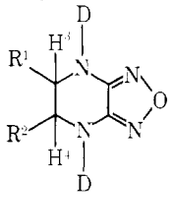
Table V. Preparation and NMR Spectral Data of Furazanopyrazines 7d-f

Compd	Registry no.	Yield,[d] %	Mp, °C	NMR[g] (Me_2SO-d_6 + D_2O) Chemical shift, δ R^1	R^2	H^3	H^4	Coupling constant, Hz $J_{3,4}$	$J_{2,3}$	$J_{2,4}$	J_{Me,H^4}
7d[a]	64163-44-6	84	189-190[e]	7.37	3.16	4.53	3.40	3.5	8.0	12.0	
e[b]	64163-45-7	87	203[f]	7.2-7.4	0.84	4.52	*h*	3.5			6.5
f[c]	64163-46-8	84	234-235[e]	7.0-7.2		4.80		0			

[a] Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.39; H, 4.98; N, 27.71. Found: C, 59.33; H, 5.22; N, 27.38. [b] Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.09; H, 5.59; N, 25.90. Found: C, 61.02; H, 5.52; N, 25.70. [c] Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 68.91; H, 4.83; N, 20.13. [d] These result from the reduction of 5 with sodium borohydride. [e] Recrystallized from benzene. [f] Recrystallized from benzene/petroleum ether. [g] Structure



[h] This peak can not be determined because of overlap with one of water.

of **6** with sodium borohydride, but compounds **6** were inert to lithium aluminum hydride. On the other hand, furazanopyrazines **5** were reduced with lithium aluminum hydride, as well as sodium borohydride, to yield furazanopiperazines **7**. The NMR spectra of **7** give the same results as those of **8**.

Recently, syntheses of 3,4-diamino-1,2,5-thiadiazole and 1,2,5-thiadiazolo[3,4-*b*]pyrazines were reported,[9] and the latter would be expected to give diaminopyrazines **1** under reductive conditions.

Experimental Section

All melting points were determined in a capillary and are corrected. NMR spectra were measured on a JEOL Model JNM-MH-100 instrument with tetramethylsilane as an internal standard.

Condensation of 3,4-Diaminofurazan (3)[10] or 4,5-Diamino-2-phenyl-1,2,3-triazole (4)[11] with 1,2-Dicarbonyl Compounds 2. The results are summarized in Tables I and II, respectively.

Method A. A solution of **3** or **4** (0.01 mol) and **2** (0.011 mol) in 20 mL of acetic acid/ethanol (1:3 v/v) was refluxed for 2 h. After cooling to room temperature, the precipitate which formed was collected by filtration and recrystallized to afford **5** or **6**, respectively.

Method B. A mixture of **3** (0.01 mol), **2f** (0.01 mol), and boron trifluoride etherate (1 mL) was heated at 120–130 °C for 10 min. The precipitate that formed after cooling to room temperature was collected by filtration, washed with water, and recrystallized from ethanol to provide **5f**.

Method C. A warm (~80 °C) solution of **2** (bisulfite salt, 0.011 mol) in 20 mL of water was added to a stirred solution (at 80 °C) of **4** in 50 mL of water. The resulting solution was maintained at 80 °C for 1 h. Sodium carbonate (0.011 mol) was added to the cooled solution, and the precipitates were collected by filtration. The filtrate was extracted with three 10-mL portions of ether, and the extracts were washed with water, dried over magnesium sulfate, and evaporated. The combined products were recrystallized to give **6**.

Hydrogenation of 5 or 6 in the Presence of Palladium Catalyst. A solution of **5** or **6** (0.01 mol) in 30–200 mL of ethyl acetate, except for **6c** where tetrahydrofuran was used, was hydrogenated in the presence of 10% palladium on carbon (~2g) under atmospheric pressure until the uptake of hydrogen ceased (~20 h) and then was filtered. The filtrate was evaporated to dryness under reduced pressure, and the residue was recrystallized to give **1** or **8**, respectively. These results are summarized in Tables III and IV, respectively.

Reduction of 5 or 6 with Sodium Borohydride. A mixture of **5** or **6** (3 mmol) and sodium borohydride (6 mmol) in 50 mL of ethanol was refluxed for 1 h. A small amount of acetic acid was added to the cooled mixture to decompose excess sodium borohydride, and the mixture was then evaporated to dryness under reduced pressure. The residual solid was triturated with diluted aqueous sodium hydroxide, filtered, and recrystallized to provide **7** or **8**, respectively. The results of **7** are summarized in Table V.

Reduction of 5 with Lithium Aluminum Hydride. A solution of lithium aluminum hydride (6 mmol) in 20 mL of dry tetrahydrofuran was added dropwise to a solution of **5** (3 mmol) in 10 mL of the same solvent, and the mixture was refluxed for 2 h. Excess lithium aluminum hydride was decomposed by the addition of water and diluted aqueous sodium hydroxide. The resulting solution was evaporated to dryness under reduced pressure, and the residue was extracted with hot chloroform. The solution was evaporated, and the residue was recrystallized to afford **7**.

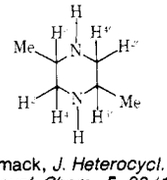
The procedure for reaction of **6** with lithium aluminum hydride is as follows. A mixture of **6** (3 mmol) and lithium aluminum hydride (15 mmol) in 100 mL of dry dioxane was refluxed for 5 h under nitrogen atmosphere and then treated in the predescribed manner to recover a 95–97% yield of **6**.

Acknowledgment. The authors are grateful to Dr. T. Nakagawa for his helpful suggestions.

Registry No.—**2a,** 107-22-2; **2b,** 78-98-8; **2c,** 431-03-8; **2d,** 1074-12-0; **2e,** 579-07-7; **2f,** 134-81-6; **3,** 17220-38-1; **4,** 53543-28-5; **2a** bisulfite salt, 18381-20-9; **2b** bisulfite salt, 64163-47-9.

References and Notes

(1) Part 2: N. Sato and J. Adachi, *J. Org. Chem.*, this issue, companion paper.
(2) J. Adachi and N. Sato, *J. Org. Chem.*, **37,** 221 (1972).
(3) F. G. McDonald and R. C. Ellingson, *J. Am. Chem. Soc.*, **69,** 1034 (1947).
(4) R. C. Ellingson and R. L. Henry, *J. Am. Chem. Soc.*, **70,** 1257 (1948).
(5) R. H. Martin and Z. Tarasiejska, *Bull. Soc. Chim. Belg.*, **66,** 136 (1957).
(6) Hydrogenolytic cleavage of the furazan ring has been also reported on conversion of furazano[3,4-*b*]pyrimidine to 4,5-diaminopyrimidine derivatives; E. C. Taylor, S. F. Martin, Y. Maki, and G. P. Beardsley, *J. Org. Chem.*, **38,** 2238 (1973).
(7) J. L. Sudmeier, *J. Phys. Chem.*, **72,** 2344 (1968).
(8)



(9) A. P. Komin and M. Carmack, *J. Heterocycl. Chem.*, **13,** 13 (1976).
(10) M. D. Coburn, *J. Heterocycl. Chem.*, **5,** 83 (1968).
(11) J. Thiele and K. Schleussner, *Justus Liebigs Ann. Chem.* **295,** 138 (1897).

Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones Related to Epimaalienone[1]

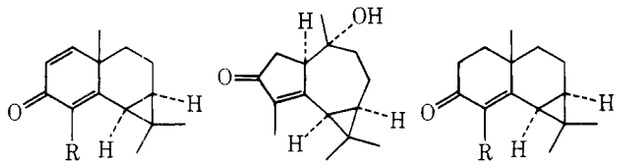
Drury Caine,* Howard Deutsch, and John T. Gupton III

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received June 27, 1977

Recently, we reported that the tricyclic cross-conjugated cyclohexadienone **1a,** derived from epimaalienone, was pho-

tochemically converted into the tricyclic hydroxyenone **2** on irradition in aqueous acetic acid.[2] Compound **2** was utilized in a synthesis of (−)-4-epiglobulol and (+)-4-epiaromadendrene.[2] Since examples of successful photochemical rearrangements of cross-conjugated cyclohexadienones containing a conjugated cyclopropane ring are rare,[3,4] further investigation of the photochemistry of compounds of type **1** appeared to be of interest. In this paper we wish to report the results of irradiation of **1a** in the aprotic solvent dioxane and of the related ring-A unsubstituted dienone **1b** in both dioxane and glacial acetic acid.

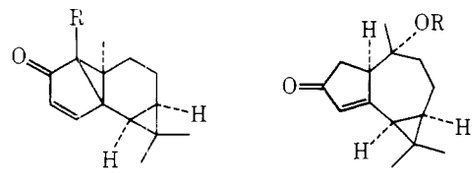


1a, R = CH_3
b, R = H

2 **3**

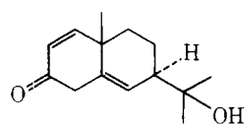
The synthetic route employed for the preparation of **1b** was similar to that used for the synthesis of **1a**,[2,5] except that the phenylselenenylation–selenoxide elimination procedure,[6] involving the conversion of enone **3** to the homoannular lithium dienolate with lithium diisopropylamide (LDA) in THF at −70 °C,[7] was used instead of oxidation with DDQ (dichlorodicyanoquinone) in dioxane.

Irradiation of a dilute solution of **1a** in anhydrous dioxane using a 2537-Å light source for 2.7 h at room temperature led to the formation of a single photoproduct which was isolated in 52% yield after column chromatography on silica gel. The spectral properties of this compound (see Experimental Section) were completely consistent with the tetracyclic enone structure **4a.** Under similar conditions irradiation of dienone **1b** for 9.0 h produced a single photoproduct having spectral properties consistent with structure **4b** in 60% yield (based upon unrecovered starting material).[8]



4a, R = CH_3
b, R = H

5a, R = H
b, R = $COCH_3$



6

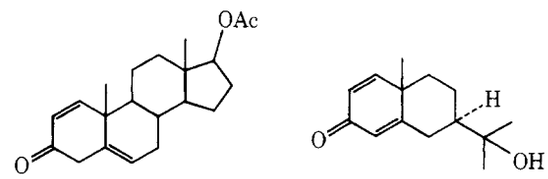
Irradiation of **1b** in 45% aqueous acetic acid gave erratic results. A compound having spectral properties consistent with hydroxyenone **5a** was apparently formed in low yield in some runs, but in others the NMR and IR spectral properties of the photolysis mixture indicated that the major component had the ring-opened structure **6.** Compound **6** was isolated by chromatography when a dilute solution of **1b** was allowed to stand in 45% aqueous acetic acid in the dark for 1.0 h. Apparently, in aqueous acetic acid, 1,6 addition of water to the vinylogous cyclopropyl ketone system in **1b** is an especially favorable process which largely prevents photochemical rearrangement of the dienone. The inconsistent results obtained during irradiation of **1b** were presumably related to variations in time between dissolution of the sample and the start of the irradiation period.

The structural assignment for **6** is based upon its NMR spectral and chemical properties (see Experimental Section). The absorption pattern for the methylene protons at C-4 was similar to that observed for the deconjugated steroidal dienone **7.**[9] The lower field absorption at δ 3.18 was expected to be due to the axial (4β) proton, and this was strongly supported by a deuterium-exchange experiment. Thus, when **6** was mixed with 0.01 equiv of NaOD in acetone-d_6/D_2O, the peak at δ 3.18 rapidly disappeared, whereas the absorption at δ 2.82 simply changed from a doublet to a broad singlet. Axial protons α to ketones generally exchange much faster than equatorial protons.[10]

The deconjugated dienone **6** was converted to conjugated dienone **8** on treatment with methanolic sodium hydroxide. The structural assignment for **8** followed readily from the close similarity of its NMR and IR spectral properties to those of related cross-conjugated dienones, e.g., **1b.**

When dienone **1a** was treated with aqueous acetic acid under conditions similar to those described for **1b,** its slow conversion into a product apparently related to **6** was observed. However, the rate of this reaction was much too slow to be competitive with the normal dienone photochemical rearrangement.

Photochemical rearrangement of **1b** could readily be accomplished using glacial rather than aqueous acetic acid as the solvent. Thus the acetoxyenone **5b** was produced in 71% yield when a dilute solution of **1b** in glacial acetic acid was irradiated for 0.75 h using ultraviolet light with a wavelength greater than 3000 Å. No other products were isolated from the photolysis.



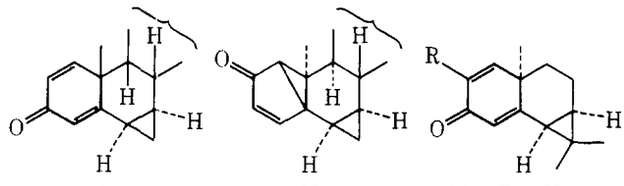
7 **8**

These results show that the predominate modes of photochemical rearrangement of dienones of type **1** parallel those which are commonly observed for related systems in which the cyclopropane ring is absent.[11] The steroid derivative *O*-acetyl-1-dehydro-6β,7β-methylenetestosterone (**9**), which like **1** has a cis relationship between the cyclopropane ring and the angular methyl group, has been reported to be readily converted into the bicyclohexenone derivative **10** on irradiation in dioxane at 2537 Å.[4] The photolability of dienones of types **1** and **9** is in marked contrast to that of the isomeric systems **11** and **12,** respectively, which have a trans relationship between the cyclopropane ring and the angular methyl substituent. For example, dienone **11a** has been found to be stable on direct irradiation in aprotic[12] and protic media,[3,13] while **12** was shown to be unchanged on irradiation in dioxane.[4]

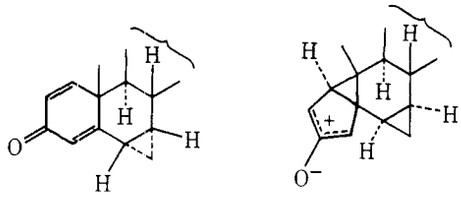
It has been suggested[11c] that the conversion of **9** into **10** proceeds via the generally accepted zwitterionic intermediate **13,** which would have a trans relationship between the adjacent cyclopropane rings on the six-membered B RING/ The failure of **12** to undergo an analogous rearrangement was attributed to the fact that the zwitterionic intermediate corresponding to **13** would be highly strained because the two adjacent cyclopropane rings on the six-membered B ring would have a cis relationship to each other. A similar explanation could account for the photostability of **11a.** However, it is not obvious that the strain associated with adjacent cis cyclopropane rings would be of such magnitude as to preclude the formation of an intermediate related to **13.** We have shown that the 2-carboxydienone **11b** undergoes rearrangement to 5/7-fused products having the cyclopropane ring intact on irradiation in dioxane and aqueous acetic acid.[3,14] However, whether the presence of the carboxyl group in some way pro-

vides stabilization of the zwitterionic intermediate derived from **11b** or allows an alternative rearrangement pathway to intervene is not clear.

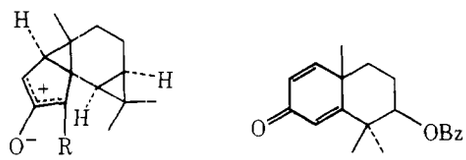
The photochemical behavior of **1a** and **1b** may be explained in terms of the zwitterionic intermediate **14** which is analogous to **13** derived from the steroidal system.[15] In dioxane the usual symmetry-allowed 1,4-sigmatropic rearrangement can lead to products of type **4**, while in aqueous or glacial acetic acid protonation of **14** on oxygen followed by solvolytic cleavage



9 **10** **11a**, R = H; **b**, R = CO_2H



12 **13**



14a, R = CH_3; **b**, R = H **15**

of the 5,10 bond would lead to fused-ring products such as **2** or **5**. Normally, ring-A unsubstituted dienones yield mixtures of fused-ring and spirocyclic products because solvolytic cleavage of both bonds of the cyclopropane ring of the mesoionic intermediate derived from protonation of **14** is possible. However, in the case of **14**, the topside attack of solvent at C-10, which would lead to a spirocyclic hydroxy ketone, is hindered by the dimethylcyclopropane ring.[16] A similar steric argument has been used to account for the fact that a spirocyclic hydroxy ketone was not produced on irradiation of the ring-A unsubstituted dienone **15**.[17]

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were determined using a Perkin-Elmer Model 457 instrument, NMR spectra (Me_4Si internal standard) were obtained using a Varian Model T-60 spectrometer, and ultraviolet spectra were measured using a Beckman Model 25 instrument. Mass spectra were determined with a Hitachi Perkin-Elmer RMU-7 or a Varian Model M-66 spectrometer. Combustion analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga.

For column chromatography either Florisil (Fisher Scientific Co.) or silica gel (Grace, 60–200 mesh; deactivated with acetone before use) were employed as adsorbants.

A Hanovia 450-W high-pressure mercury lamp housed in a Pyrex probe was used for irradiation in acetic acid. A Hanau NK 20 7-W low-pressure mercury lamp was used for all irradiations in dioxane. When either solvent was used, dry nitrogen was bubbled through the reaction vessel for a few minutes preceeding and during the period of irradiation.

Preparation of 4-Normethyl-1,2-dehydroepimaalienone (1b). (−)-2-Carone was reacted with methyl vinyl ketone according to the procedure of Caine and Gupton.[5] (−)-3-(2-Oxobutan-4-yl)-2-carone (bp 100–135 °C) (0.30 °C (0.30 mm)) was obtained in 64% yield and showed the following properties: UV λ_{max} (95% EtOH) 220 nm (ϵ 3540); IR (CCl_4) 1720, 1690 cm^{-1}; NMR δ (CCl_4) 0.85 (s, 3 H), 1.05 (s, 3 H), 1.15 (s, 3 H), 2.10 (s, 3 H); MS *m/e* (70 eV) 222.161 (EMC = 222.162).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.51; H, 9.96.

The product of the previous reaction (23.25 g, 0.105 mol) was added dropwise to 200 mL of anhydrous saturated ethanolic hydrogen chloride at 5 °C. After warming to room temperature and stirring for 30 min, the reaction mixture was poured into 200 mL of ice water and extracted with $CHCl_3$. Removal of the solvent gave 24.0 g (95%) of *cis*-6-(2-chloropropan-2-yl)-3-oxo-9-methyl-Δ^4-octahydronaphthalene: mp 106–107 °C (from hexane); IR (CCl_4) 1675, 1620 cm^{-1}; NMR δ (CCl_4) 1.25 (s, 3 H), 1.60 (s, 6 H), 5.65 (broad s, 1 H); MS *m/e* (70 eV) 204 (M^+ − HCl).

Anal. Calcd for $C_{14}H_{21}OCl$: C, 69.84; H, 8.79. Found: C, 69.72; H, 8.80.

To a suspension of 10.7 g (ca. 0.25 mol) of sodium hydride in 50 mL of dry dimethoxyethane (DME) was added 20.4 g (0.085 mol) of the above chloroenone in 500 mL of dry DME. The mixture was heated at reflux overnight, and 25 mL of ethanol was added. Removal of the solvents and partitioning between ether and water followed by distillation yielded 11.8 g (68%) of an amber oil, **3**: bp 109–119 °C (0.08 mm); UV λ_{max} (95% EtOH) 277 nm (ϵ 18 200); IR (CCl_4) 1663, 1592 cm^{-1}; NMR δ (CCl_4) 1.10 (s, 3 H), 1.16 (s, 3 H), 1.20 (s, 3 H), 5.86 (s, 1 H); MS *m/e* (70 eV) 204.151 (EMC = 204.151). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.10; H, 9.88.

Although compound **3** could be converted to **1b** by DDQ oxidation, as reported for **1a**,[2] the yields were erratic and low. In the preferred method, 5.00 g (0.0245 mol) of **3** in 25 mL of dry THF was added slowly to 1.2 equiv of lithium diisopropylamide (LDA) in 100 mL of THF in a dry ice–acetone bath. After stirring for an additional 30 min at this temperature, a solution prepared from 4.59 g (0.0147 mol, 1.2 equiv) of diphenyl diselenide and 0.76 mL (2.35 g, 0.0147 mol) of bromine in 25 mL of THF was added quickly, and the reaction mixture was allowed to warm to room temperature. The crude phenyl selenide was isolated and dissolved in 75 mL of methylene chloride. To this solution was added, over a 20-min period, 6.66 g (0.0588 mol, 2.4 equiv) of 30% aqueous hydrogen peroxide dissolved in 20 mL of water. Slight external cooling was necessary to maintain the temperature at 25 °C. Extraction of the methylene chloride layer with aqueous $NaHCO_3$ and removal of the solvent yielded 5.1 g of yellow oil. Chromatography on Florisil (20% ether in hexane) afforded 3.00 g (60%) of crystalline dienone **1b**: mp 87–88 °C (from pentane); UV λ_{max} (95% EtOH) 243 (ϵ 10 000), 303 nm (8600); IR (CCl_4) 1660, 1622, 1588 cm^{-1}; NMR δ (CCl_4) 1.18 (s, 6 H), 1.25 (s, 3 H), 5.95 (q, J = 1.5, 10 Hz, 1 H), 6.13 (broad, $J \sim 1.5$ Hz, 1 H), 6.72 (d, J = 10 Hz, 1 H); MS *m/e* (70 eV) 202.139 (EMC = 202.136).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.02; H, 8.99.

Irradiation of 1b in Dioxane. A 375-mg sample of dieneone **1b** was dissolved in 100 mL of dry dioxane and irradiated for 9.0 h. The solvent was removed under reduced pressure and the crude material chromatographed on Florisil. Elution with 10% ether in hexane afforded 133 mg (60%, based on unrecovered starting material) of **4b**: mp 58–60 °C (from pentane); IR (CCl_4) 1700 cm^{-1}; NMR δ (CCl_4) 1.07 (s, 6 H), 1.20 (s, 3 H), 5.78 (d, J = 6 Hz, 1 H), 7.37 (d, J = 6 Hz, 1 H).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.09; H, 8.97.

Further elution with 50% ether in hexane afforded 149 mg of starting material.

Irradiation of 1a in Dioxane. A solution of 516 mg of **1a** was irradiated for 2.7 h in 100 mL of dry dioxane. After removal of solvent, the residue was chromatographed on silica gel. Elution with hexane yielded 267 mg (52%) of **4a**: bp 78–105 °C (bath temperature), 0.05 mm; UV λ_{max} (95% EtOH) 220 (ϵ 5450), 280 nm (2490), IR (CCl_4) 1695, 1651 cm^{-1}; NMR δ (CCl_4) 0.98 (s, 3 H), 1.03 (s, 3 H), 1.12 (s, 3 H), 1.38 (s, 3 H), 5.84 (d, J = 6 Hz, 1 H), 7.34 (d, J = 6 Hz, 1 H); MS *m/e* (70 eV) 216.155 (EMC = 216.151).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.09; H, 9.40.

Reaction of 1b with Aqueous Acetic Acid. A solution of 100 mg (0.495 mm) of **1b** in 10 mL of 45% aqueous acetic acid was allowed to stand for 1.0 h. The reaction mixture was poured into excess aqueous sodium bicarbonate and extracted with 50 mL of ether. After drying and solvent removal, approximately 110 mg (101%) of yellow oil was isolated. After chromatography on Florisil (60% ether in hexane), 100 mg (92%) of **6** was isolated and showed the following properties: mp 75–76 °C (from ether/pentane); IR (CCl_4) 3310, 2970, 2920, 2860, 1678, 1615 cm^{-1}; NMR δ (CCl_4) 1.02 (s, 3 H), 1.10 (s, 3 H), 1.21 (s, 3 H), 2.82 (d, J = 17 Hz, 1 H), 3.18 (d, each member split into a triplet, J = 17,

2.5 Hz, 1 H), 5.50 (broad s, 1 H), 5.70 (d, J = 10 Hz, 1 H), 6.50 (d, J = 10 Hz, 1 H).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.30; H, 9.17.

Irradiation of the signal at δ 5.50 changed the absorption at δ 3.18 into a doublet, each member of which was split into a doublet (J = 17 and 2.5 Hz). Irradiation at δ 2.25 produced the same effect on the signal at δ 3.18 as did irradiation at 5.50.

When a solution of ca. 100 mg of **6** in 0.5 mL of acetone-d_6 containing 0.01 equiv of NaOD and 0.10 mL of D_2O was allowed to stand for ca. 15 min, the following changes in the NMR spectrum were observed: the signal at δ 3.18 disappeared, whereas the signal at δ 2.82 changed from a doublet to a broad singlet; the signal at δ 5.50 became much sharper and appeared as a doublet ($J \sim 2$ Hz). When ca. 100 mg of **6** was treated with excess NaOH in methanol, a mixture of compounds (77 mg) could be isolated. Chromatography on Florisil (75% ether in hexane) yielded 40 mg of a pale yellow oil, tentatively identified as **8**: IR (CCl_4) 3420, 2960, 2860, 1662, 1622, 1607 cm^{-1}; NMR δ (CCl_4) 1.20 (s, 6 H), 1.27 (s, 3 H), 3.03 (s, 1 H), 6.00 (s, 1 H), 6.08 (d, J = 10 Hz, 1 H), 6.73 (d, J = 10 Hz, 1 H).

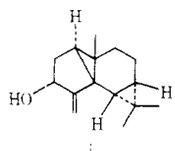
Irradiation of 1b in Glacial Acetic Acid. A solution of 1.00 g (0.00495 mol) of **1b** in 250 mL of freshly distilled glacial acetic acid was irradiated for 0.75 h. The excess solvent was removed at reduced pressure and the resulting yellow oil taken up in ether/water. Extraction of the ether with saturated aqueous sodium bicarbonate followed by drying and removal of solvent yielded 1.31 g (101%) of a yellow oil. This material was carefully chromatographed on Florisil, with each fraction being monitored by TLC. The only identifiable material that was isolated was eluted with 25% ether in hexane. This fraction yielded 0.920 g (71%) of **5b**: mp 64–66 °C (from hexane); IR (CCl_4) 2990, 2920, 2870, 1737, 1718, 1610 cm^{-1}; NMR δ (CCl_4) 1.05 (s, 3 H), 1.12 (s, 3 H), 1.17 (s, 3H), 1.93 (s, 3 H), 3.73 (t, J = 3 Hz, 1 H), 5.97 (t, J = 1.6 Hz, 1 H); UV λ_{max} (95% EtOH) 241 nm (ϵ 11 800).

Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.39; H, 8.43.

Registry No.—1a, 55659-72-8; **1b**, 64057-42-7; **3**, 64090-80-8; **4a**, 64057-43-8; **4b**, 64057-44-9; **5b**, 64057-45-0; **6**, 64070-26-4; **8**, 64057-46-1; (−)-2-carone, 5561-14-8; methyl vinyl ketone, 78-94-4; (−)-3-(2-oxobutan-4-yl)-2-carone, 64057-41-6; *cis*-6-(2-chloropropan-2-yl)-3-oxo-9-methyl-Δ^4-octahydronaphthalene, 64057-47-2.

References and Notes

(1) This investigation was supported by Public Health Service Research Grants No. GM 15044 from the National Institute of General Medicine and CA 12193 from the National Cancer Institute.
(2) D. Caine and J. T. Gupton III, *J. Org. Chem.*, **40**, 809 (1975).
(3) D. Caine and P. F. Ingwalson, *J. Org. Chem.*, **37**, 3751 (1972).
(4) J. Pfister, H. Wehrli, and K. Schaffner, *Helv. Chim. Acta*, **50**, 166 (1967).
(5) D. Caine and J. T. Gupton III, *J. Org. Chem.*, **39**, 2654 (1974).
(6) (a) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975); (b) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Am. Chem. Soc.*, **95**, 6137 (1973); (c) D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 695 (1973).
(7) R. A. Lee, C. McAndrews, K. M. Patel, and W. Reusch, *Tetrahedron Lett.*, 965 (1973).
(8) It is of interest to note that the tetracyclic enones of type **4** contain the same ring skeleton and relative stereochemistry as that recently established for myliol (i), a tetracyclic sesquiterpene alcohol from *Mylia taylorii* (A. Matsuo, H. Nozaki, M. Nakayama, Y. Kushi, and S. Hayashi, *J. Chem. Soc., Chem. Commun.*, 1006 (1976)).



i

(9) B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **48**, 1680 (1963).
(10) S. K. Malhotra and H. J. Ringold, *J. Am. Chem. Soc.*, **86**, 1997 (1964).
(11) For reviews see: (a) P. J. Kropp, *Org. Photochem.*, **1**, 1 (1967); (b) K. Schaffner, *Adv. Photochem.*, **4**, 81 (1966); (c) K. Schaffner, "Organic Reactions in Steroid Chemistry", Vol. II, J. Fried and J. A. Edwards, Ed., Van Nostrand-Reinhold, New York, N.Y., 1972, Chapter 13, pp 330–338.
(12) P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, **32**, 4118 (1967).
(13) J. Streith and A. Blind, *Bull. Soc. Chim. Fr.*, 2133 (1968).
(14) P. F. Ingwalson, Ph.D. Dissertation, Georgia Institute of Technology.
(15) Woodward and Hoffmann (R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969)) have suggested a $_{\pi}2_a + _{\sigma}2_a$ cycloaddition mechanism to account for the formation of products such as **4** and **10** from the corresponding dienones. However, mechanisms involving the intervention of zwitterionic intermediates appear to be more generally accepted and readily account for the different types of photoproducts which are obtained in protic and aprotic solvents.
(16) Examination of models of **14** indicates that it is more sterically crowded than **13** because of the β-methyl group on the dimethylcyclopropane ring. Steric crowding is particularly severe in **14a** where a methyl substituent is present at C-4.
(17) P. J. Kropp, *J. Am. Chem. Soc.*, **85**, 3779 (1963).

A Convenient Preparation of Methyl 2,5-Dihydro-2-oxo-3-furancarboxylate

Martha L. Quesada and Richard H. Schlessinger*

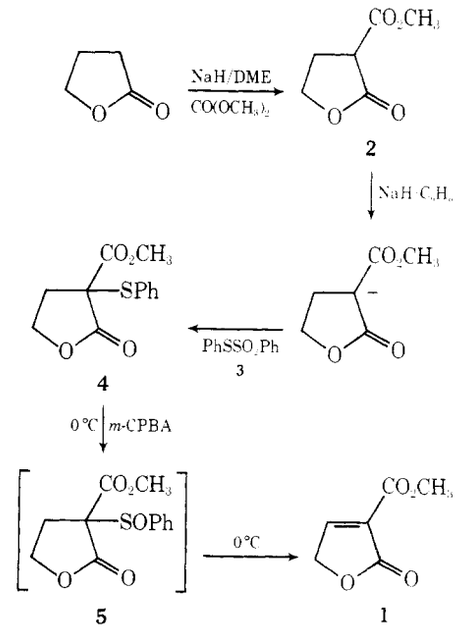
Department of Chemistry, University of Rochester, Rochester, New York 14627

Received June 10, 1977

We have recently had need for the C-5 synthon methyl 2,5-dihydro-2-oxo-3-furancarboxylate (**1**) within the context of several total synthetic efforts. Compound **1** can serve as an electron-deficient olefin both in the Michael addition reaction and the Diels–Alder reaction, thus providing a convenient entry into a variety of complex molecular systems. Careful search of the literature revealed that, while several closely related systems were known,[1] compound **1** itself was unknown. The previously described syntheses of compounds related to **1** proved not to be synthetically applicable to the preparation of **1** itself.[1] As a result, we have developed a new approach to the synthesis of **1** (Scheme I) which, in principle, should be general for the synthesis of a variety of systems related to **1**.

Butyrolactone, on treatment with diethyl carbonate and sodium hydride in dimethoxyethane (DME), affords the corresponding carbomethoxy lactone **2** in 72% yield. Treatment of **2** with sodium hydride gives rise to the corresponding β-dicarbonyl anion which, on reaction with the sulfide sulfone **3**, undergoes thiophenylation to compound **4** in 55% yield. Reaction of the β-dicarbonyl anion derived from **2** with diphenyl disulfide does not yield compound **4** as the starting materials are recovered unreacted, even after prolonged reaction times. Thus, for unreactive anions such as those derived from β-dicarbonyl systems the sulfide sulfone **3** is a clearly superior thiophenylating agent.[2]

Scheme I



0022-3263/78/1943-0346$01.00/0