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Intramolecular Ortho [2+2] Photocycloaddition of 5-(p-Acylphenyl)-1-pentenes

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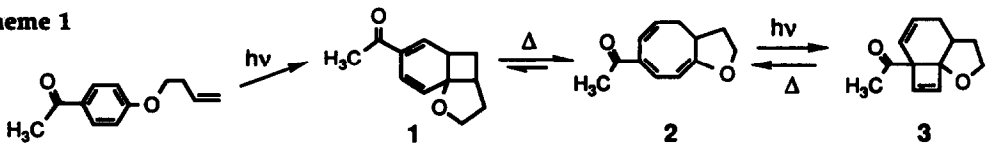
Abstract: The title compounds undergo intramolecular 2+2 ortho photocycloadditions to generate tricycloundecadienes 4 and 5. These are formed stereoselectively, with the four and five-membered rings anti to each other. Compounds 4 undergo low temperature Cope rearrangements to generate epimers of 5 and also open to equilibrium mixtures of bicycloundecatrienes and tricycloundecadienes 7. The latter revert photochemically to the original phenyl ketones.

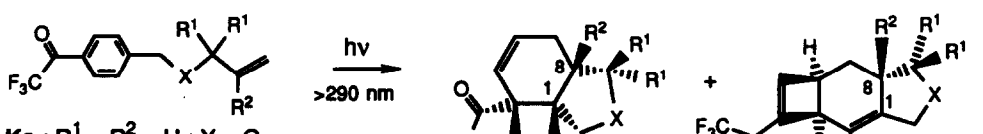
Several years ago we reported that UV irradiation of p-(3-butenoxy)phenyl ketones forms bicycloöctadienes **3** that convert thermally to cycloöctatrienes.[1] The overall process results from an intramolecular ortho photocycloaddition of the double bond to the π,π^* triplet of the benzene ring, to form **1**, which then undergoes the efficient electrocyclic rearrangements in Scheme 1.

Scheme 1



The anchoring oxygen atom present in our original studies has a strong effect on electron distribution in the lowest triplet of the phenyl ketone and probably strongly influences the rates of the thermal electrocyclic rearrangements. Therefore we have studied several compounds in which the unsaturated tether is anchored to the benzene ring with a methylene group. Scheme 2 summarizes the results for several α,α,α-trifluoromethylacetophenones.[2] In all cases, irradiation produced a mixture of two isomeric tricyclo[6.3.0.0]undecadienes **4** and **5**, with the latter favored at low conversion, the former at high conversion. The products were isolated by flash chromato-

Scheme 2

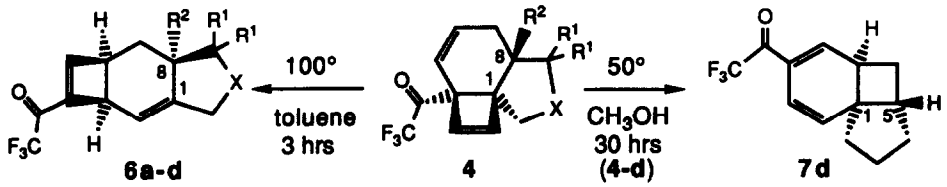


Ka : $R^1 = R^2 = H$; X = O
Kb : $R^1 = H$; $R^2 = Me$; X = O
Kc : $R^2 = H$; $R^1 = Me$; X = O
Kd : $R^1 = R^2 = H$; $X = CH_2$

graphy; their stereochemistry was determined by ^1H and ^{13}C NMR, including nOe.[3] Yields were determined by GC analysis. Total chemical yields averaged 60% at 25% conversion, with that of 5 dropping at higher conversions. Quantum yields at 10% conversion were: **4a**, .017; **5a**, .045; **4b**, .021; **5b**, .026; **4c**, .005; **5c**, .009; **4d**, .0034; **5d**, .0064.

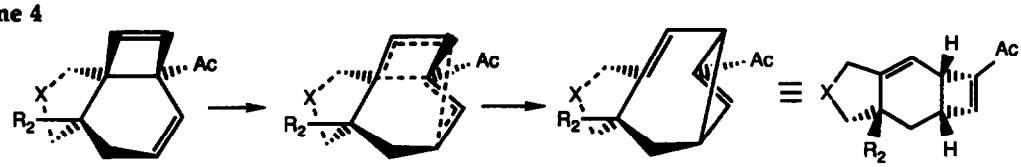
Photoproducts **4a-d** are analogous to compounds 3 structurally and also undergo thermal pericyclic rearrangements. However, as shown in Scheme 3, compounds 4 undergo a Cope rearrangement instead of the electrocyclic ring opening that occurs in 3.[4] Photoproducts **5a-d** are stable under the same conditions but undergo electrocyclic openings at higher temperatures.

Scheme 3

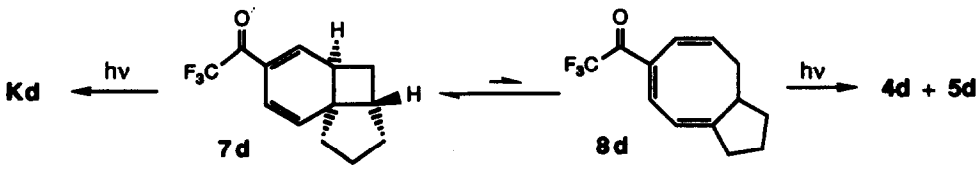


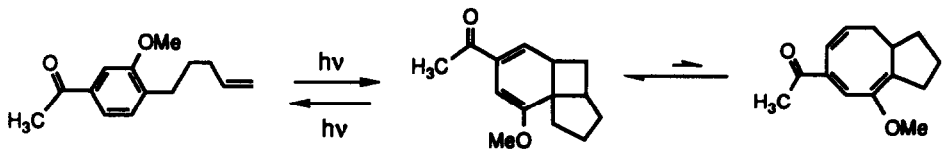
Heating each of the products 4 at 100° quantitatively produces the C-8 epimer 6 of the corresponding linear photoproduct 5. The NMR spectra of **6a-d** are very similar to those of **5a-d**; the exact stereochemistries of **6a-d** were confirmed by nOe experiments. Similar Cope rearrangements have been reported before.[5] Scheme 4 shows how the Cope rearrangement produces the stereochemistry of 6. It is noteworthy that this Cope rearrangement must be faster than the normal bicycloöctadiene→cycloöctatriene rearrangement exemplified by 3 → 2..

Scheme 4



We have found independently that methanol or added acid accelerates the 3 → 2 rearrangement.[6] The slow low temperature rearrangement of **4d** → **7d** presumably arises from the same electrocyclic cyclobutene ring opening, with the cyclohexadiene structure being favored in equilibrium with its cycloöctatriene isomer **8d**. There is too little **8d** present to be detected in the NMR spectrum of **7d**, but its presence is revealed by strong absorption in the near uv (ε = 2160 cm^{-1} M^{-1} at 328 nm). Uv irradiation of isolated **7d** forms **Kd** as well as **4d** and **5d**. The same is true for **Ke**, which yields mainly **7e** as a photoproduct; irradiation of isolated **7e** regenerates **Ke**.[7]





Ke **7e** **8e**

We can summarize our findings as follows. Changing the anchoring atom from oxygen to carbon does not change the initial photochemistry of the unsaturated ketones. (Triplet reaction rates may vary; we shall measure them.) However, rates of the subsequent thermal electrocyclic rearrangements are changed substantially, so that the overall quantum efficiency is lowered. The quantum yields for formation of products **4** and **5** depend on the competitive photochemistry of **7** and **8**. The **7** → **8** rate apparently is slower than the **1** → **2** rate and allows more photoreversion of **7** to starting phenyl ketone than occurs for **1** Likewise, the **4** → **8** ring opening is slower than the corresponding **3** → **2** reaction, so that the Cope **4** → **6** rearrangement can compete Both observations further support the idea that the thermal openings of both **1** and **3** to **2** are accelerated by strong donor-acceptor interactions from oxygen to carbonyl.[1] One reason that we studied the trifluoroacetophenones was to maintain as strong a donor-acceptor interaction in the bicycloöctadienes as possible, as well as to maintain a π,π^* lowest triplet.[8] In fact p-(4-penten-1-yl)acetophenone, which also has a π,π^* lowest triplet,[9] undergoes photocyclization just like **Kd**.

Whereas all the oxygen-tethered ketones that we have studied produce only the angular compound **3**, as Scheme 1 shows, these carbon-tethered compounds are unique in giving both linear and angular tricyclo[6.3.0.0]undecadiene photoproducts. We are now studying their competitive formation more closely, to see why cycloöctatrienes **8** cyclize at both diene units. It is possible that the strong oxygen-to-carbonyl donor-acceptor conjugation present in one diene unit of **2** localizes excitation mostly on that diene unit; the CH_2-to-CF_3CO donor-acceptor interaction may be too weak to ensure predominant formation of **4** from **8**. It is also interesting that the angular products **4** are stable to light, whereas the linear **5**'s are destroyed by continued irradiation. Thus **5** is more stable to heat but less stable to light than **4**. Heating **5c** to 200° causes it to revert to **7c**. We conclude that the linear tricyclo[6.3.0.$0^{3,6}$]undeca-1,4-dienes cannot undergo the Cope rearrangement and instead undergo a slow but typical cyclobutene ring opening to regenerate an equilibrium mixture of **8** and **7** which favors **7**.

We note that the stereochemistry for formation of both **4** and **5** is the same as reported separately for the photocyclizations of several oxygen-anchored systems.[10] The four-membered ring is cis-fused to the six-membered ring and anti to the five-membered ring in both the angular and the linear bicycloöctadiene isomers.

Acknowledgement: This work was supported by NIH grant No. GM-39821. The NMRs were purchased with funds provided by NIH Grant No. RR04750 and NSF Grant No. CHE88-00770.

References

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2 The reactants K were prepared by treating the Grignard reagents of the corresponding p-bromobenzyl ethers or -butene with ethyl trifluoroacetate at -78°C. 5-(4-Bromophenyl)-1-pentene was prepared by reaction of 4-bromobutene with the Grignard reagent of p-bromobenzyl bromide stabilized by HMPA.

3 *e.g.* **4b** : IR (CCl_4) 1738 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.27 (d, J=3.0 Hz, H_2) 6.22 (d, J=3.0 Hz, H_3) 5.92 (dt, J=10.2, 5.60 Hz, H_8) 5.73 (br d, J=10.4 Hz, H_6) 3.89 (d, J=10.7 Hz, $H_{9\beta}$) 3.73 (d, J=8.0 HZ, $H_{11\alpha}$) 3.66 (d, J=10.9 Hz, $H_{9\alpha}$) 3.50 (d, J=8.1 Hz, $H_{11\beta}$) 2.20 (dd, J=17.1 ,5.22 Hz, $H_{7\alpha}$) 1.96 (dd, J=17.1,3.85 Hz, $H_{7\beta}$) 1.06 (s, CH_3). nOe : H-11β > H-2 = H-7β = H-9β > H-7α were enhanced when the (β) methyl group at C-8 was irradiated. ^{13}C NMR ($CDCl_3$) δ 192.4 (q, J = 36 Hz), 138.6, 136.2, 129.0, 122.7, 115.9 (q, J = 296 Hz), 77.3, 71.2, 64.65, 61.2, 43.7, 31.1, 22.4..**5b** : IR (CCl_4) 1709 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.29 (br s, H_5) 5.79 (br d, J = 4 H_2) 4.22 , 4.02 (AB quar, J=13.5 Hz, H_{11}) 3.51, 3.04 (AB quar, J=7.8 Hz, H_9) 3.22 (t, J=5.7 Hz, H_3) 2.54 (m, H_6) 2.08 (d, J=14.1, $H_{7\beta}$)) 1.53 (dd, J = 14, 6 Hz, $H_{7\alpha}$) 1.10 (s, CH_3). nOe : H-9β > H-7β > H-5 > H-11β were enhanced when the (β) methyl group at C-8 was irradiated Irradiation of H-6 enhanced H-5 and H-7α but not the C-8 methyl. ^{13}C -NMR ($CDCl_3$) δ 174.8 (q, J = 37 Hz) 158.8, 147.0, 142.7, 116.0 (q, J = 290 Hz) 114.5, 81.7, 69.9, 41.9, 41.0, 40.3, 34.1, 24.1.

4 **5b** :^{1}H-NMR (C_6D_6) δ 6.53 (br s, H_5) 5.49 (br d, J = 4 Hz, H_2) 4.22, 4.02 (AB quar, J=13.5 Hz, 2 H_{11}) 3.51, 3.04 (AB quar, J=7.8 Hz, 2 H_9) 3.22 (t, J=5.7 Hz, H_3)) 2.54 (m, H_6) 1.38 (d, J=14.1, $H_{7\beta}$) 0.87 (s, CH_3) 0.86 (dd, J = 14, 6 Hz, $H_{7\alpha}$). **6b** : ^{1}H-NMR (C_6D_6) δ 6.48 (br s, H_5) 5.47 (m, H_2) 4.24, 3.97 (AB q, J=13.4 Hz, 2 H_{11}) 3.53, 3.09 (AB q, J=8.3 Hz, 2 H_9) 3.17 (br d, J = 8.2 Hz, H_3) 2.53 (m, J = 8.2, 2.6 Hz, H_6) 1.39 (dd, J=11.7, 2.6Hz, $H_{7\beta}$) 0.83 (s, CH_3) 0.73 (dd, J=11.7, $H_{7\alpha}$); nOe: Irradiation of either H-9 or the C-8 methyl enhances the other and H_1 strongly. ^{13}C NMR ($CDCl_3$) δ 175.9 (quar), 158.2, 148.4, 141.2, 116.0 (quar), 113.9, 80.4, 69.5, 43.8, 41.2, 39.0, 34.9, 23.1. **7d** : ^{1}H NMR ($CDCl_3$) δ 6.90 (d, J = 1.58 Hz, H_8) 6.26, 5.60 (AB q, 2 H, $J_{10,11}$ = 10.0 Hz) 2.95 (m, H_5) 2.88 (m, H_7) 2.40 (m, $H_{6\alpha}$) 2.10 (m, $H_{3\alpha}$) 1.98 (m, $H_{6\beta}$) 1.91 (m, $H_{4\alpha}$) 1.72 (m, $H_{2\beta}$) 1.66 (m, $H_{4\beta}$) 1.46 (m, $H_{2\alpha}$) 1.31 (m, $H_{3\beta}$). ^{13}C NMR ($CDCl_3$) δ 179.65, 145.33, 145.29, 134.07, 116.59, 115.96, 53.21, 46.78, 40.56, 35.81, 35.78, 33.79, 25.58.

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