36803-46-0; **2b**, 36803-47-1; **4a**, 36807-69-9; **4b**, 36807-70-2; **4c**, 36807-71-3; **4d**, 36807-72-4.

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## Photochemical Syntheses of Spiro[4.5]decane-1,6-dione

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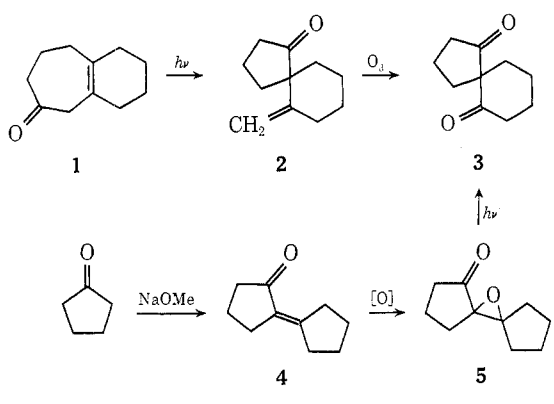
Recently the photoisomerization of the $\beta,\gamma$-unsaturated ketone bicyclo[5.4.0]undec-1(7)-en-3-one (**1**) to the $\beta,\gamma$-unsaturated spiro ketone 6-methylenespiro-[4.5]decan-1-one (**2**) was reported.[1] We now wish to describe the ozonolysis of **2** to the spiro 1,3 diketone **3** and the facile photochemical synthesis of **3**.




1 2 3 4 5

The structure of the spiro ketone **2** was proved by physical methods and by catalytic reduction of the exocyclic methylene group to two isomeric methyl ketones, one of which is known.[2] To confirm that the exocyclic methylene group was attached to the six-membered ring, **2** was ozonized to yield the spiro 1,3 diketone **3**. The infrared spectrum of **2** showed $\bar{\nu}_{max}$ at 1735 $cm^{-1}$ due to the carbonyl stretching frequency of a cyclopentanone, whereas **3** had $\bar{\nu}_{max}$ at 1732 and 1698 $cm^{-1}$ due to cyclopentanone and cyclohexanone rings, respectively.

Since it is well known in the steroid series that photolysis of $\alpha,\beta$-epoxy ketones yields 1,3 diketones,[3] photolysis of the epoxy ketone **5** should yield the desired spiro 1,3 diketone **3**. The precursor required for this photorearrangement was the ketone **5**. This epoxy ketone **5** can be readily obtained by an aldol condensation of cyclopentanone followed by epoxidation. Epoxidation of the aldol product **4** with perbenzoic acid or with 30% hydrogen peroxide and base gave the epoxide **5** in low yield; however, *m*-chloroperbenzoic acid gave **5** in 47% yield.

Direct irradiation of **5** in benzene, hexane, ether, and methanol with a medium-pressure mercury arc (Hanovia type L), using a Pyrex filter, afforded the spiro 1,3 diketone **3** in 25% yield. A second unidentified product **6** was also observed in trace amounts such that the ratio of formation of **3**:**6** was 7:1.

Photolysis of **5** in the presence of a series of photosensitizers such that the sensitizer absorbed >90% of the light gave the following results: benzaldehyde ($E_T$ = 72 kcal)[4] and benzophenone (69 kcal)[4] led to a substantial decrease in the rate of formation of **3**, whereas acetone (77 kcal)[5] and acetophenone (74 kcal)[4] led to an increase in the rate of reaction. These results indicate that a triplet state with an energy level above 72 kcal and below 74 kcal leads to the spiro 1,3-diketone **3**. Furthermore, sensitized photolysis of **5** also leads to the formation of **3** and **6** in the ratio of 7:1. Since the product distribution in such sensitized runs provides a "fingerprint" characteristic of the triplet, it would be exceedingly fortuitous for another species to give the same "fingerprint," and we therefore conclude that the triplet is the reacting species in the direct runs as well.[6]

Photolysis of **5** in the presence of the quenchers piperylene, naphthalene, and biphenyl indicated a slight increase in the rate of photoisomerization in the case of naphthalene. These results indicate that the triplet state has an extremely short lifetime and does not undergo diffusion-controlled quenching. The increase in the rate of reaction in the case of naphthalene is probably due to sensitization of the singlet state of **5**.[7]

The photorearrangement described here offers a rapid method for the synthesis of the spiro[4.5]decanes found as the skeletons of a number of interesting sesquiterpenes.[8,9] Furthermore, this method should be general and provide an alternative synthetic route to spiro molecules.

### Experimental Section[10]

**Ozonolysis of 6-Methylenespiro[4.5]decan-1-one (2).**—A solution of 30 mg (0.183 mmol) of 6-methylenespiro[4.5]decan-1-one,[1] one drop of water, and 10 ml of ethyl acetate was stirred at 0° for 10 min while ozone was passed through the solution. Then 1.0 ml of water and 0.2 g of zinc dust were added, and the mixture was stirred at room temperature overnight. The ethyl acetate solution was filtered, washed with water until neutral, dried

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(10) Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Ir spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined in methanol with a Cary 14 recording spectrometer. Nmr spectra were obtained with Varian A-60-A and XL100 spectrometers. The mass spectra were on an AE1 MS-9 mass spectrometer at an ionizing energy of 70 eV. Microanalysis were performed by Micro-Analysis Inc., Wilmington, Del.

($Na_2SO_4$), and concentrated. The product was separated by preparative vpc[11] to yield 10 mg (33%) of spiro[4.5]decane-1,6-dione as a clear oil: bp 238–241° dec; ir ($CHCl_3$) 1732 (cyclopentanone C=O), 1698 $cm^{-1}$ (cyclohexanone C=O); mass spectrum (70 eV) *m/e* (rel intensity) 166 (38, $M^+$), 148 (14), 138 (35), 137 (20), 121 (21), 111 (100), 110 (90), 95 (34), 91 (27), 67 (52), 55 (74), 44 (95), 41 (67).

**Preparation of 2-Cyclopentylidenecyclopentan-1-one Oxide (5).**—A solution of 2.84 g (85% pure, 0.0140 mol) of *m*-chloroperbenzoic acid in 60 ml of chloroform was added slowly to an ice-cold solution of 2.00 g (13.3 mmol) of 2-cyclopentylidenecyclopentan-1-one (**4**)[12] in 20 ml of chloroform. This mixture was stirred at 3° for 18 hr. The reaction mixture was then filtered, washed with $NaHCO_3$ solution and brine until neutral, dried ($Na_2SO_4$), and concentrated. The residue was chromatographed on 50 g of silica gel (activity IV, 27.8 × 2.3 cm), with 9:1 hexane–ethyl acetate. The product obtained (1.04 g, 47%) crystallized from hexane to give holohedral plates of 2-cyclopentylidenecyclopenten-1-one oxide (**5**): mp 38–40°; uv max (EtOH) 307 nm (ε 43); ir ($CHCl_3$) 1743 (cyclopentanone C=O), 1160, 960 $cm^{-1}$; nmr ($CDCl_3$) δ 2.6–1.4 (m); mass spectrum (70 eV) *m/e* (rel intensity) 166 (50, $M^+$), 148 (40), 138 (55), 125 (21), 110 (100), 109 (32), 96 (34), 95 (75), 91 (44), 67 (80), 66 (40), 55 (65), 44 (48), 41 (64).

*Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.27; H, 8.54.

**Preparation of Spiro[4.5]decane-1,6-dione (3).**—A solution of 132 mg of 2-cyclopentylidenecyclopentan-1-one oxide (**5**) in 110 ml of acetone was stirred with a stream of nitrogen and irradiated with a 450-W Hanovia lamp through a Pyrex filter. The reaction was stopped after 90 min. The acetone solution was concentrated and preparative vpc[13] was used to collect 6 mg of an unidentified oil, **6**,[14] 15 mg of reactant, and 40 mg (30%) of spiro[4.5]decane-1,6-dione (**3**) as a clear oil: bp 238–240° dec; uv max (EtOH) 287 nm (ε 126); ir ($CHCl_3$) 1732 (cyclopentanone C=O) and 1698 $cm^{-1}$ (cyclohexanone C=O); nmr ($CDCl_3$) δ 2.9–1.1 (m); mass spectrum (70 eV) *m/e* (rel intensity) 166 (62, $M^+$), 148 (19), 138 (33), 137 (25), 121 (19), 111 (100), 110 (91), 95 (50), 91 (28), 67 (55), 55 (67), 44 (100), 41 (66).

*Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.25; H, 8.74.

The spiro[4.5]decane-1,6-dione was shown to be identical (boiling point, ir, mass spectrum) with the diketone **3**, previously prepared by ozonolysis of the spiro[4.5]undecene **2**. Nmr spectra indicate that **3** and **6** are the only products. The low yield of **3** obtained is due to preparative vpc. Similar results were obtained when **5** was photolyzed in benzene, hexane, ether, and methanol.

**Quenching Studies with 2-Cyclopentylidenecyclopentan-1-one Oxide (5).**—In a typical experiment approximately 0.010 g of **5** was weighed into a 5-ml volumetric flask. The sample was dissolved in benzene, and 0.5-ml aliquots were placed in 7-mm Pyrex test tubes. Quenchers were added to prepare the following solutions: 0.01, 0.1, and 2.0 *M* piperylene; 0.01 and 0.1 *M* naphthalene; and 2 *M* biphenyl. The test tubes were degassed with nitrogen and irradiated on a merry-go-round with a 450-W Hanovia lamp. The resulting solutions were analyzed by vpc.[11]

**Sensitization Studies with 2-Cyclopentylidenecyclopentan-1-one Oxide (5).**—The same procedure was used as in the quenching studies, except that the solutions were prepared so that the sensitizer absorbed over 90% of the light at 313.0 nm. The following solutions were used: 0.0615 *M* acetophenone, 0.0324 *M* benzophenone, 0.258 *M* benzaldehyde, and acetone (neat).

**Registry No.**—**3**, 36803-48-2; **5**, 36803-49-3.

**Acknowledgment.**—We acknowledge partial support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Mr. Kuhlman of Wyeth Laboratories for the mass spectra.

(11) The column (6 ft × 0.25 in.) used was packed with 20% Carbowax 20M on 60–80 mesh Chromosorb P.

(12) O. Wallach, *Ber.*, **29**, 2955 (1896).

(13) The column (4 ft × 0.25 in.) used was packed with 20% Carbowax 20M on 60–80 mesh Chromosorb WAW DMCS.

(14) This product is currently under investigation.

## Studies in Purine Chemistry. XVI. A One-Step Synthesis of 7-Aryltheophyllines[1,2]

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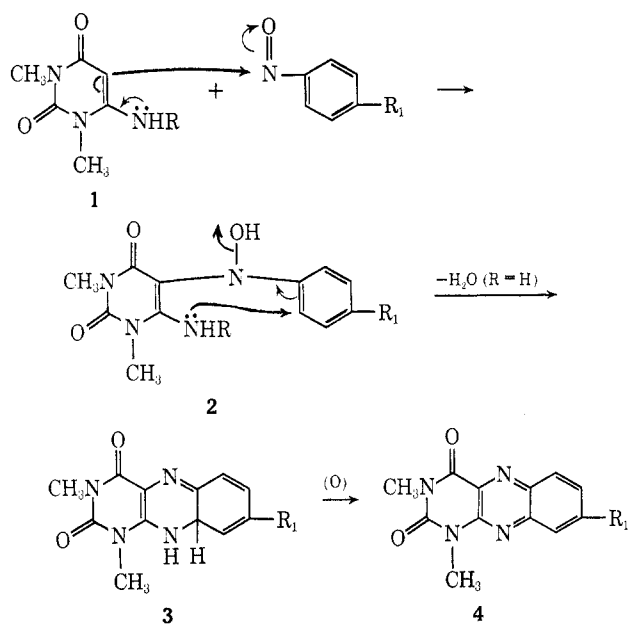
Some time ago we described a new route to 1,3-dimethylalloxazines which involves the condensation of 1,3-dimethyl-6-aminouracil (**1**, R = H) with nitrosobenzenes in the presence of acetic anhydride.[4] A reasonable intermediate in this condensation is the hydroxylamine **2**; the intramolecular dehydrative-cyclization step (**2** to **3**) is presumably facilitated by prior acetylation of the hydroxylamine. Dehydrogenation with excess nitrosobenzene then gives **4**. It appeared that the use of a 6-alkylamino derivative of **1** (R = alkyl) would prevent the final aromatization step (**3** to **4**) and lead to a synthesis of 1,3-dimethyl-5-acetyl-10-alkylleucoflavins.




1 2 3 4

We have found, however, that the reaction of 1,3-dimethyl-6-methylaminouracil (**1**, R = $CH_3$) with nitrosobenzene in the presence of acetic anhydride gave 7-phenyltheophylline (**8**, $R_1$ = H; Ar = $C_6H_5$).[5] Analogous reactions were observed with 1,3-dimethyl-6-ethylaminouracil (**1**, R = $C_2H_5$) and with 1,3-dimethyl-6-benzylaminouracil (**1**, R = $CH_2C_6H_5$) in condensations with nitrosobenzene and with *p*-chloronitrosobenzene; in all cases, the α-C atom of the 6-alkylamino group becomes the 8-carbon atom of the

(1) Part XV: E. C. Taylor, G. P. Beardsley, and Y. Maki, *J. Org. Chem.*, **36**, 3211 (1971).

(2) This investigation was supported by the U. S. Army Medical Research and Development Command (Contract No. DA-49-193-MD-2777) and is Contribution No. 1089 in the Army research program on malaria.

(3) Kumamoto University, Kumamoto, Japan.

(4) E. C. Taylor, F. Sowinski, T. Yee, and F. Yoneda, *J. Amer. Chem. Soc.*, **89**, 3369 (1967).

(5) H. Dolman, J. van der Goot, G. H. Mos, and H. D. Moed, *Recl. Trav. Chim. Pays-Bas*, **83**, 1215 (1964), have reported the preparation of this compound by arylation of theophylline with *p*-chloronitrobenzene, followed by reduction and reductive diazotization. This is the only 7-aryltheophylline previously reported.