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≡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

Thomas Gibson

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

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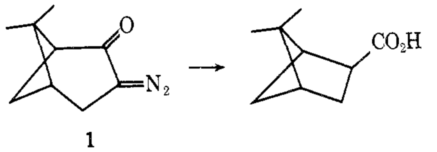
In pursuance of our interest in the development of methods for the synthesis of compounds of the bicyclo[2.1.1]hexane series,[1,2] we have turned our attention to the ring contraction of bicyclo[3.1.1]heptanes.

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]



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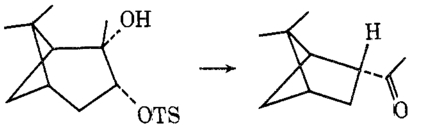
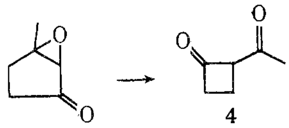


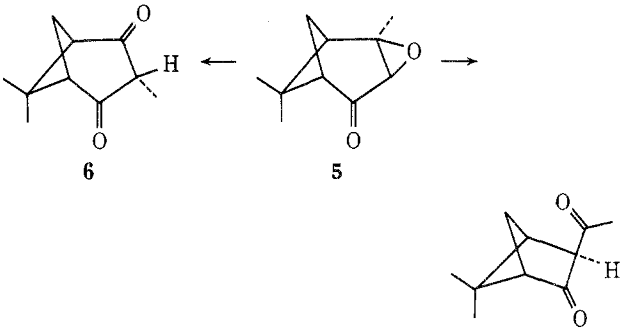
2

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**.



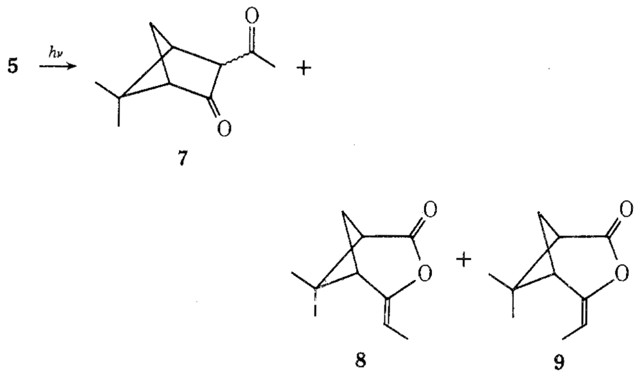
3 4



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°,



7

8 9

Table I

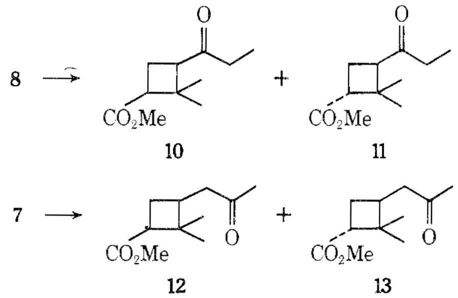
Solvent	Concn, *M*	Time, hr	Yield,[a] %	5	8	9	7
Benzene[b,c]	4.5×10^{-2}	12	50	56	30	2	12
Benzene[b,c,e]	1.6×10^{-2}	12	78	16	71	6	7
Acetonitrile[b,d,e]	4.8×10^{-2}	100	70	19	46	4	31
Acetonitrile[d,f]	3.1×10^{-2}	72	80	83			17

[a] Distilled volatile product. Relative proportions of individual products were determined by area measurement of glc peaks. [b] 450-W mercury lamp, Hanovia 679-A36. [c] Vycor. [d] Pyrex. [e] 4 equiv of 1,3-pentadiene added. [f] 300-nm lamps in Rayonet reactor.

showed infrared bands at 5.61 and 5.89 μ, and nmr signals at τ 8.34 and 5.47. The latter signals, which appear as a doublet and a quartet, can be atributed to the protons of the methyl group on the double bond and to the olefinic proton, respectively. The isomeric enol lactone **9** showed similar data. The assignment of configuration to **8** and **9** is based on the chemical shifts of the olefinic protons. Using the additive increment values determined by Matter, *et al.*,[10] the chemical shifts for the olefinic protons in **8** and **9** were calculated to be τ 5.16 and 4.93, respectively. The observed values of τ 5.47 and 4.79 for the major and minor products are in relatively good agreement with these values.

The mixture of isomers **7** showed two maxima in the carbonyl region of the infrared spectrum at 5.68 and 5.86 μ. These values are in good agreement with those expected for the isolated carbonyl groups in the bicyclo[2.1.1]hexanone[2] and acetyl moieties, respectively. That no extensive enolization of the two carbonyl groups in **7** occurs is reasonable in view of the difficulty of introduction of a double bond into the bicyclohexane framework.[11] The presence of a mixture of epimers in **7** was indicated by the nmr spectrum, which showed, among other signals, two singlets at τ 9.03 and 9.29 with relative weights of 3:1, respectively. These are assigned to the endo methyl groups in the two isomers, but we could not find a sufficient precedent to assist in the specific assignment to the two isomers.[12] All attempts to separate the two diketones by glc methods were unsuccessful.

Further evidence for the structures of compounds **7–9** was obtained as follows. Treatment of the enol lactone **8**, isolated by preparative glc and contaminated with about 25% of verbenone epoxide, with sodium methoxide in anhydrous methanol produced the keto esters **10** and **11** in good yield in a ratio of approximately 2:1. The verbenone epoxide was recovered unchanged, and its unreactivity under these conditions was confirmed by a control experiment. Treatment of the mixture of isomers **7** under similar conditions produced the keto esters **12** and **13** in a ratio of 7:3. Since the keto esters are formed under equilibrating conditions, it is expected that the pseudo-diequatorial cis isomers should predominate, and the ratios of products observed in these reactions are closely similar to those obtained in similar systems. For example, the equilibrium mixture of methyl *cis*- and *trans*-pinonate is reported to contain 75% of the cis isomer.[13] The nmr spectra of the isomeric keto esters are also in good agreement with their assignments. Subramanian and Krishna Rao have established the effects of substituents in 2,2-dimethyl 1,3-disubstituted cyclobutanes on the chemical shifts of the quaternary methyl groups.[13] Application of the rules derivable from their data to the keto esters **10–13** shows that in each instance the cis diequatorial isomer is formed in major amount. A detailed presentation of the spectroscopic data for all isolated compounds is given in the Experimental Section.



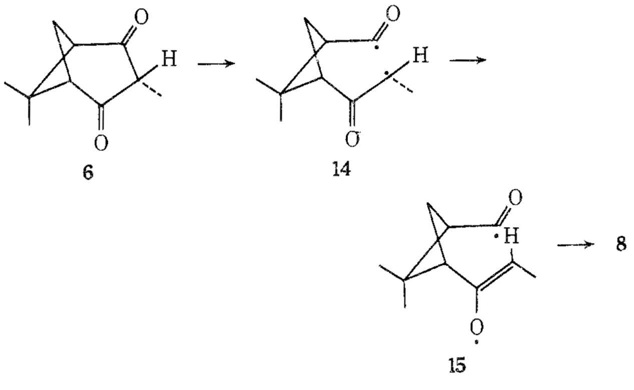
10 11

12 13

In an effort to detect the transient formation of the diketone **6** which would result from methyl transfer, the irradiation of verbenone epoxide was carried out in the presence of a 3-molar excess of 1,3-pentadiene. Previous work on similar systems has shown that conversion of nonenolic β-diketones to enol lactones proceeds by way of the n-π^* triplet state and can be quenched by 1,3-pentadiene.[7] However, we could obtain no evidence for the formation of **6** under these conditions, although it was found that the formation of products **7–9** took place more cleanly and rapidly. Furthermore, when the light was filtered with a Pyrex sleeve, the rate of disappearance of verbenone epoxide dropped considerably, but the relative yield of the ring-contraction products increased. Finally, when the irradiation was performed with a bank of lamps emitting at 300 nm, only the ring-contracted diketones were formed, although very slowly. The results are presented in Table I.

Discussion

No direct evidence could be obtained for the formation of the β-diketone **6** during the course of the irradiations. The inability to quench the formation of the enol lactones with 1,3-pentadiene shows that, if **6** is indeed an intermediate in this process, it either does not rearrange by way of a triplet excited state or the reaction is very rapid with respect to the quenching process.[14] However, support for the presence of a symmetrical intermediate such as **6** was provided by the lack of optical rotation of **8**. Assuming that **6** is an intermediate, its photocleavage would generate the diradical **14**. Rotation of the methyl group at the

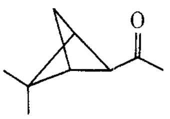


6 14

15

radical site of **14** during conversion to diradical **15** should occur in such a way as to minimize interaction with the bulky *gem*-dimethyl substituted bridge, leading to the trans stereochemistry as depicted. Closure would then generate **8** as the initial product in agreement with the stereochemical conclusion reached on the basis of the nmr spectra.

The apparent photostability of **7** under these conditions is surprising, since nonenolic β-diketones such as these are generally observed to be much more reactive than their enolic counterparts. Also, since transfer of the substituent has been shown to be stereospecific in rigid systems,[6] only the trans isomer would be expected to form in the rearrangement. One possible process by which epimerization could occur would involve photocleavage of the C_2–C_3 bond of **7** followed by rotation of the C_3–C_4 bond and recombination. This process gains some support from the observation that the base peak in the high-resolution mass spectrum of the mixture of diketones results from loss of carbon monoxide, which can be most easily rationalized by formation of the bicyclo[1.1.1]pentane derivative **16**. In fact, a monoketone with molecular ion corresponding to that of **16** was isolated in trace amount from one irradiation run, but too little material was obtained to determine its structure. No compound with structure **17**, the product which would result from a process analogous to the rearrangement of **6**, was observed in any of these experiments. The lack of formation of the bicyclohexanone **18** during methoxide treatment of **7** is easily rationalized by the lack of stabilization of the enolate anion in the strained ring system, by the same argument as that applied to the interpretation of the infrared spectra of these compounds.



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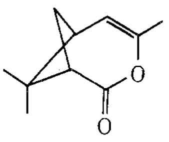

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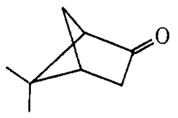

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Experimental Section[16]

In a typical irradiation, a solution of 0.965 g of verbenone epoxide, $[\alpha]_D - 114°$, in 130 ml of pentane was irradiated through Vycor glassware with a 450-W medium-pressure mercury arc lamp for 12 hr. The solution was flushed with argon for 0.5 hr before irradiation and maintained under argon for the duration of the reaction. Removal of solvent and bulb-to-bulb distillation of the residue gave 0.465 g, bp (bath) 65–75° (1.2 mm). Gc analysis on the SE-30 column showed the presence of a leading shoulder under the verbenone epoxide peak and two resolved peaks, the latter two being formed in about 30 and 2%, respectively. On the BDS column only two peaks appeared in the ratio of 88:12. Verbenone epoxide under these conditions exhibits no decomposition. Collection of the three peaks by preparative gc gave samples for analysis.

Peak 1 (SE-30) was a mixture of verbenone epoxide and **7**.

Peak 2 (SE-30) was **8** (30%), isolated as a solid. Sublimation gave material with mp 46–47°, $[\alpha]_D \sim 0°$, ir 3.27, 5.61, 5.89, and 9.61 μ, and a molecular ion at *m/e* 166. The nmr spectrum showed signals at τ 9.05 (3 H, s), 8.67 (3 H, s), 8.34 (3 H, d, *J* = 6.8 Hz), 8.30 (1 H, d, *J* = 10 Hz), 7.2–7.4 (2 H, m), 5.47 (1 H, q, *J* = 6.8 Hz), and 7.48 (1 H, q, *J* = 5.2 Hz). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.20; H, 8.40.

Peak 3 (SE-30) was **9** (2%), a liquid: ir 5.63, 5.90, and 9.50 μ; molecular ion at *m/e* 166.1005 (calcd for $C_{10}H_{14}O_2$, 166.0994); and nmr signals at τ 9.03 (3 H, s), 8.59 (3 H, s), 8.41 (3 H, d, *J* = 7 Hz), 8.27 (1 H, d, *J* = 9.6 Hz), 7.37 (1 H, dd, *J* = 9.6, 5.8 Hz), 7.22 (1 H, t, *J* = 5.8 Hz), 6.88 (1 H, t, *J* = 5.8 Hz), and 4.78 (1 H, q, *J* = 7 Hz).

Peak 1 (BDS) was a mixture of verbenone epoxide and **8**.

Peak 2 (BDS) was **7** (12%), a liquid: ir 5.68 and 5.86 μ; molecular ion at *m/e* 166.0989 ($C_{10}H_{14}O_2$); and nmr signals at τ 9.29 and 9.03 (3 H, 2 s, ratio 1:3), 8.72 (1 H, d, *J* = 9 Hz), 8.59 (3 H, s), 8.45 (1 H, d, *J* = 8 Hz), 7.68 and 7.63 (3 H, 2 s, ratio 3:1), 7.43 (3 H, m), 6.88 and 6.58 (1 H, s and d, *J* = 5 Hz, ratio 1:3).

Sodium Methoxide Cleavage of 8. To a solution of *ca.* 0.2 g of sodium in 2 ml of dry methanol was added 0.100 g of **8**, which had been isolated by preparative gc and which was contaminated with about 20% of verbenone epoxide. The solution was brought to reflux for 2 hr, cooled, diluted with ether, washed with saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Removal of solvent gave 0.072 g of oil, which was shown by gc analysis on the BDS column to be composed of three materials in the ratio of 21:25:54. The minor constituent was identified as verbenone epoxide. The 25% constituent (**11**) showed ir bands at 5.76 and 5.85 μ, a molecular ion at *m/e* 198.1275 (calcd for $C_{11}H_{18}O_3$, 198.1256), and nmr signals at τ 8.95 (3 H, t, *J* = 7.2 Hz), 8.92 (3 H, s), 8.79 (3 H, s), 7.68 (2, H, q, *J* = 7.2 Hz), 7.23 (1 H, dd, *J* = 6.0, 8.5 Hz), 6.90 (1 H, dd, *J* = 6.7, 8.5 Hz), and 6.31 (3 H, s). The major constituent (**10**) showed ir bands at 5.75 and 5.85 μ, a molecular ion at *m/e* 198.1240 ($C_{11}H_{18}O_3$), and nmr signals at τ 9.14 (3 H, s), 8.96 (3 H, t, *J* = 7 Hz), 8.59 (3 H, s), 7.0–8.25 (6 H), and 6.34 (3 H, s).

Sodium Methoxide Cleavage of 7. To a solution of *ca.* 0.2 g of sodium in 1 ml of methanol was added 37.4 mg of a mixture of isomers of **7** isolated by preparative glc. After reflux for 2 hr, the solution was cooled, diluted with ether, and washed with saturated $NaHCO_3$ solution. After drying over $MgSO_4$, the solvent was carefully evaporated to give 28.6 mg of yellow oil. Gc analysis on the BDS column showed the presence of two peaks in a ratio of 7:3, both of which were isolated by preparative gc. The minor constituent (**13**) showed ir bands at 5.78 and 5.83 μ, a molecular ion at *m/e* 198.1231 ($C_{11}H_{18}O_3$), and nmr signals at τ 8.95 (3 H, s), 8.92 (3 H, s), 8.35 (1 H, m), 7.88 (3 H, s), 7.49 (2 H, m), 7.2–7.7 (3 H), and 6.34 (3 H, s). The major constituent (**12**) showed ir bands at 5.77 and 5.84 μ, a molecular ion at *m/e* 198.1263 ($C_{11}H_{18}O_3$), and nmr signals at τ 9.12 (3 H, s), 8.78 (3 H, s), 7.90 (3 H, s), 7.6–8.2 (3 H), 7.57 (2 H, d, *J* = 2 Hz), 7.26 (1 H, dd, *J* = 10 and 7.8 Hz), and 6.38 (3 H, s).

Registry No.—**(−)-5**, 33967-70-3; **7** (epimer A), 49830-06-0; **7** (epimer B), 49830-07-1; **8**, 49830-08-2; **9**, 49830-09-3; **10**, 49830-10-6; **11**, 49830-11-7; **12**, 49830-12-8; **13**, 49830-13-9.

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(12) Presumably, the chemical shift of the endo methyl group in 5,5-dimethylbicyclo[2.1.1]hexanone could be used to settle this problem, but, unfortunately, the nmr spectrum of this substance does not appear to have been determined.[3]

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(14) The intermediacy of the triplet state in the photoreactions of β-diketones may not be well established, since the work cited to support this hypothesis was carried out in neat 1,3-pentadiene solution.[7] It is known that at high quencher concentration it is possible to quench the singlet state of some systems.[15]

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(16) Melting points were determined on a micro hot stage and are corrected; boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer 257 and 137 spectrophotometers as neat films. Nuclear magnetic resonance spectra were obtained on a Varian Associates HA-100 spectrometer using TMS as an internal reference in $CDCl_3$. Nmr data are recorded in this order: chemical shift (integration, multiplicity where s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and coupling constant in hertz). High-resolution mass spectra were determined with an Atlas SM-1 spectrometer in which exact masses were obtained from element maps. Glc analyses were carried out on a Varian Aerograph Model 202B instrument using thermal conductivity detectors. Columns used were 5 ft × 0.25 in. stainless steel packed with 15% butanediol succinate (BDS) or 15% SE-30 silicone oil on HMDS-treated 60–80 mesh Chromosorb W support. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.