slope of the appropriate graph[8] with the numerical values computed by least squares.

The rate constants in Table I are the average of three to four runs for each compound. Average deviation from the mean is less than 4.5%. Temperature control was ±0.05°. Initial concentration of hydroxamic acids in the kinetics runs was 0.012 *M*.

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Skipped Diynes. IV. Diacetylenic Ketone Reactions[1]

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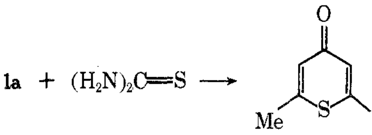
Ketones with geminal triple bonds (**1**) are vulnerable to attack at several sites. As is the case with the more common monoethynyl ketones, additions of nucleophiles,[2-10] electrophiles,[11,12] dienes,[2] and dipolarophiles[13] to **1** have been observed. These were particularly interesting to us when both ethynyl groups became involved in conversions to families such as cyclopentenones, thiolenones, (5-triazolyl)isoxazoles, (pyrazolyl)pyrazoles, etc.[2,7] To expand this still relatively unfamiliar area, we investigated the chemistry of **1** with emphasis on **1a**.

$$(RC{\equiv}C)_2C{=}O$$

1a, $R = CH_3$
b, $R = C_6H_5$

Those reactions of **1a** which proceed as expected will simply be mentioned, while those with new features will be described.[2,3,6] Thus, with primary or secondary amines, **1a** yields isolable monoadducts which may be cyclized to pyridones; with hydrazines and **1a**, the monoadduct may not always be isolable but the cyclization can usually be made to take place; with thiols, **1a** yields symmetrical diadducts; with tetracyclone, **1a** forms a Diels-Alder monoadduct.

The reaction of diethynyl ketones with thiourea and substituted thioureas occurs readily but often unpredictably. Penta-1,4-diyn-3-one is reported to react with *N,N'*-diphenylthiourea to give an adduct of unspecified structure.[5] Compound **1b** reacted with both thiourea and *N,N'*-diphenylthiourea to give the same dihydrothiophene derivative,[2] but **1a** reacted with thiourea to give 2,6-dimethyl-4*H*-thiopyran-4-one as the only isolable product (eq 1).

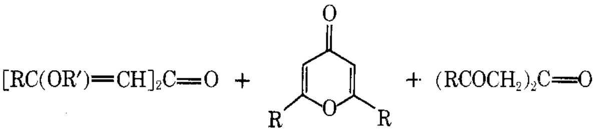


(1)

Our reaction conditions are quite different from the formally similar addition of hydrogen sulfide to **1b**, which proceeds in a bomb at 180° to give an analogous thiopyranone.[11]

While not defined in every detail, the course of the additions of alcohols or water to **1** has been clarified. With **1b** Russian workers have recently shown that a monoalkoxy adduct of **1** as well as the products of eq 2 may be formed.[4] In the presence of acid the γ-pyrone is generally the major product.[12]

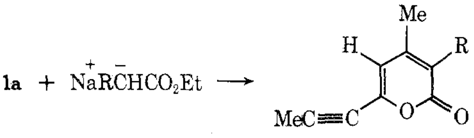
$$1 + R'OH \longrightarrow$$



(2)

When **1a** was treated with sodium ethoxide in ethanol, the only isolable product was 2,6-diethoxyhepta-2,5-dien-4-one, but with sodium methoxide in methanol, a 3:2 mixture of 2,6-dimethyl-4-pyrone and 2,6-dimethoxyhepta-2,5-dien-4-one was produced. The pyrone presumably arises from the slow acid-catalyzed hydrolysis of the bis(enol) ether to 2,4,6-heptanetrione, which then spontaneously condenses under the reaction conditions to give the pyrone. Indeed, **1a** yields 2,6-dimethyl-4-pyrone upon treatment with aqueous acid.[12]

Additions of Grignard reagents to the carbonyl group are possible, but additions of other carbon nucleophiles to **1** have varying success.[2,9] In the case of **1a** these additions are usually foiled by its sensitivity to the strongly basic conditions usually employed in such reactions. This problem was circumvented by employing inverse addition of the anions of diethyl malonate and ethyl cyanoacetate in solution to a cold solution of **1a**.



(3)

$R = CO_2Et$, CN

The mode of attack and the resulting products are typical of monoethynyl ketones.[2] Under similar reaction conditions, **1b** reacts with carbon nucleophiles to give exclusively cyclopentenones.[2]

Experimental Section

For general details see ref 1, 2, and 14. **1a** had mp 80-81° (lit.[6a] mp 78-80°); ir (CCl_4) 2260, 2230, 1630 cm^{-1}; nmr (CCl_4) δ 2.05 (s, 6 H). **1b** had mp 65° (lit.[2] mp 64-66°); ir (CCl_4) 2240, 2180, 1605 cm^{-1}.

3-Propynyl-5-methylpyrazole. To a solution of **1a** (0.5 g) in 10 ml of methanol at 0°, hydrazine hydrate (1 ml) was added dropwise. Work-up followed by chromatography (twice) on silica gel with ether-chloroform (2:1, v/v) gave a yellow solid: mp 93.5-94.5°; ir ($CHCl_3$) 3490 (NH), 2230 (C≡C), 1580, 1465, 1410 cm^{-1}; nmr ($CDCl_3$) δ 2.0 (s, 3 H), 2.4 (s, 3 H), 6.0 (s, 1 H), 12.1 (broad, 1 H).

Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.76. Found: C, 69.86; H, 6.75.

2,4-Dinitrophenylhydrazone of 1a, as orange needles from ethyl acetate, had mp 201-203°; ir (KBr) 3220 (NH), 2220 (C≡C), 1618 cm^{-1} (C=N); nmr ($CDCl_3$) δ 2.1 (s, 3 H), 2.3 (s, 3 H), 8.6 (m, 3 H), 12.0 (broad, 1 H).

Anal. Calcd for $C_{13}H_{10}N_4O_4$: C, 54.54; H, 3.57. Found: C, 54.55; H, 3.05.

1-(2,4-Dinitrophenyl)-3-propynyl-5-methylpyrazole. A solution of sodium methoxide (0.2 g) in methanol (20 ml) and the above DNP (0.25 g) was heated to boiling. Water (10 ml) precipitated a solid which was recrystallized twice from absolute ethanol to give silky yellow needles (0.2 g): mp 137–139°; ir (KBr) 2230, 1610, 1550 cm^{-1}; nmr ($CDCl_3$) δ 2.0 (s, 3 H), 2.2 (s, 3 H), 6.4 (s, 1 H), 8.12 (m, 3 H).

Anal. Calcd for $C_{13}H_{10}N_4O_4$: C, 54.54; H, 3.57. Found: C, 54.33; H, 3.36.

2-(*o*-Carboxyanilino)-hept-2-en-5-yn-4-one. A solution of **1a** (0.5 g) and anthranilic acid (0.64 g) in absolute ethanol was refluxed for 1 hr. Work-up and recrystallization from chloroform gave a yellow solid whose melting point could not be determined since ring closure to the pyridone occurred on slow heating: ir (KBr) 2240, 2280 (C≡C), 1700 (CO_2H), 1610 (C=O), 1570 cm^{-1} (C=C); nmr (DMSO) δ 2.0 (s, 6 H), 5.5 (s, 1 H), 7.6 (m, 4 H), 8.3 (s, 1 H), 12.9 (broad, 1 H).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.39. Found: C, 68.77; H, 5.23.

***N*-(*o*-Carboxyphenyl)-2,6-dimethyl-4-pyridone.** 2-(*o*-Carboxyanilino)-hept-2-en-5-yn-4-one (0.5 g) was suspended in xylene (50 ml) and refluxed for 4 hr. Filtration of the cooled reaction mixture gave white crystals (0.5 g) from methanol: mp 360° dec; ir (KBr) 3100 (OH), 1690 (CO_2H), 1650 cm^{-1} (C=O); nmr (H_2SO_4, external TMS) δ 2.8 (s), 7.7 (s), 8.6 (m): neut equiv 244 ± 2.

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.39. Found: C, 69.09; H, 5.30.

***N*-(*m*-Carboxyphenyl)-2,6-dimethyl-4-pyridone.** Dipropynyl ketone (0.25 g) and *m*-aminobenzoic acid (0.34 g) were dissolved in absolute ethanol and heated at *ca.* 65° for 20 min. Removal of the solvent gave a nearly quantitative yield of the adduct, 2-(*m*-carboxyanilino)hept-2-en-5-yn-4-one: mp 143–145°; ir (KBr) 2260, 2230 (C≡C), 1690 (CO_2H), 1620 (C=O), 1570 cm^{-1} (C=C). This adduct (0.5 g) was heated as a suspension in refluxing xylene (30 ml) for 6 hr. Filtration of the cooled reaction mixture gave a gray solid: mp 333° dec from methanol; ir (KBr) 3100 (OH), 1710 (CO_2H), 1640 cm^{-1} (C=O); nmr (H_2SO_4, external TMS) δ 2.9 (s), 7.8 (s), 8.5 (m), 9.0 (m); neut equiv 242 ± 2.

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.39. Found: C, 69.13; H, 5.23.

2-(3,4-Xylidino)-hept-2-en-5-yn-4-one. A solution of **1a** (0.4 g) and 3,4-xylidine (0.48 g) in 30 ml of absolute ethanol was boiled on a steam bath for 5 min. On cooling in ice, 0.95 g of a solid was deposited. Two recrystallizations from ethanol (Norit) gave yellow needles (0.6 g): mp 107.5–108.5°; ir (KBr) 2280, 2240 (C≡C), 1595 (C=O), 1540 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.95 (s, 6 H), 2.25 (s, 6 H), 5.3 (s, 1 H), 7.0 (m, 3 H), 12.4 (broad, 1 H).

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54. Found: C, 79.36; H, 7.25.

***N*-(3,4-Dimethylphenyl)-2,6-dimethyl-4-pyridone.** 2-(3,4-Xylidino)-hept-2-en-5-yn-4-one (0.3 g) in 20 ml of xylene was refluxed for 19 hr and the resulting solution was cooled and poured into ligroin at 0°. This yielded 0.3 g of a white-gray solid: mp 199–200°; ir (KBr) 1645 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.95 (s, 6 H), 2.35 (s, 6 H), 6.2 (s, 2 H), 7.1 (m, 3 H).

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54. Found: C, 79.18; H, 7.25.

2,6-Bis(*o*-aminobenzenethio)hepta-2,5-dien-4-one. Dipropynyl ketone (0.25 g) and *o*-aminobenzenethiol (0.65 g) were dissolved in 20 ml of methanol. To this solution was added dropwise with stirring 1 ml of a saturated solution of sodium methoxide in methanol. Within seconds, a light yellow solid precipitated out. The solid was collected and recrystallized twice from absolute ethanol to give 0.4 g of yellow needles which melted at 154–160°, presumably because of cis-trans isomerization: ir ($CHCl_3$) 3500, 3400 (NH), 1615 (C=O), 1560 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.9 (d, 6 H), 4.05 (broad, 4 H), 6.3 (q, 2 H), 6.75 (m, 4 H), 7.25 (m, 4 H).

Anal. Calcd for $C_{19}H_{20}N_2S_2O$: C, 64.0; H, 5.66. Found: C, 63.84; H, 5.71.

2,6-Bis(*p*-tolylthio)hepta-2,5-dien-4-one. This compound, which isomerizes on heating to 130°, was prepared in the same manner as above: mp 188–189°; ir ($CHCl_3$) 1625 (C=O), 1560 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.9 (d, 6 H), 2.4 (s, 6 H), 6.25 (q, 2 H), 7.25 (m, 8 H).

Anal. Calcd for $C_{21}H_{22}S_2O$: C, 71.14; H, 6.26. Found: C, 71.13; H, 6.12.

2,6-Bis(*p*-chlorobenzenethio)hepta-2,5-dien-4-one. This compound, which isomerizes on heating to 130°, was prepared in the same manner as above: mp 187–188°; ir ($CHCl_3$) 1630 (C=O), 1560 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.9 (d, 6 H), 6.35 (q, 2 H), 7.45 (m, 8 H).

Anal. Calcd for $C_{19}H_{16}Cl_2S_2O$: C, 57.72; H, 4.08. Found: C, 57.57; H, 4.01.

2,6-Diethoxyhepta-2,5-dien-4-one. To a freshly prepared solution of sodium ethoxide (0.4 g of sodium metal in 20 ml of absolute ethanol) was added dropwise a solution of **1a** (0.75 g) in 15 ml of absolute ethanol. The resulting solution was refluxed for 8 hr and then poured into ice water. Vigorous stirring of this mixture produced a precipitate which was then filtered off and recrystallized from chloroform–ligroin. Two further recrystallizations from isopropyl alcohol–water gave white needles: mp 91–93°; ir ($CHCl_3$) 1665 (C=O), 1585 (C=C), 1068 cm^{-1} (C=CO); nmr ($CDCl_3$) δ 1.35 (t, 3 H), 2.3 (s, 6 H), 3.85 (q, 4 H), 5.4 (s, 2 H).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.65; H, 9.15. Found: C, 66.99; H, 9.34.

2,6-Dimethoxyhepta-2,5-dien-4-one and 2,6-Dimethyl-4-pyrone. A solution of **1a** (0.5 g) in 30 ml of freshly prepared methanolic sodium methoxide (0.2 g of Na) was refluxed for 24 hr and then poured into water. Ether extraction gave a yellow oil which proved to be an inseparable mixture of dienone and pyrone. The dienone had nmr ($CDCl_3$) δ 2.35 (s, 6 H), 3.65 (s, 6 H), 5.14 (s, 2 H); the pyrone[12] had nmr ($CDCl_3$) δ 2.25 (s, 6 H), 6.06 (s, 2 H).

2,6-Dimethyl-4*H*-thiapyran-4-one. A solution of **1a** (0.5 g) and thiourea (0.35 g) in 15 ml of dry DMF was allowed to stand at room temperature for 14 hr. The reaction mixture was then poured into ice water and extracted with chloroform. Work-up yielded a reddish-brown semisolid, which after two sublimations at 75° (0.3 mm) gave a solid: mp 104° (lit.[15] mp 104°); ir (CCl_4) 1625 (C=O), 1595 cm^{-1} (C=C); nmr ($CDCl_3$) δ 2.35 (s, 6 H), 6.7 (s, 2 H).

4-Methylhepta-2,5-diyn-4-ol. A freshly prepared solution of methylmagnesium iodide (10 mmol, 1.58 g, prepared from 0.25 g of magnesium metal and 1.34 g of iodomethane) in ether was added dropwise to a solution of **1a** (1.0 g, 10 mmol) in ether at 0°. The resulting yellow-brown suspension was then refluxed for 30 min and poured into an excess of cold, saturated ammonium chloride solution. Work-up gave white needles (0.3 g): mp 37–38° from ligroin–carbon tetrachloride (lit.[9,10] mp 35°); ir (CCl_4) 3675 (free OH), 3435 (H-bonded OH), 2275 (C≡C), 1230, 1325 cm^{-1} (CO); nmr (CCl_4) δ 1.62 (s, 3 H), 1.83 (s, 6 H), 3.08 (broad, 1 H).

3-Cyano-4-methyl-6-propynyl-2*H*-pyran-2-one. A solution of freshly prepared sodioethyl cyanoacetate [ethyl cyanoacetate (0.54 g) and excess sodium hydride (50% dispersion in oil, washed with pentane before use)] in benzene-DMF (1:1) was added dropwise to a solution of **1a** (0.5 g) in dry benzene (10 ml) at 5°. The dark red solution was stirred at 25° for 90 min, poured into ice-cold 2% acetic acid, and extracted with chloroform (3 × 100 ml). The extracts were washed in turn with water, saturated sodium bicarbonate, and saturated salt solution and finally filtered through anhydrous sodium sulfate. Removal of the chloroform yielded a viscous, dark red oil which was chromatographed on silica gel with chloroform as the eluting solvent. The middle fractions gave a reddish solid, which on recrystallization from ligroin–chloroform and sublimation at 95° (0.5 mm) yielded a yellow solid: mp 137–138°; ir ($CHCl_3$) 2265, 2250 (C≡N, C≡C), 1745 (C=O), 1615, 1540 (C=C), 1120 (=CO), 640 cm^{-1} (cis C=C); nmr ($CDCl_3$) δ 2.2 (s, 3 H), 2.45 (s, 3 H), 6.65 (s, 1 H).

Anal. Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.08. Found: C, 69.12; H, 4.12.

3-Carboethoxy-4-methyl-6-propynyl-2*H*-pyran-2-one. A freshly prepared solution of diethylsodio malonate [0.8 g of diethyl malonate and 0.3 g of sodium hydride dispersion (50% in oil, washed with pentane before use)] in dry benzene was added dropwise to a solution of **1a** (0.5 g) in benzene at 5° under a nitrogen atmosphere. When the addition was completed, the mixture was stirred at 5° for 30 min and then poured into cold 2% acetic acid. Work-up yielded a red oil which was chromatographed on silica gel with ligroin–ethyl acetate (2:1) as the eluting solvent. The late fractions yielded the pure pyranone as a yellow oil: ir (CCl_4) 2225 (C≡C), 1745 (C=O), 1630 (C=C), 1265 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.37 (t, 3 H), 2.07 (s, 3 H), 2.2 (s, 3 H), 4.38 (q, 2 H), 6.2 (s, 1 H); mass spectrum *m/e* (rel intensity) 220 (P^+, 70), 192 (100), 175 (70), 164 (70), 148 (50), 120 (50).

1-(2-Methyl-3,4,5,6-tetraphenylphenyl)-but-2-yn-1-one. Dipropynyl ketone (1.0 g) and tetracyclone (3.85 g) were refluxed in *o*-dichlorobenzene under nitrogen for 24 hr. The reaction mixture was then poured into 100 ml of hexane, cooled to −80° for 5 min, and then allowed to stand at 0° for 1 hr. The solid (2 g) which deposited was recrystallized from hexane–dichloromethane to give 1.0 g of an off-white solid: mp 234–235°; ir (KBr) 2200 (C≡C), 1650 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.78 (s, 3 H), 2.16 (s, 3 H), 6.78 (d, 10 H), 7.07 (s, 10 H); uv (99.5% ethanol) λ_{max} 280 nm (ϵ

7300), 236 (33,200).

Anal. Calcd for $C_{35}H_{26}O$: C, 90.87; H, 5.67. Found: C, 90.79; H, 5.94.

1-(Pentaphenylphenyl)-3-phenylprop-2-yn-1-one. Diphenyl ethynyl ketone (1.15 g) and tetracyclone (1.9 g) were refluxed in *o*-dichlorobenzene under nitrogen for 24 hr. The resulting brown-red solution was cooled to 25°, poured into cold hexane (100 ml), and kept at 0° for 2 hr. The brown solid which precipitated was recrystallized several times from dichloromethane–methanol to give 1.0 g of an off-white solid: mp 279–281°; ir (KBr) 2210 ($C{\equiv}C$), 1645 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.86, 7.1, 7.25 (m, 10 H); uv (ethanol) λ_{max} 310 nm (ϵ 12,400), 280 (20,500), 240 (51,700), 226 (49,000); mol wt (osmometric in benzene) 585 (calcd, 587).

Anal. Calcd for $C_{45}H_{30}O$: C, 92.12; H, 5.15. Found: C, 91.95; H, 5.14.

Registry No.—**1a,** 34793-66-3; **1a** 2,4-DNP, 50278-05-2; **1b,** 15814-30-9; 3-propynyl-5-methylpyrazole, 50278-07-4; hydrazine hydrate, 10217-52-4; 2,4-dinitrophenyl)-3-propynyl-5-methylpyrazole, 50278-08-5; 2-(*o*-carboxyanilino)hept-2-en-5-yn-4-one, 50278-09-6; anthranilic acid, 118-92-3; *N*-(*o*-carboxyphenyl)-2,6-dimethyl-4-pyridone, 50278-10-9; *m*-aminobenzolic acid, 99-05-8; *N*-(*m*-carboxyphenyl)-2,6-dimethyl-4-pyridone, 50278-11-0; 2-(*m*-carboxyanilino)hept-2-en-5-yn-4-one, 50278-12-1; 2-(3,4-xylidino)-hept-2-en-5-yn-4-one, 50278-13-2; 3,4-xylidine, 95-64-7; *N*-(3,4-dimethylphenyl)-2,6-dimethylpyridone, 50278-14-3; 2,6-bis(*o*-aminobenzenethio)hepta-2,5-dien-4-one, 50278-15-4; *o*-aminobenzenethiol, 137-07-5; 2,6-bis(*p*-tolylthio)hepta-2,5-dien-4-one, 50278-16-5; *p*-toluenethiol, 106-45-6; 2,6-bis(*p*-chlorobenzenethio)hepta-2,5-dien-4-one, 50278-17-6; *p*-chlorobenzenethiol, 106-54-6; 2,6-diethoxy-2,5-dien-4-one, 50278-18-7; 2,6-dimethoxy-2,5-dien-4-one, 50278-19-8; 2,6-dimethyl-4-pyrone, 1004-36-0; 2,6-dimethyl-4*H*-thiapyran-4-one, 1073-80-9; 4-methylhepta-2,5-diyn-4-ol, 32156-89-1; iodomethane, 74-88-4; thiourea, 62-56-6; sodioethyl cyanoacetate, 18852-51-2; 3-cyano-4-methyl-6-propynyl-2*H*-pyran-2-one, 50278-24-5; diethylsodio malonate, 996-82-7; 3-carboethoxy-4-methyl-6-propynyl-2*H*-pyran-2-one, 50278-26-7; *o*-dichlorobenzene, 95-50-1; 1-(2-methyl-3,4,5,6-tetraphenyl)but-2-yn-1-one, 50278-27-8; 1-(pentaphenylphenyl)-3-phenylprop-2-yn-1-one, 50278-28-9; tetracyclone, 479-33-4.

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The Photochemistry of (−)-*trans*-Verbenone Epoxide

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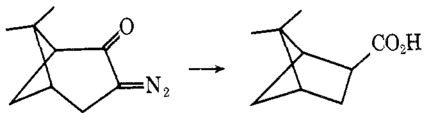
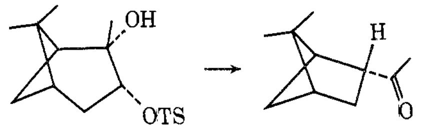
In pursuance of our interest in the development of methods for the synthesis of compounds of the bicyclo[2.1.1]hexane series,[1,2] we have turned our attention to the ring contraction of bicyclo[3.1.1]heptanes.

Two methods have been developed previously based on this model, one of which involved the photochemical ring contraction of the diazo ketone **1**,[3] while the other utilized the base-catalyzed rearrangement of *cis*-pinene glycol monotosylate (**2**).[4,5]



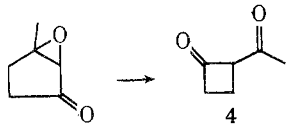
1



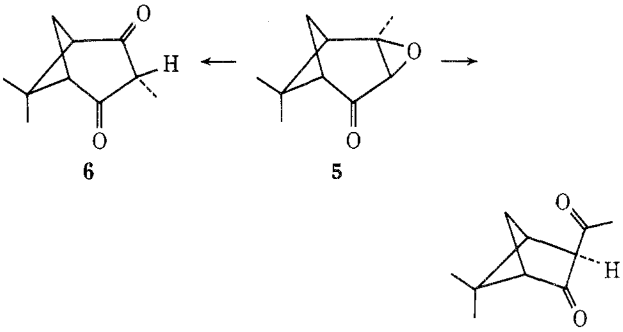
2

A reaction which has received relatively little attention as a ring contraction method is the photochemical rearrangement of α,β-epoxy ketones. Extensive studies of this reaction in steroid systems have shown that β-diketones can be generated in good yields, where product formation occurs by stereospecific shift of a β substituent to the α position.[6] Generally, yields are better in those systems which form readily enolizable β-diketones, as nonenolic diketones are relatively susceptible to further photochemical reaction by photocleavage processes.[7]

The possibility that the photochemical rearrangement of α,β-epoxy ketones might be useful for the generation of the strained bicyclo[2.1.1]hexanone ring system was supported by the reasonably efficient ring contraction of the epoxy ketone **3** to the cyclobutanone **4**.[8] Verbenone epoxide (**5**) appeared to be a convenient compound to examine as a test of the hypothesis, especially with regard to competition between transfer of the methyl group to give compound **6** and ring contraction to give **7**.



3 **4**



6 **5** **7**

Results

Irradiation of a solution of (−)-**5**[9] (*ca.* 0.01 *M*) in pentane or benzene with a 450-W medium-pressure mercury arc lamp for 12 hr produced a mixture of starting material and three volatile products in 50% yield. Analysis by gas chromatography showed that starting material comprised 56% of the mixture. Isolation of the products by preparative glc and analysis by spectroscopic methods allowed the identification of the enol lactone **8** (30%), its isomer **9** (2%), and an inseparable 3:1 mixture of the ring-contracted diketones **7** (12%). The enol lactone **8**, mp 46–47°,