664-93-9; 3,3-dimethyl-2-butanone-1-^{14}C, 17032-76-7; 3,3-dimethyl-2-butanone-2-^{14}C, 17032-75-6.

Photochemical Addition of 4,4-Dimethyl-2-cyclohexenone to Tetramethylethylene[1]

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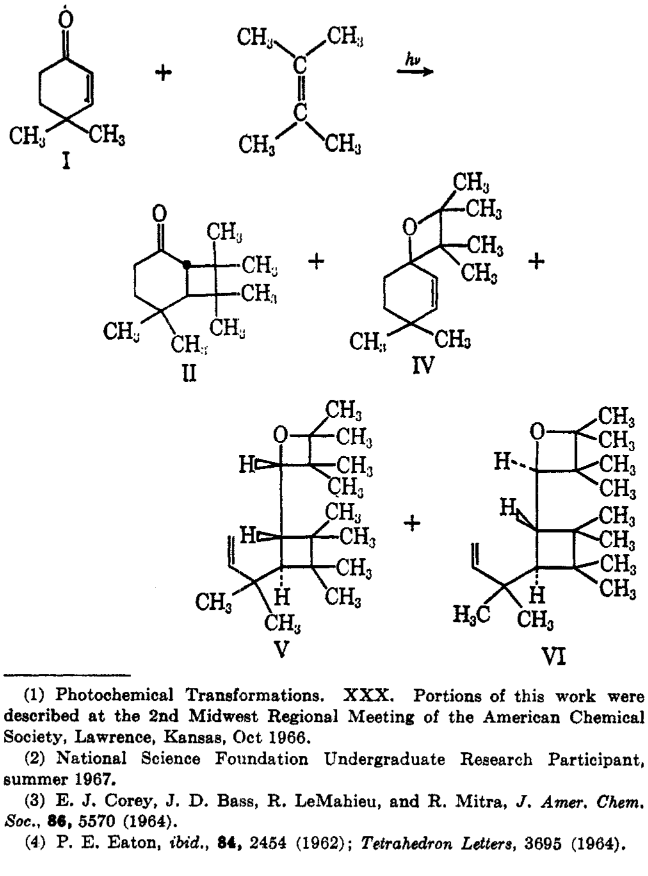
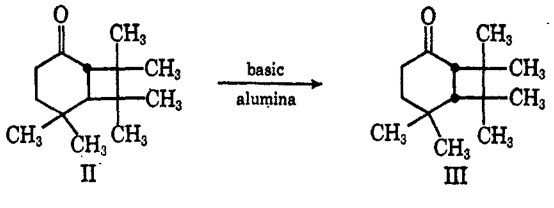
Irradiation of 4,4-dimethyl-2-cyclohexenone in the presence of tetramethylethylene gives *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one and an oxetane as major products. In addition, two novel secondary photoproducts are isolated and characterized.

Photochemical addition of cycloalkenones to olefins has found substantial use in synthesis since the initial investigations by Corey[3] and Eaton.[4] We wish to describe the photochemical addition of 4,4-dimethyl-2-cyclohexenone to tetramethylethylene which has three special features. First, only *trans*-cyclobutane adduct is formed, second the oxetane is a major product, and third two novel minor products are formed.

Irradiation of 4,4-dimethyl-2-cyclohexenone (I) in neat tetramethylethylene or in *t*-butyl alcohol containing tetramethylethylene in a Pyrex vessel using a Rayonet reactor with 3500-Å lamps gives two major products and several minor products (Scheme I). The products isolated are shown below. The major products account for 89% of the starting material destroyed. The *trans* adduct II shows the expected spectroscopic properties, molecular weight, and elemental analysis (see Experimental Section) and is isomerized by basic alumina to *cis*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one (III). Vapor chromatography of the crude product from the irradiation showed the absence of *cis* adduct III. The oxetane IV showed no infrared carbonyl absorption but did show double bond absorption. The nmr spectrum (see Experimental Section) showed the presence of six methyl groups on saturated carbon, two olefinic protons as an AB pattern, $^3J_{AB}$ = 10.3 Hz, and four methylene protons. Elemental analysis was consistent with the formula $C_{14}H_{24}O$. The mass spectrum did not show a significant parent ion but did show intense ions at *m/e* 150 (M − C_3H_6O) and 135 [(M − C_3H_6O) − CH_3]. These fragment ions correspond to sequential loss of acetone and a methyl group from the parent ion. The minor oxetane products (V and VI) were first isolated from the crude reaction mixture but were more easily prepared by a reaction described in Scheme II.

Scheme I





The minor oxetane products (V and VI) were best prepared by irradiation of *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one in the presence of tetramethylethylene in *t*-butyl alcohol (Scheme III). They

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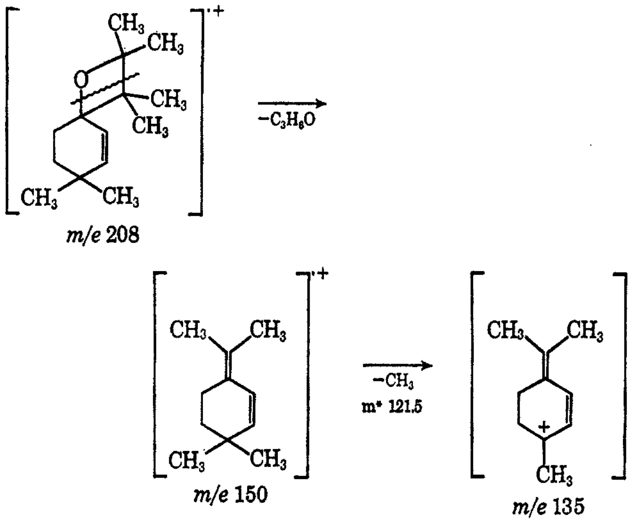
[1] Photochemical Transformations. XXX. Portions of this work were described at the 2nd Midwest Regional Meeting of the American Chemical Society, Lawrence, Kansas, Oct 1966.

[2] National Science Foundation Undergraduate Research Participant, summer 1967.

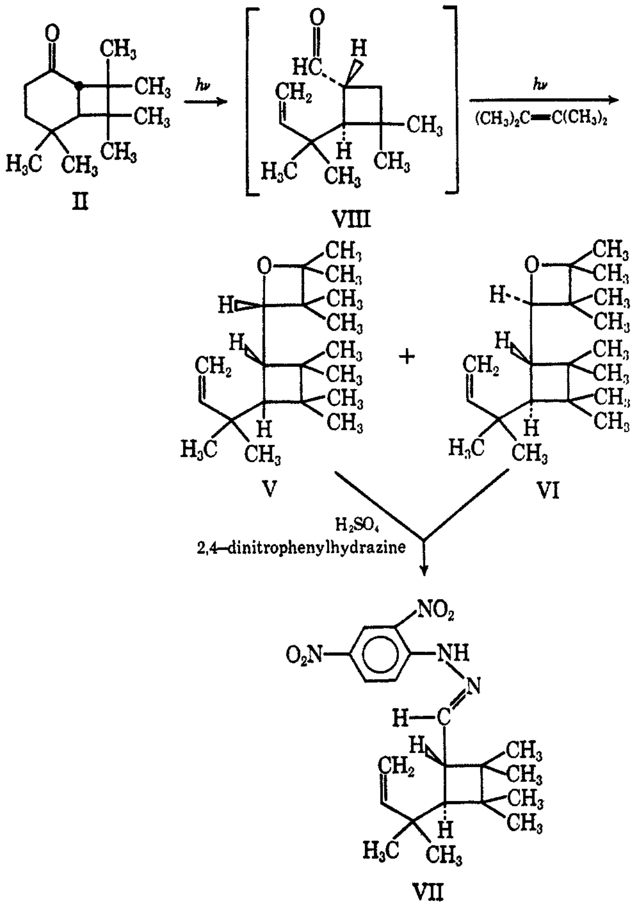
[3] E. J. Corey, J. D. Bass, R. LeMahieu, and R. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

[4] P. E. Eaton, *ibid.*, **84**, 2454 (1962); *Tetrahedron Letters*, 3695 (1964).

SCHEME II

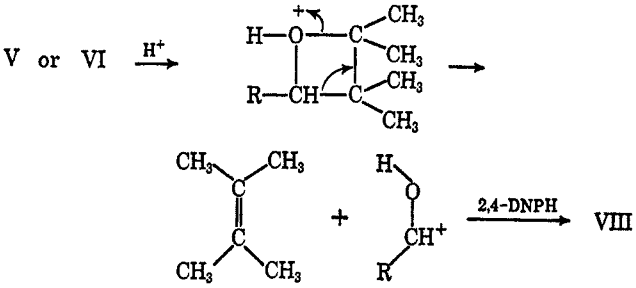


SCHEME III



are thus not primary photoproducts in the irradiation of I. The two isomeric products could be differentiated by their infrared spectra in solution and by their behavior on thin layer chromatography. Both products showed parent ions at *m/e* 292 and analyzed for $C_{20}H_{36}O$. Neither isomer showed carbonyl absorption, but both showed double-bond absorption in the infrared. The nmr spectrum of both isomers showed a monosubstituted vinyl group, ten methyl groups on saturated carbon, and three methine protons as an ABX pattern. Treatment of either isomer with 2,4-dinitrophenylhydrazine reagent in methanolic sulfuric acid gave the same 2,4-dinitrophenylhydrazone (VII). The molecular weight (388) and elemental analysis of the derivative show that formation of the 2,4-dinitrophenylhydrazone involves loss of the elements of tetramethylethylene. This loss is easily formulated as shown in Scheme IV. The nmr spectrum of the derivative shows the monosubstituted vinyl group, six methyl groups on saturated carbon, two methine protons and one aldimine proton as an ABX pattern, and the expected aromatic and N–H protons. Formation of the two oxetanes from *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one and the formation of the same 2,4-dinitrophenylhydrazone from both oxetanes suggest that both have *trans* stereochemistry on the cyclobutane ring.

SCHEME IV



Irradiation of *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one in the absence of tetramethylethylene gave a complex mixture of products which we were not able to separate. Irradiation at −40° in an infrared cell did permit observation of characteristic aldehyde absorption bands at 2720 and 1390 cm^{-1} and monosubstituted ethylene bands at 3090, 1640, 1420, 990, and 910 cm^{-1}. Aldehyde carbonyl absorption was not resolved from that of the starting ketone. Some ketene absorption (2110 cm^{-1}) was observed. This is in accord with expectation for an α cleavage which can give either aldehydes or ketenes.[5] Formation of the oxetanes from II requires cleavage on the less substituted side of the carbonyl group. This abnormal direction of cleavage may be caused by the presence of the *trans* ring fusion. The conversion of the aldehyde VIII to V and VI is a normal Paterno–Büchi reaction.

The formation of only *trans* adduct II rather than a *cis–trans* mixture is surprising. Apparently, the excited state responsible for formation of *cis* adduct in the addition of 4,4-dimethyl-2-cyclohexenone to 1,1-dimethoxyethylene[6] does not react with tetramethylethylene to give a cyclobutane derivative.

Experimental Section

Irradiation of 4,4-Dimethyl-2-cyclohexenone in Tetramethylethylene.—A solution of 4,4-dimethyl-2-cyclohexenone (6.2 g) in tetramethylethylene (25.2 g) was irradiated for 111 hr in a Pyrex vessel using a Rayonet reactor with 3500-Å lamps. The excess tetramethylethylene was removed under vacuum with a rotary evaporator. Thin layer chromatography revealed the presence of several products. Preparative-scale vpc gave workable amounts of the two major products (II and IV). Analysis of the crude mixture (11.3 g) by vpc using ethyl cinnamate as

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[5] R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963); O. L. Chapman, *ibid.*, **1**, 366 (1963).

[6] O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, **90**, 1657 (1968).

an internal standard and known thermal conductivity ratios showed II (42%) and IV (47%).

Compound IV did not show carbonyl absorption in the infrared. The mass spectrum of IV did not show a significant parent ion but did show intense ions at *m/e* 150 (M − C_3H_6O) and 135 [(M − C_3H_6O) − CH_3]. The nmr spectrum of IV shows an AB pattern (δ_A 5.72, δ_B 5.38, $^3J_{AB}$ = 10.3 Hz, olefinic protons), a complex four-proton multiplet (δ 1.2–2.2, methylene protons), and five singlets (δ 1.23, 6 H; 1.13, 3 H; 1.05, 3 H; 0.99, 3 H; 0.92, 3 H; six methyl groups).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.71; H, 11.76.

Compound II showed infrared carbonyl absorption at 5.83 μ. The nmr spectrum of II (CCl_4) showed an AB pattern (δ_A 2.57, δ_B 1.92, $^3J_{AB}$ = 15 Hz, bridgehead protons), a complex four-proton multiplet (δ 1.3–2.4, methylene protons), and six three-proton singlets (δ 0.90, 0.95, 1.02, 1.06, 1.13, and 1.19). In a separate experiment II was isolated in 42% yield by repeated chromatography on silica gel. An analytical sample prepared by distillation (67°, 0.07 mm) followed by sublimation (55° at 0.2 mm) had mp 38–39°.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.86; H, 11.47.

Isomerization of *trans*-5,5,7,7,8,8-Hexamethylbicyclo[4.2.0]-octan-2-one.—A solution of *trans*-5,5,7,7,8,8-hexamethylbicyclo-[4.2.0]octan-2-one in pentane was added to a column of basic alumina and left in contact with the basic alumina for 30 min. Elution with 1:1 ether–pentane gave *cis*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one, $\lambda_{\max}^{CCl_4}$ 5.91 μ. Distillation (120°, 15 mm) gave an analytical sample. The nmr spectrum (CCl_4) showed a complex six-proton multiplet (δ 1.0–2.5) and six methyl groups (δ 0.90, 3 H; 0.94, 3 H; 1.03, 9 H; 1.13, 3 H).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.97; H, 11.46.

Irradiation of *trans*-5,5,7,7,8,8-Hexamethylbicyclo[4.2.0]-octan-2-one in the Presence of Tetramethylethylene.—A solution of tetramethylethylene (2.27 g) and *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one (0.46 g) in *t*-butyl alcohol (9 ml) was irradiated for 245 hr in a Pyrex vessel in a Rayonet reactor with 3500-Å lamps. Removal of the solvent and excess tetramethylethylene gave a crude mixture (0.72 g). Thin layer chromatography showed several products. Chromatography on silica gel gave two isomeric products (A and B). Recrystallization from pentane gave the pure products both having mp 53–55°. Neither product showed carbonyl absorption in the infrared, but both products showed double-bond absorption (A, $\lambda_{\max}^{CCl_4}$ 6.13 and 11.04 μ, and B, $\lambda_{\max}^{CCl_4}$ 6.13 and 10.99 μ). Both A and B showed parent ions at *m/e* 292. The nmr spectrum (CCl_4) of product A showed three olefinic protons as an ABC pattern (δ ~5.95, q, 1 H; 4.6–5.1, m, 2 H), three methine protons as an ABX pattern (δ 4.18, d, 1 H; 2.25, t, 1 H; 1.67, d, 1 H), and ten methyl groups (δ 0.82, 6 H; 0.87, 3 H; 0.98, 3 H; 1.03, 9 H; 1.08, 3 H; 1.12, 3 H; 1.18, 3 H). The nmr spectrum (CCl_4) of B showed three olefinic protons as an ABC pattern (δ ~5.85, q, 1 H; 4.6–5.1, m, 2 H) three methine protons (δ 4.22, d, 1 H; 2.18, t, 1 H; 2.65, d, 1 H), and ten methyl groups (δ 0.87, 3 H; 0.92, 6 H; 0.95, 3 H; 1.02, 6 H; 1.10, 6 H; 1.14, 3 H; 1.22, 3 H). The infrared spectra of A and B in solution were clearly differentiated, each containing bands not found in the other. The behavior of A and B on thin layer chromatography also differed significantly.

Anal. Calcd for $C_{20}H_{36}O$: C, 82.19; H, 12.33. Found for product A: C, 82.12; H, 12.18. Found for product B: C, 82.11; H, 12.37.

Treatment of either A or B with 2,4-dinitrophenylhydrazine in methanolic sulfuric acid gave the same 2,4-dinitrophenylhydrazone, mp 179–180°. The nmr spectrum ($CDCl_3$) of the derivative showed a broad N-H resonance (δ 11.0, lost on shaking with D_2O), three aromatic protons (δ 9.08, d; 8.28, q; 7.95, d), an aldimine proton (δ 7.48, d), three olefinic protons (δ 5.95, q, 1 H; 4.6–5.1, m, 2 H), two methine protons coupled to each other and one coupled to the aldimine proton (δ 2.92, q; 2.18, d), and six methyl groups (δ 0.96, 3 H; 1.00, 3 H; 1.03, 3 H; 1.07, 6 H; 1.10, 3 H).

Anal. Calcd for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.92; H, 7.20; N, 14.55.

Irradiation of *trans*-5,5,7,7,8,8-Hexamethylbicyclo[4.2.0]octan-2-one at Low Temperature.—A neat film of *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one was irradiated in an Air Products low-temperature infrared cell at −180° with an unfiltered mercury lamp for 1110 min. No change in the infrared absorption of the sample was observed during this period. Similar irradiation at −40° produced significant new bands at 3090 (olefin C–H stretch), 2720 (aldehyde C–H stretch), 2110 (ketene), 1640 (C=C stretch), 1420 (C–H deformation), 1390 (aldehyde H-rock), 990 (*trans* C–H wag), and 910 cm^{-1} (=CH^2 wag).

Registry No.—I, 1073-13-8; II, 19018-67-8; IV, 19019-03-5; tetramethylethylene, 563-79-1; III, 19018-68-9.

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The Photolysis of Dihydro-1,2-oxazines

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Photolysis of nitrosobenzene-1,3-diene adducts (dihydro-1,2-oxazines) gives 1-phenylpyrroles. The reaction provides a convenient preparation for these compounds. Evidence for a mechanism involving intramolecular hydrogen abstraction and a γ-amino ketone intermediate is presented.

Recent articles have described photochemical transformations of heterocycles incorporating the N–O linkage. Thus isoxazoles[1,2] and 3-hydroxyisoxazoles[3] were found to rearrange to oxazole and oxazolone derivatives, oxaziranes[4] undergo fragmentation, and N-alkylisoxazolidines[5] ring expand to tetrahydro-1,3-oxazines. A common feature of these diverse photoprocesses is the cleavage of the endocyclic N–O bond.

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(4) E. Meyer and G. W. Griffin, *Angew. Chem. Intern. Ed. Engl.*, **6**, 634 (1967).

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