HETEROCYCLES, Vol. 62, 2004, pp. 387 - 397
Received, 7th July, 2003, Accepted, 7th October, 2003, Published online, 7th November, 2003

8-OXABICYCLO[3.2.1]OCTA-3,6-DIEN-2-ONE SYNTHESIS USING A PYRYLIUM 3-OXIDE PRECURSOR DERIVED FROM A 4-OXO-4*H*-PYRAZOLE 1,2-DIOXIDE

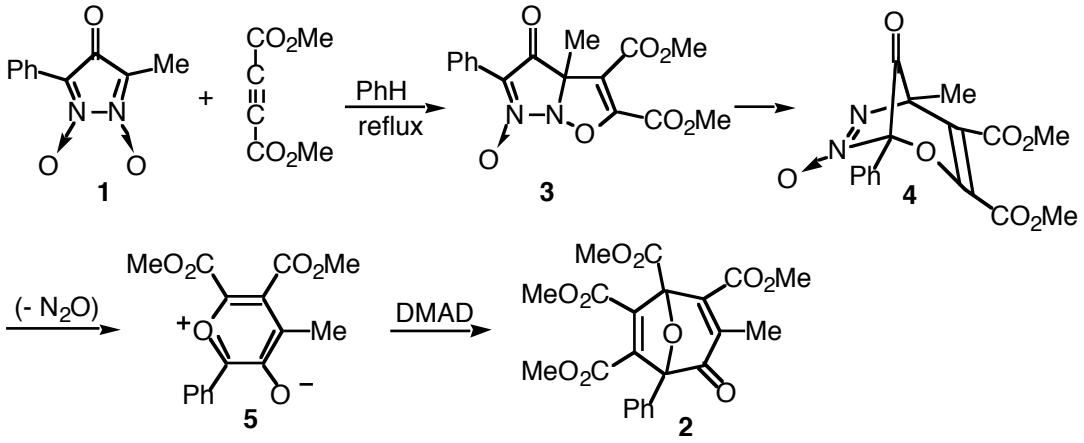
John F. Hansen,*‡ Andre L. Kilpatrick, and Anita Durairaj

Department of Chemistry, Illinois State University, Normal, IL 61790-4160, USA

Abstract-Dimethyl acetylenedicarboxylate reacts with 3-methyl-5-phenyl-4-oxo-4*H*-pyrazole 1,2-dioxide in CH_2Cl_2 and water to give 3,4-bis(carbomethoxy)-8,8-dihydroxy-5-methyl-1-phenyl-2-oxa-6,7-diazabicyclo[3.2.1]octa-3,6-diene 7-oxide. This compound loses water and N_2O when heated, producing a 3-oxidopyrylium derivative which reacts, *in situ*, with alkynes to give 8-oxabicyclo[3.2.1]octa-3,6-dien-2-one derivatives.

Freeman and Hoare, in 1971, reported that 3-methyl-5-phenyl-4-oxo-4*H*-pyrazole 1,2-dioxide (**1**) reacted with dimethyl acetylenedicarboxylate (DMAD) in refluxing benzene to give an 8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (**2**).[1] The sequence illustrated in Scheme 1 was proposed to account for the observed transformation.

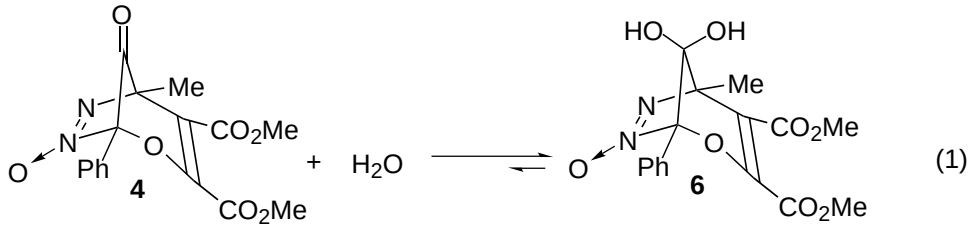
Scheme 1. Proposed origin of **2**



Freeman suggested that a 1,3-dipolar cycloaddition of DMAD to the methyl nitrone group in **1** produced an unstable 2,3-dihydroisoxazole derivative (**3**). Rearrangement of **3** to **4** by a 1,3-oxygen shift, and loss of nitrous oxide from **4**, *in situ*, gave a pyrylium 3-oxide betaine (**5**), which underwent cycloaddition with a second molecule of DMAD to give **2**.

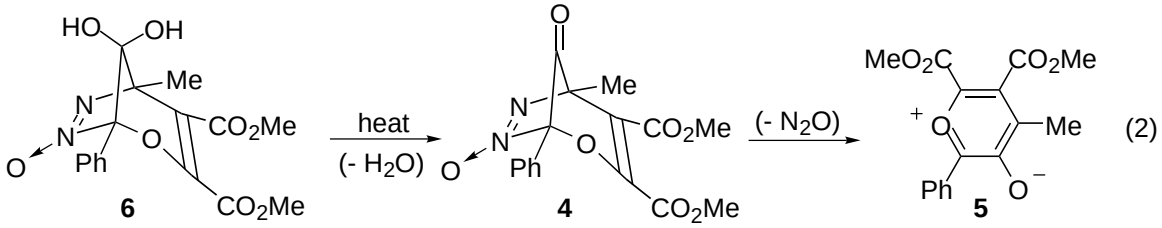
The cycloaddition of DMAD with **5** proposed by Freeman and Hoare was similar to earlier reports of the addition of DMAD to 1,3-diphenylbenzo[*c*]pyrylium 4-oxide.[2] Other reactions of alkynes with pyrylium oxide betaines were subsequently reported by Potts and coworkers,[3] Ibata and Jitsuhiro,[4] Sammes and Whitby,[5] and Hendrickson and Farina.[6] Related cycloadditions with alkene dipolarophiles were reported earlier by Woods[7] and by Hurd,[8] although the involvement of pyrylium oxides in those reactions was not established until several years later.[9] Since that time numerous reports of the reaction of pyrylium 3-oxides with alkenes to form seven-membered carbocyclic rings have appeared.[10]

Neither **4** nor **5** was observed directly by Freeman and Hoare in the reaction of **1** with DMAD. However, they reported that reaction of **1** with DMAD at room temperature resulted in the formation of a colorless solid, which gave elemental analysis results consistent with a molecular formula of $C_{16}H_{16}N_2O_8$. Based upon these results and upon spectral evidence, they suggested that this compound was **6**, the hydrate derivative of the ketone (**4**) (equation 1). The water required for hydration was presumed to have been supplied from the atmosphere.



(1)

It occurred to us that Freeman and Hoare's hydrate (**6**) might serve as a convenient precursor to the pyrylium 3-oxide betaine (**5**), through a sequence involving dehydration of **6** to **4** and subsequent thermal decomposition of **4** to **5** (equation 2).



(2)

The pyrylium oxide (**5**) might then undergo cycloaddition with alkenes or alkynes to form seven-membered carbocycles. We report herein our initial investigations in support of this hypothesis.

The preparation of **6** as reported by Freeman and Hoare involved the use of neat DMAD, serving as solvent as well as reactant. This method is not entirely satisfactory, due to the hazards and inconvenience of handling the large quantities of DMAD, a notorious lachrymator. To obtain **6** more conveniently**,** we

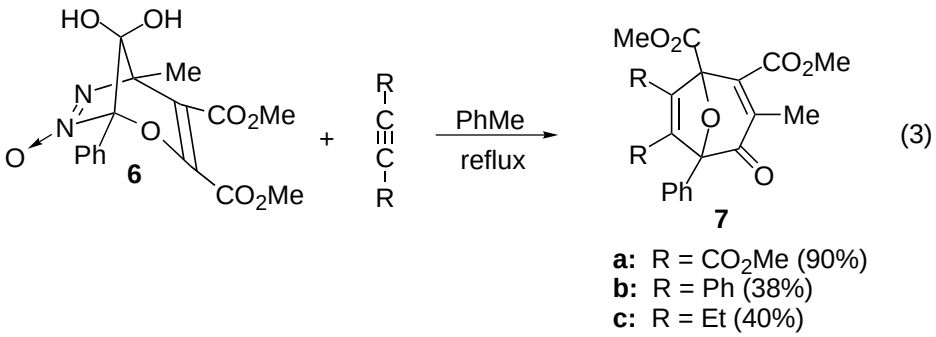
developed an improved method in which a solution of **1** and excess DMAD in dichloromethane, along with a little water, was heated under reflux for about 40 hours. The Freeman-Hoare hydrate (**6**), which is insoluble in dichloromethane, separated from the reaction mixture and could be isolated by suction filtration. After washing with cold dichloromethane and drying, **6** was obtained in a yield of about 70%, and no further purification was required. The product was identical with a sample of **6** prepared using the literature method.[1]

The Freeman-Hoare hydrate is remarkably stable, and no decomposition was observed in samples of **6** stored for several years in colorless glass vials under normal atmosphere at room temperature. This stability contrasts with the *gem*-diols, or hydrates, derived from most carbonyl compounds, which are unstable and generally cannot be isolated. Notable exceptions are seen in cases of the hydrates of some cyclic ketones, where the tetrahedral geometry of the carbon atom of the hydrate can be accommodated with less ring strain than the trigonal geometry of the carbonyl carbon, or in cases in which electron-withdrawing groups are attached to the □-carbons of the carbonyl group.[11] It is likely that both of these factors contribute to the stability of the Freeman-Hoare hydrate (**6**) when compared with the ketone (**4**). An example of the formation of stable hydrates from a bridged-bicyclic ketone was recently described by Kobayashi and Kobayashi.[12]

A logical first test of the hypothesis that the Freeman-Hoare hydrate might serve as a pyrylium 3-oxide precursor was the reaction of **6** with DMAD. In our initial studies, a mixture of **6** and excess DMAD in benzene was stirred under reflux. The hydrate (**6**) is not soluble in benzene, so the progress of the reaction could be evaluated by observing the gradual disappearance of **6**. It was found that the reaction was very slow, requiring several days to proceed to completion. Presumably, the slow step in this process is the dehydration of **6** to **4**, since Freeman and Hoare's results suggest that subsequent loss of nitrous oxide from **4** to give **5** should occur readily at the temperature of refluxing benzene.

In order to effect a decrease in the reaction time, subsequent experiments were carried out under reflux in toluene. Standard conditions applied in this study involved the use of 0.5 mmol of **6** and a 50% molar excess of the alkyne in 1 mL of toluene under reflux. The disappearance of **6** in those experiments was complete within six hours. The results of reactions with DMAD, with diphenylacetylene, and with 3-hexyne are summarized in equation 3. The product (**7a**) was formed in excellent yield when **6** reacted with DMAD. Compound (**7a**) was identical with an authentic sample of **2**, which was prepared as

described by Freeman and Hoare.[1] The compounds (**7b**) and (**7c**) were characterized from elemental analyses and spectral properties consistent with the assigned structures. All products were yellow solids, which were easily purified by flash chromatography on silica gel. The yields reported represent isolated quantities of material after chromatographic purification.



(3)

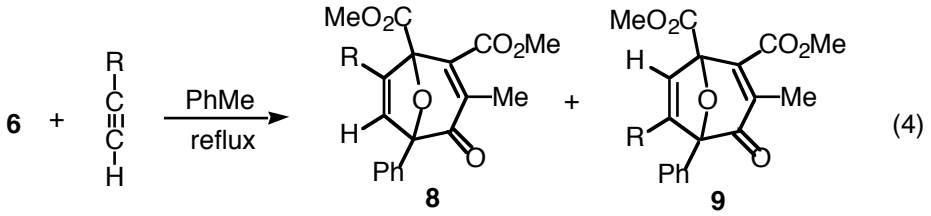
a: R = CO_2Me (90%)
b: R = Ph (38%)
c: R = Et (40%)

The modest yields obtained for **7b** and **7c** appeared to be a consequence of a relatively slow reaction of the pyrylium oxide intermediate (**5**) with diphenylacetylene or 3-hexyne. In those reactions, darkening of the reaction mixture occurred, and the ^{1}H NMR spectrum of the crude product showed numerous additional signals besides those of the desired product. It was found that NMR patterns similar to those for the impurities in these reactions could be observed in the mixture that resulted when **6** was heated under reflux in toluene for six hours in the absence of a dipolarophile. No attempt was made to characterize the products of this thermal decomposition; however, it is known that pyrylium oxides are capable of undergoing self-condensation to form a variety of dimeric products.[10a,13,14,15]

Improved yields of **7b** and **7c** were realized when the alkynes, diphenylacetylene or 3-hexyne, were used in greater excess. Reaction of **6** with eight-fold molar amounts of the alkynes in toluene under reflux resulted in yields approaching 70% for both **7b** and **7c**. Sammes and Street[10a] applied a similar strategy, using a large excess of a dipolarophile of relatively low reactivity, when the rate of cycloaddition was slow enough that dimerization of a pyrylium oxide became competitive

The reaction study was extended to include two unsymmetrically-substituted acetylenes, methyl propiolate and phenylacetylene. The standard conditions, 50% excess of the alkyne in toluene under reflux for six hours, were used, and the results obtained are summarized in equation 4. In both cases high yields of oxabicyclo[3.2.1]octa-3,6-dien-2-ones were obtained. However, in each case a mixture of isomers was obtained, which differed in the orientation of addition of the alkyne. In both reactions, there was a slight

preference for the product (**8**) in which the substituent R is located at C-6 of the ring, over the isomer (**9**) in which the substituent R is located at C-7. In fact, the isomer ratio of **8** to **9** was about 11:9 in both reactions.



(4)

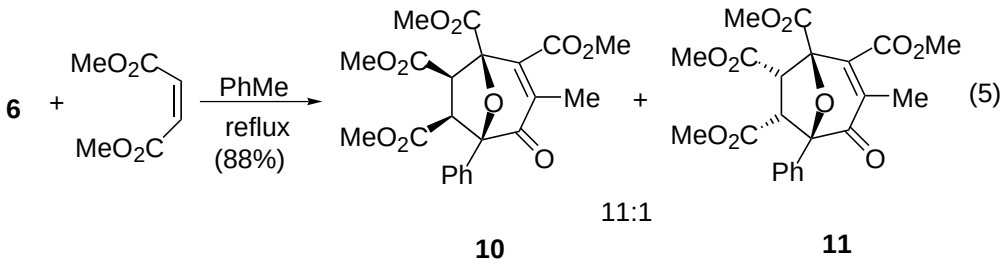
a: R = CO_2Me (91%)(**8a:9a** = 11:9)
b: R = Ph (87%)(**8b:9b** = 11:9)

In the case of **8a** and **9a**, the assignment of structures for the isomers was based upon a comparison of the signal pattern for the phenyl substituent at C-1 with the corresponding pattern seen for the phenyl group in **2**. The ^{1}H NMR signal pattern for the phenyl group in **9a**, which appeared as a two-proton multiplet at 7.62-7.66 and a three-proton multiplet centered at 7.38, very closely resembled that for **2**, which gave a two-proton multiplet at 7.61-7.66 and a three-proton multiplet centered at 7.39 ppm. The signal for the protons on the phenyl group of **8a** gave a much different pattern, consisting of a two-proton multiplet at 7.45-7.51 and a three-proton multiplet centered at 7.42 ppm. From these observations, we infer that the ester group in **9a** must be located at C-7, so that the environment of the phenyl group in **9a** is similar to that of the phenyl group in **2**. The signal for the vinylic proton at C-6 in **9a** appears downfield at 7.85 ppm, consistent with strong deshielding by the two ester functional groups at C-5 and C-7. The vinylic proton at C-7 in **8a** is not so strongly deshielded, appearing at 7.32 ppm.

The structural assignments for **8b** and **9b** were based mainly upon a correlation of the ^{1}H NMR signals for the vinylic protons in these compounds with the signals for the vinylic protons in the spectra of **8a** and **9a**. As noted above, the vinylic proton in **9a** is more strongly deshielded (7.85 ppm) than is the vinylic proton in **8a** (7.32 ppm). By analogy, the products from the addition of phenylacetylene are assigned as **9b** for the isomer in which the vinylic proton is more strongly deshielded (7.31 ppm), and **8b** for the isomer in which the vinylic proton is less strongly deshielded (6.72 ppm). The greater deshielding of the vinylic protons at C-6 in each of the compounds (**9a**) and (**9b**) we ascribe to their proximity to the carbomethoxy group at C-5 in each of those compounds.

We have also investigated the reaction of the hydrate (**6**) with an alkene dipolarophile, dimethyl maleate. This reaction was also carried out in toluene under reflux for six hours, using a 50% molar excess of the

alkene. In this case two diastereomeric products are possible, depending upon whether the orientation of addition of the dipolarophile is *exo* or *endo* to the pyrylium oxide (equation 5). After purification by flash chromatography, a total yield of 88% of a mixture of the two diastereomers was obtained. The isomers



were present in a ratio of about 11:1, from ^{1}H NMR analysis, favoring the *exo* isomer (**10**) over the *endo* isomer (**11**). The stereochemical assignment in this case was facilitated by the fact that **11** is a known compound, which previously had been obtained by Freeman and Hoare[1] through catalytic hydrogenation of **2**. The minor isomer (**11**) corresponded in its melting point and ^{1}H NMR spectrum with the values that had been reported for the hydrogenation product.

Our results to date show that the hydrate (**6**), which is readily prepared in good yield, can function as a pyrylium 3-oxide betaine precursor in cycloaddition reactions. Investigations of the reactions of **6** are continuing. We are also examining the possibility that related pyrylium oxide precursors might be accessible from the reaction of **1** or other 4-pyrazolone 1,2-dioxides with DMAD or other alkynes.

EXPERIMENTAL

Unless otherwise noted, ^{1}H NMR spectra were obtained at 300 MHz with a Varian Gemini 300 spectrometer, on samples in deuteriochloroform containing tetramethylsilane (TMS). ^{1}H chemical shifts (d) are reported relative to tetramethylsilane at 0 ppm. ^{13}C NMR spectra were run at 75 MHz, with chemical shifts reported relative to $^{13}CDCl_3$ at 77.0 ppm. Infrared spectra were run as Nujol mulls, on a Perkin Elmer Series 1600 FTIR spectrometer or a Nicolet 5SXC FTIR spectrometer. Elemental analyses were performed at the University of Illinois-Urbana-Champaign. Silica gel used for flash chromatography was EM Silica Gel 60, 230-400 mesh. Melting points were determined in open capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected.

3,4-Bis(carbomethoxy)-8,8-dihydroxy-5-methyl-1-phenyl-2-oxa-6,7-diazabicyclo[3.2.1]octa-3,6-diene 7-Oxide (**6**).

A mixture of 1.02 g (5.0 mmol) of 3-methyl-5-phenyl-4-oxo-4*H*-pyrazole 1,2-dioxide (**1**)[16] and 2.80 g (20 mmol) of dimethyl acetylenedicarboxylate (DMAD) in 5 mL of dichloromethane and 0.20 g of water was stirred under reflux. After 42 h the mixture was cooled, and **6** was collected as a white solid, which was washed with cold dichloromethane. After drying, the yield of **6** was 1.27 g (70%), mp 163-165° C (lit.,[1] mp 162-165° C). The compound did not require recrystallization. IR: 3410 cm^{-1}, 3265, 1755, 1708, 1640, 1529. NMR spectra (in dimethyl sulfoxide-d_6, TMS): ^1H: 7.57 (m, 5H), 3.81 (s, 3H), 3.77 (s, 3H), 1.42 (s, 3H); ^{13}C (TMS at 0 ppm): 164.0, 159.9, 141.7, 130.0, 128.9, 127.3, 126.7, 122.7, 106.3, 93.0, 69.1, 53.2, 52.5, 10.8.

Reactions of Alkynes with **6**. General Procedure.

A mixture of 0.182 g (0.50 mmol) of **6** and 0.75 mmol of the alkyne in 1.0 mL of toluene was stirred under reflux. After 6 h the solvent was evaporated, and the residue was dissolved in acetone and deposited by evaporation on 0.5 g of silica gel. This was then applied at the top of a column of 5.0 g of silica gel, and the column was eluted using 5% or 10% acetone in hexane. After a forerun containing unreacted alkyne, the product was collected in a yellow solution. Yields reported are for the weight of yellow solid obtained upon evaporation of the eluate fractions and drying overnight at 0.1 torr.

Tetramethyl 3-Methyl-1-phenyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one-4,5,6,7-tetracarboxylate (**7a**).

Reaction of 0.182 g (0.50 mmol) of **6** with 0.107 g (0.75 mmol) of dimethyl acetylenedicarboxylate gave 0.201 g (90%) of **7a**, as a yellow solid, mp 114-116° C (from methanol) (lit.,[1] mp 112-114° C). IR:1758 cm^{-1}, 1743, 1722, 1706, 1660. ^1H NMR: 7.61-7.66 (m, 2H), 7.36-7.42 (m, 3H), 3.89 (s, 3H), 3.844 (s, 3H), 3.841 (s, 3H), 3.69 (s, 3H), 2.05 (s, 3H). ^{13}C NMR: 187.7, 165.3, 164.3, 162.1, 161.1, 146.0, 143.2, 143.1, 134.8, 132.0, 129.2, 129.1, 127.0, 94.0, 88.3, 53.4, 52.7, 52.6, 52.3, 12.6.

Dimethyl 3-Methyl-1,6,7-triphenyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one-4,5-dicarboxylate (**7b**).

A. Under the usual conditions, using 0.182 g (0.50 mmol) of **6** and 0.134 g (0.75 mmol) of diphenylacetylene, **7b** was obtained as a yellow, crystalline solid, 0.090 g (38%), mp 158-160° C (from

methanol). IR: 1747 cm^{-1} 1734, 1701. ^{1}H NMR: 7.51 (m, 2H), 7.23-7.30 (m, 9H), 6.99-7.08 (m, 2H), 6.88 (m, 2H), 3.80 (s, 3H), 3.53 (s, 3H), 2.11 (s, 3H). ^{13}C NMR: 192.6, 166.9, 164.9, 150.1, 145.6, 141.5, 134.22, 134.18, 132.8, 131.7, 129.4, 129.3, 128.71, 128.67, 128.2, 128.0, 127.9, 127.85, 127.80, 95.9, 90.5, 52.9, 51.8, 12.3. *Anal.* Calcd for $C_{30}H_{24}O_6$: C, 74.99; H, 5.03. Found: C, 74.97; H, 4.97.

B. The reaction was carried out using 0.182 g (0.50 mmol) of **6** and 0.712 g (4 mmol) of diphenylacetylene in 2 mL of toluene under reflux for 6 h. The yield of **7b** was 0.164 g (68%).

Dimethyl 6,7-Diethyl-3-methyl-1-phenyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one-4,5-dicarboxylate (**7c**).

A. Reaction of 0.182 g (0.50 mmol) of **6** and 0.082 g (0.75 mmol) of 3-hexyne gave 0.076 g (40%) of **7c**. Recrystallization gave yellow prisms, mp 78-80° C (from hexane). IR: 1742 cm^{-1}, 1697. ^{1}H NMR: 7.81 (m, 2H), 7.31-7.43 (m, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.46 (m, diastereotopic CH_2, 2H), 1.97-2.24 (m, diastereotopic CH_2, 2H), 1.95 (s, 3H), 1.07 (t, J = 7.5 Hz, 3H), 0.70 (t, J = 7.5 Hz, 3H). ^{13}C NMR: 192.6, 167.7, 165.5, 149.3, 146.0, 141.0, 134.7, 133.6, 128.3, 127.9, 127.1, 94.0, 89.1, 52.8, 52.1, 18.9, 18.1, 13.2, 13.1, 12.3. *Anal.* Calcd for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 68.46; H, 6.34.

B. Reaction of 0.182 g (0.5 mmol) of **6** with 0.328 g (4.0 mmol) of 3-hexyne in 2 mL of toluene under reflux gave, after 6 h, and normal work up, 0.129 g (67%) of **7c**.

Trimethyl 3-Methyl-1-phenyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one-4,5,6-tricarboxylate (**8a**) and Trimethyl 3-Methyl-1-phenyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one-4,5,7-tricarboxylate (**9a**).

Reaction of 0.182 g (0.50 mmol) of **6** with 0.108 g (0.75 mmol) of methyl propiolate in 1 mL of toluene under reflux for 6 h gave a mixture which was chromatographed to give 0.176 g (91%) of a mixture of **8a** and **9a** (11:9). Most of the major isomer, **8a**, mp 142-143° C was obtained from the mixture by recrystallization from methanol, with most of the other isomer (**9a**) remaining in solution. Pure **9a**, mp 98-99° C (from acetone-pentane), could be obtained by further chromatographic separation from the residual material after removal of **8a**.

8a: IR: 1756 $cm^{=1}$, 1726, 1704. ^{1}H NMR: 7.45-7.51 (m, 2H), 7.38-7.46 (m, 3H), 7.32 (s, 1H), 3.88 (s, 6H), 3.82 (s, 3H), 1.98 (s, 3H). ^{13}C NMR: 190.2, 165.9, 164.6, 161.5, 146.4, 144.3, 142.6, 133.9, 133.0, 129.0, 128.4, 126.5, 95.6, 88.2, 53.3, 52.3, 52.2, 12.5. *Anal.* Calcd for $C_{20}H_{18}O_8$: C, 62.18; H, 4.70. Found: C, 61.84; H, 4.45.

9a: IR: 1753 $cm^{=1}$, 1726. ^{1}H: 7.85 (s, 1H), 7.62-7.66 (m, 2H), 7.38 (m, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.68 (s, 3H), 2.11 (s, 3H). ^{13}C NMR: 189.2, 166.2, 164.5, 162.3, 149.4, 142.3, 139.4, 136.1, 133.3, 129.1, 127.93, 127.90, 93.6, 88.1, 53.2, 52.3, 52.0, 12.2. *Anal.* Calcd for $C_{20}H_{18}O_8$: C, 62.18; H, 4.70. Found: C, 61.70; H, 4.49.

Dimethyl 1,6-Diphenyl-3-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one-4,5-dicarboxylate (**8b**) and Dimethyl 1,7-Diphenyl-3-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one-4,5-dicarboxylate (**9b**).

Reaction was carried out in the usual way between **6**, 0.182 g (0.50 mmol), and phenylacetylene, 0.076 g (0.75 mmol) in 1.0 mL of toluene under reflux. After flash chromatography, 0.176 g (87%) of a mixture (11:9) of **8b** and **9b**. Recrystallization from methanol gave a first crop which consisted of nearly pure **8b**, while the second crop consisted almost entirely of **9b**. Recrystallization from methanol gave yellow prisms of **8b**, mp 163-164° C. Recrystallization of **9b** from methanol gave yellow rods, mp 161-161.5° C.

8b: IR: 1742 cm^{-1}, 1697. ^{1}H NMR: 7.52-7.61 (m, 4H), 7.33-7.47 (m, 6H), 6.72 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 1.96 (s, 3H). ^{13}C NMR: 191.3, 167.1, 165.5, 155.5, 145.0, 134.2, 133.6, 131.4, 129.1, 128.6, 128.2 (overlapping signals), 128.1, 127.3, 126.6, 94.8, 89.8, 53.1, 52.1, 12.5. *Anal.* Calcd for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 71.07; H, 4.87.

9b: IR: 1758 cm^{-1}, 1738, 1701. ^{1}H NMR: 7.40-7.45 (m, 2H), 7.31 (s, 1H), 7.25-7.32 (m, 5H), 7.19-7.23 (m, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 2.11 (s, 3H). ^{13}C NMR: 193.2, 167.4, 165.0, 146.1, 144.8, 136.0, 135.5, 134.3, 131.7, 129.3, 129.2, 128.4, 128.2, 127.3, 96.2, 88.4, 53.1, 52.2, 12.1. *Anal.* Calcd for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 70.80; H, 4.90.

Tetramethyl 3-Methyl-1-phenyl-8-oxabicyclo[3.2.1]oct-3-en-2-one-4,5,6,7-tetracarboxylate, *exo* (**10**) and *endo* (**11**) mixture.

A mixture of the Freeman-Hoare hydrate **6**, 0.182 g (0.50 mmol) and dimethyl maleate, 0.108 g (0.75 mmol) in 1.0 mL of toluene was stirred under reflux. After 6 h the solvent was evaporated, and the residual material was submitted to flash chromatography, using 5 g of silica gel with 20% acetone in hexane. This gave 0.197 g (88%) of a mixture of the *exo* isomer (**10**) and the *endo* isomer (**11**) (11:1). The major isomer (**10**) was isolated by crystallization from methanol as clear, colorless, rhombic prisms, mp 192-194° C. IR: 1762 cm^{-1}, 1738, 1706. ^{1}H NMR: 7.57-7.62 (m, 2H) 7.27-7.38 (m, 3H), 4.07 (d, J =

10 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.84 (d, J = 10 Hz, 1H), 3.60 (s, 3H), 3.17 (s, 3H), 1.85 (s, 3H). ^{13}C NMR: 191.0, 168.6, 168.0, 167.0, 164.9, 146.2, 132.9, 132.8, 128.1, 127.3, 126.6, 88.7, 85.1, 54.2, 53.5, 53.2, 52.8, 52.4, 52.0, 12.2. *Anal.* Calcd for $C_{22}H_{22}O_{10}$: C, 59.19; H, 4.97. Found: C, 58.93; H, 5.14.

The minor *endo*-isomer (**11**) was isolated by flash chromatography from the residual filtrate after isolation of the major isomer. Recrystallization gave colorless crystals from acetone-hexane, mp 103-104° C (lit.,[1] mp 100-102° C for the *endo* isomer). IR: 1742 cm^{-1}, 1707. ^{1}H NMR: 7.37 (s, 5H), 4.40 (d, J = 12 Hz, 1H), 3.94 (d, J = 12 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 2.28 (s, 3H); ^{13}C NMR: 191.8, 169.8, 168.9, 167.2, 165.8, 144.0, 138.6, 136.7, 128.5, 128.1, 125.6, 89.4, 85.6, 55.6, 53.7, 53.4, 52.8, 52.6, 52.4, 13.4.

REFERENCES AND NOTES

‡ Postdoctoral associate, 1968-69, with Professor Leo A. Paquette, to whom this paper is dedicated.

1. J. P. Freeman and M. J. Hoare, *J. Org. Chem.,* 1971, **36**, 19.
2. E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.,* 1962, **84**, 1315.
3. K. T. Potts, A. J. Elliot, and M. Sorm, *J. Org. Chem.,* 1972, **37**, 3838.
4. T. Ibata and K. Jitsuhiro, *Bull. Chem. Soc. Jpn.,* 1979, **52***,* 3582.
5. P. G. Sammes and R. J. Whitby, *J. Chem. Soc., Perkin Trans. 1,* 1987, 195.
6. J. B. Hendrickson and J. S. Farina, *J. Org. Chem.,* 1980, **45**, 3359.
7. L. L. Woods, *J. Am. Chem. Soc.,* 1952, **74**, 3959.
8. (a) C. D. Hurd and S. Trofimenko, *J. Am. Chem. Soc.,* 1958, **80**, 2526; (b) C. D. Hurd, R. J. Sims, and S. Trofimenko, *Ibid.,* 1959, **81**, 1684.
9. R. A. Volkmann, P. D. Weeks, D. E. Kuhla, E. B. Whipple, and G. N. Chmurny, *J. Org. Chem.,* 1977, **42**, 3976.
10. (a) P. G. Sammes and L. J. Street, *J. Chem. Soc., Perkin Trans. 1,* 1983, 1261; (b) P. G. Sammes and L. J. Street, *J. Chem. Soc., Chem. Commun.,* 1983, 666; (c) P. G. Sammes and L. J. Street, *J. Chem. Res. (S),* 1984, 196; (d) P. G. Sammes, L. J. Street, and R. J. Whitby, *J. Chem. Soc., Perkin Trans. 1,* 1986, 281; (e) P. G. Sammes, L. J. Street, and P. Kirby, *J. Chem. Soc., Perkin Trans. 1,* 1983, 2729; (f) S. M. Bromridge, P. G. Sammes, and L. J. Street, *J. Chem. Soc., Perkin Trans. 1,* 1985, 1725; (g) P. G. Sammes and L. J. Street, *Gazz. Chim. Ital.,* 1986, **116**, 106; (h) A. R.

Katritzky and N. Dennis, *Chem. Rev.,* 1989, **89**, 827; (i) P. A. Wender, H. Y. Lee, R. S. Wilhelm, and P. D. Williams, *J. Am. Chem. Soc.,* 1989, **111**, 8954; (j) P. Magnus, L. Diorazio, T. J. Donohoe, M. Giles, P. Pye, J. Tarrant, and S. Thom, *Tetrahedron,* 1996, **52**, 14147; (k) K. A. Marshall, A. K. Mapp, and C. H. Heathcock, *J. Org. Chem.,* 1996, **61**, 9135; (l) J. L. Mascareñas, A. Rumbo, and L. Castedo, *J. Org. Chem.,* 1997, **62**, 8620; (m) J. R. Rodríguez, A. Rumbo, L. Castedo, and J. L. Mascareñas, *J. Org. Chem.,* 1999, **64**, 966; (n) J. R. Rodríguez, L. Castedo, and J. L. Mascareñas, *J. Org. Chem.,* 2000, **65**, 2528; (o) N. Ohmori, T. Miyazaki, S. Kojima, and K. Ohkata, *Chemistry Letters,* 2001, 906; (p) A. Delgado, L. Castedo, and J. L. Mascareñas, *Org. Lett.,* 2002, **4**, 3091; (q) R. M. Adlington, J. E. Baldwin, A. V. W. Maywegand, and G. J. Pritchard, *Org. Lett.,* 2002, **4**, 3009.

11. M. B. Smith and J. March, "March's Advanced Organic Chemistry, 5th ed." (John Wiley and Sons, Inc., New York, NY, 2001) p 1176.
12. T. Kobayshi and S. Kobayshi, *Eur. J. Org. Chem.,* 2002, 2066.
13. R. H. Furneaux, J. M. Mason, and I. J. Miller, *J. Chem. Soc., Perkin Trans. 1,* 1984, 1923.
14. E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.,* 1964, **86**, 3814.
15. J. B. Hendrickson and J. S. Farina, *J. Org. Chem.,* 1980, **45**, 3361.
16. J. P. Freeman, J. J. Gannon, and D. L. Surbey, *J. Org. Chem.,* 1969, **34**, 187.