(with an equatorial X = OMe substituent). The boat-twist-boat conformers of these α-methoxy epimers were 7 and 10 kcal higher in energy, respectively. Based on these findings, neither an axial R^2 = Me nor an axial X = alkoxy substituent would be expected to compromise the equatorial preference of the R^3 = Me substituent in cyclizations leading to kijanolide-type structures II.

To test this stereochemical prediction we prepared the 1:1 mixture of C-7 epimeric benzyl ether enal dienes **B10** from the mono TBS derivative **B1** of (±)-2,4-dimethyl-1,5-pentanediol[16] (Chart II). Treatment of the 1:1 mixture **B10** with ethylaluminum dichloride at −78 to −23 °C produced an inseparable 1:1 mixture of products in 70% chromatographed yield. Reduction of this mixture with DIBAH afforded a separable 1:1 mixture of alcohols **B13** and **B14**. The C-8 carbinyl proton of the former appeared as a doublet of doublets at 3.22 ppm with J = 10 and 5 Hz whereas the corresponding proton of the latter gave rise to an unresolved envelope at 3.35 ppm in full accord with the structure assignments. Had the diastereomeric pair **B15** and **B16** been produced, the axial carbinyl proton of the latter would have expectedly given rise to a pattern showing two diaxial couplings.

In principle, the undesired C-8 epimer **B14** could be inverted via benzyl ether cleavage, oxidation–reduction. However, the foregoing results indicate that an acyclic precursor with the correct configuration at C-7 (e.g., **B10a**) should afford the desired bicyclic aldehyde diastereoisomer **B11** directly. Work along these lines is currently in progress.

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Supplementary Material Available: Spectral data for compounds in Charts I and II (9 pages). Ordering information is given on any current masthead page.

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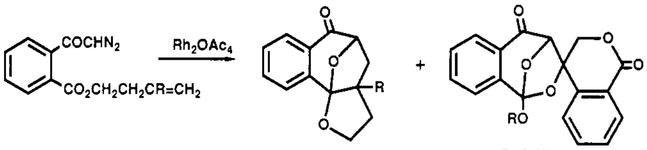
Tandem Cyclization–Cycloaddition Reactions of α-Diazoacetophenone Derivatives[†]

Summary: Treatment of *o*-alkyl-2-enoxycarbonyl-α-diazoacetophenones with rhodium acetate results in an initial cyclization to give a six-ring carbonyl ylide which undergoes a subsequent intramolecular dipolar cycloaddition with the neighboring double bond.

Sir: The reaction of carbenes with heteroatoms bearing a lone pair of electrons to give ylides has been known for some time.[1] Nestled in this area are some examples of carbenes undergoing reaction with carbonyl groups to give carbonyl ylides.[2-8] In recent years there has been a growing interest in the potential use of carbonyl ylides as 1,3-dipoles for total synthesis.[9-11] Their dipolar cycloaddition to olefinic, acetylenic, and hetero multiple bonded dipolarophiles has been well demonstrated.[12] The intramolecular trapping of carbonyl ylides by multiple bonds represents a useful method for the synthesis of some novel carbocyclic ring systems.[10-15] An attractive feature of this reaction is the opportunity to control the stereochemistry of the product at several centers. In this communication we present results which show that cyclic six-membered ring carbonyl ylides, produced from *o*-alkyl-2-enoxycarbonyl-α-diazoacetophenones, undergo intramolecular cycloaddition with a C–C double bond suitably located within the molecule. The resulting product represents a multiply functionalized rigid bicyclic system which is capable of subsequent synthetic elaboration.

The synthesis of α-diazoacetophenone **1** consisted of treating phthalic anhydride with 1-buten-4-ol followed by conversion of the resulting acid to the diazoketone in the usual fashion. Treatment of **1** with a catalytic quantity of rhodium(II) acetate at 25 °C in benzene afforded cyclohepta[1,2-*b*]furanone **3** in 87% yield (NMR ($CDCl_3$,360 MHz) δ 1.15–1.25 (m, 1 H), 1.55–1.68 (m, 3 H), 1.96–2.67 (m, 1 H), 3.90 (dt, 1 H, J = 8.3 and 5.7 Hz), 4.17 (dt, 1 H, J = 8.3 and 6.8 Hz), 4.79 (dd, 1 H, J = 7.4 and 2.0 Hz), and 6.90–8.14 (m, 4 H). In addition to cycloadduct **3**, a 10% yield of spiroisochromanedione **4** was also obtained.



1; R=H
2; R=CH₃

3; R=H
5; R=CH₃

4; R=C₄H₇

This material could be prepared in larger quantities by adding a sample of 1*H*-2-benzopyran-1,4(3*H*)-dione (**6**) to the initial reaction mixture. This would suggest that **6** is formed from **1** by a competitive hydrolysis and is followed by a cycloaddition reaction with **9** across the carbonyl group to produce **4**.

The NMR spectrum of cycloadduct **3** was a bit complicated since a number of overlapping peaks were present. In order to simplify the spectrum, the reaction of **2** with rhodium diacetate was carried out. The cyclization–cycloaddition sequence proceeded quite smoothly producing

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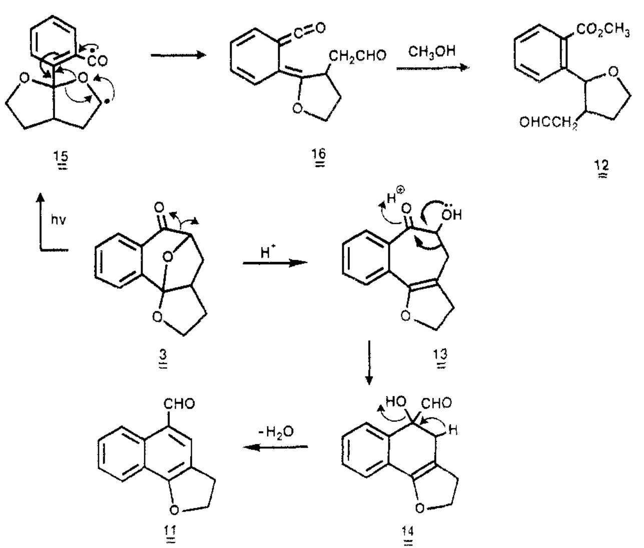
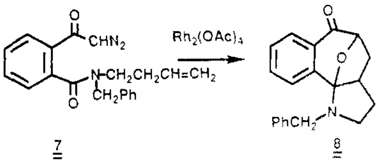
[†] Dedicated to Howard E. Zimmerman on the occasion of his 60th birthday.

0022-3263/86/1951-1157$01.50/0

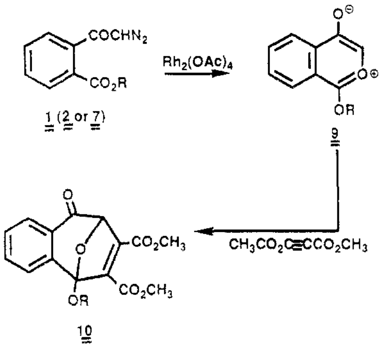
Scheme I



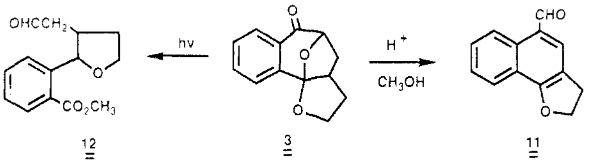
cycloadduct **5** in 80% yield (NMR ($CDCl_3$, 360 MHz) δ 0.40 (s, 3 H), 1.31 (dd, 1 H, J = 12 and 1.4 Hz), 1.40 (ddd, 1 H, J = 12.0, 8.0, and 4.3 Hz), 1.80 (ddd, 1 H, J = 12.0, 8.4, and 8.0 Hz), 2.09 (dd, 1 H, J = 12.2 and 9.0 Hz), 3.94 (q, 1 H, J = 8.0 Hz), 4.20 (ddd, 1 H, J = 12.2, 8.7, and 4.3 Hz), 4.77 (dd, 1 H, J = 9.0 and 1.4 Hz), 7.01 (dt, 1 H, J = 9.0 and 1.6 Hz), 7.12 (dt, 1 H, J = 9.0 and 1.6 Hz), 7.53 (dd, 1 H, J = 9.0 and 1.2 Hz), and 8.14 (dd, 1 H, J = 9.0 and 1.2 Hz). We also studied the metal catalyzed reaction of the closely related diazoamide **7** and found that an analogous reaction occurred.



The above results are consistent with a mechanism in which the key step involves intramolecular cyclization of the ketocarbenoid onto the oxygen atom of the ester carbonyl to give a resonance-stablized six-membered carbonyl ylide intermediate (**9**). The ylide dipole is then trapped internally by the neighboring double bond to give the internal cycloadduct. Support for this contention was obtained by carrying out the reaction of **1** (**2** or **7**) in the presence of excess dimethyl acetylenedicarboxylate. Under these conditions, the formation of the internal cycloadduct, which is produced in high yield in the absence of a trapping agent, is entirely supressed. The only product obtained corresponds to the expected bimolecular dipolar cycloadduct **10**.



During the course of our studies we found that cycloadduct **3** undergoes some unusual rearrangement reactions. Treatment of **3** with hydrochloric acid in methanol gave 2,3-dihydronaphtho[1,2-*b*]furan-5-carboxaldehyde (**11**) in 85% yield. On irradiation in methanol, a rearrangement occurred producing methyl (tetrahydrofuranyl)benzoate **12** in 73% yield. The unexpected conversion of **3** to **11** can be rationalized in terms of an initial protonation on the bridged ether oxygen followed by ring opening and proton loss to give **13** as a transient species. This compound then undergoes a subsequent acid-induced rearrangement to **14** followed by loss of water to produce **11** (Scheme I).



The formation of benzoate **12** is readily explicable in terms of a photoinduced Norrish type I ring cleavage of **3** to give diradical **15**. Fragmentation of this species produces ketene **16** which reacts with methanol to give benzoate **12**.

Work is currently underway utilizing this methodology for the construction of the perhydroazulene ring system.

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Supplementary Material Available: Experimental details and spectral data for **1**, **2**, **3**, and **7** (3 pages). Ordering information is given on any current masthead page.

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