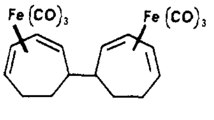
(Et_2O, 0 °C)[7] resulted in a low yield (20–25%) of product **4** of terminal methylation,[8] together with ca. 25% yield of the dimeric species **5**, the latter being indicative of electron-transfer processes.



5

Hydride abstraction from **4** ($Ph_3C^+PF_6^-$, CH_2Cl_2, 20 °C, 45 min) proceeded in high yield to give the substituted dienyl complex **6**.[8]

Reaction of **6** with lithium dimethylcuprate gave a 3:1 mixture of complexes **7** and **8** (NMR), while reaction with methyllithium gave only **8**, both reactions being accompanied by dimer formation and proceeding in low overall yield (20%;[8] Scheme I). Despite the low yields, formation of **7** does indicate the potential for attaining 1,3-stereocontrol by using a seven-membered ring. Surprisingly, reaction of **1a** with dimethyl malonate anion gave low yields of multiple products.[9]

During the above study we consistently observed the formation of considerable amounts of polar material (TLC), which was too unstable for characterization. This might arise from nucleophile attack at a CO ligand[10] and might be effectively overcome by increasing the electron density at the metal. We therefore examined reactions of complexes **1b** and **1c**, summarized in Scheme II. Treatment of **1b** with MeLi (CH_2Cl_2, −78 °C) gave the product **9b** of methylation at C-2 of the dienyl ligand, while reaction of **1b** or **1c** with Me_2CuLi (Et_2O, 0 °C) gave the product **10** of terminal methylation,[8] in 85–90% yield. Reaction of **1b** or **1c** with dimethyl sodiomalonate (THF, 20 °C) gave **11**; reaction with methyl sodioacetoacetate gave an equimolar mixture of diastereomers **12** and with methyl phenylsulfonylsodioacetate gave **13**, all reactions occurring in 90–100% yield and at the dienyl terminus, as shown conclusively by NMR spectra of the products.[8] Hydride abstraction ($Ph_3C^+PF_6^-$, CH_2Cl_2, 20 °C, 45 min) from the methyl-substituted complex **10** proceeded in excellent yield to give **14**, which upon treatment with Me_2CuLi, gave a single crystalline product in 83% yield, readily identified as **15** from its *symmetrical* 200-MHz ^1H NMR spectrum.[8] (Addition of the second methyl group *syn* to the metal would have given a compound showing widely differing CH_3 chemical shifts.) Reaction of **14** with dimethyl sodiomalonate occurred with equal regio- and stereospecificity to give **16** in essentially quantitative yield.[8] Decomplexation of **16c** (Me_3NO, dimethylacetamide, 55 °C, 36 h) afforded the stereochemically defined cycloheptadiene derivative **17**[8] in 80% yield. Finally, treatment of the methylated dienyl complex **14** with methyl phenylsulfonylsodioacetate gave the diene complex **18** as a mixture of distereomers in 90% yield after preparative TLC.

In conclusion, we have now demonstrated that (a) alteration of the electronic character of the metal in cycloheptadienyl–Fe-$(CO)_2L$ complexes has a profound effect on the reactivity of these molecules toward a range of synthetically useful nucleophiles, (b) changes in the nature of the nucleophile have a profound effect on regioselectivity of the reaction, and (c) the metal can be successfully removed in high yield in the presence of functional groups. Thus, it is possible to synthesize stereochemically defined substituted cycloheptadiene derivatives via iron complexes. We are currently studying functionalization of the diene unit of compounds related to **17**.

Acknowledgment. 200-MHz NMR spectra were recorded on a Varian XL-200, purchased with the aid of a grant from the National Science Foundation.

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(8) Structural types **2** and **3** show significant differences in their ^1H NMR spectra, and our data agree with published spectra of similar compounds.[2,4] Spectral data of representative compounds follow. **4**: IR ν_{max} ($CHCl_3$) 2039, 1964 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (2 H, m, 2-H, 3-H), 3.07, 2.86 (1 H, m, each, 1-H, 4-H), 1.97 (3 H, br m), 1.43 (1 H, m), 1.28 (1 H, m), 0.95 (3 H, d, J = 6 Hz). **6**: IR ν_{max} (CH_3CN) 2103, 2056 cm^{-1}; ^1H NMR (CD_3CN) δ 7.12 (1 H, t, J = 7 Hz, 3-H), 6.20 (1 H, dd, J = 8, 6 Hz), 5.80 (1 H, dd, J = 10, 7 Hz), 4.85 (2 H, m, 1-H, 5-H), 3.4 (1 H, m, 6-H), 2.4 (1 H, m, endo-7-H), 0.93 (3 H, d, J = 7 Hz), 0.9 (1 H, m, obscured, exo-7-H). **7**: IR ν_{max} ($CHCl_3$) 2040, 1970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.18 (2 H, m, 2-H, 3-H), 2.79 (2 H, m, 1-H, 4-H), 1.98 (2 H, m), 1.19 (2 H, m) 0.86 (6 H, d, J = 7 Hz). **8**: IR ν_{max} ($CHCl_3$) 2045, 1975 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.59 (1 H, t, J = 8 Hz, 4-H), 4.3 (2 H, m, 3-H, 5-H), 2.79 (1 H, m, 2-H), 2.35 (2 H, m), 1.68 (1 H, m), 1.39 (1 H, d, J = 8.8 Hz), 0.86 (3 H, d, J = 7.2 Hz), 0.85 (3 H, d, J = 6.3 Hz). **9**: IR ν_{max} ($CHCl_3$) 1972, 1911, cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3 (15 H, m), 3.94 (1 H, t, J = 8 Hz, 4-H), 3.58 (2 H, m, 3-H, 5-H) 2.85 (1 H, m, 2-H), 2.13 (1 H, m, 1-H), 1.88 (2 H, m), 1.50 (2 H, m), 0.60 (3 H, d, J = 7.1 Hz). **10b**: IR ν_{max} ($CHCl_3$) 1968, 1907 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (15 H, m), 4.57 (2 H, m, 2-H, 3-H), 2.28 (2 H, m, 1-H, 4-H), 1.83 (3 H, m), 1.10 (1 H, m), 0.77 (3 H, d, J = 6 Hz). **11b**: IR ν_{max} (CCl_4) 1980, 1923, 1760, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4 (15 H), 4.4 (2 H, m, 2-H, 3-H), 3.64 (3 H, s), 3.60 (3 H, s), 3.12 (1 H, d, J = 6.3 Hz, malonate CH), 2.8–1.9 (5 H, m), 1.25 (2 H, m). **12b**: IR ν_{max} (CCl_4) 1977, 1923, 1738, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (15 H), 4.63 (2 H, m, 2-H, 3-H), 3.60 and 3.56 (3 H, two s), 3.0 (1 H, s), 2.05 (2 H, m, 1-H, 4-H), 2.06 and 2.02 (3 H, two s), 1.95 (3 H, m), 1.15 (2 H, m). **14**: IR ν_{max} (CH_3CN) 2042, 2002 cm^{-1}; ^1H NMR (CD_3CN) δ 7.06 (15 H), 6.09 (1 H, m, 3-H), 5.36 (2 H, m, 2-H, 4-H), 4.4 (1 H, m, 1-H or 5-H), 3.74 (1 H, m, 5-H or 1-H), 3.31 (1 H, m), 2.2 (1 H, m), 0.84 (3 H, d, J = 6 Hz, and 1 H, m). **15**: IR ν_{max} ($CHCl_3$) 1968, 1908 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (15 H), 4.59 (2 H, m, 2-H, 3-H), 2.20 (4 H, m, 1-H, 4-H, 5-H, 7-H), 1.48 (1 H), 0.98 (1 H), 0.79 (6 H, d, J = 6.5 Hz). **16**: IR ν_{max} ($CHCl_3$) 1976, 1917, 1758, 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (15 H), 4.53 (2 H, m, 2-H, 3-H), 3.57 (3 H, s), 3.53 (3 H, s), 3.0 (1 H, d, J = 7 Hz, malonate CH), 2.2 (2 H, m, 1-H, 4-H), 1.8 (2 H, m), 1.2–0.8 (2 H, m), 0.8 (3 H, d, J = 6.5 Hz). **17**: IR ν_{max} ($CHCl_3$) 1750, 1733 cm^{-1}; ^1H NMR (CCl_4) δ 5.58 (4 H, s, olefinic), 3.75 (6 H, s), 3.36 (1 H, d, J = 7 Hz), 2.8–2.5 (2 H, m), 1.9–1.5 (2 H, m), 1.12 (3 H, d, J = 7 Hz).

(9) Contrast with the following: Genco, N.; Marten, D.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1976**, *98*, 848.

(10) See, for example: Bryan, E. G.; Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Schiavon, G. M. *J. Organomet. Chem.* **1977**, *127*, C19. Cowles, R. J. H.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. *Chem. Commun.* **1969**, 392. Hine, K. E.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1975**, 81.

2-Indanol Formation from Photocyclization of α-Arylacetophenones

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Received March 7, 1983

Part of the elegance of Paquette's dodecahedrane synthesis[1] was his anticipation of efficient δ-hydrogen abstraction by photoexcited ketones of restricted conformational mobility. There had been a few examples[2-5] of efficient photocyclization due to triplet state δ-hydrogen abstraction in ketones in which the only reactive C–H bonds are situated δ to the carbonyl, but the controlling conformational factors were not explicitly considered. We report an apparently overlooked example of a very efficient δ-hydrogen transfer process that leads cleanly to 2-indanols and that provides unique information about a rotational equilibrium.

We have studied a group of α-(*o*-tolyl)acetophenones, which undergo quantitative photocyclizations to 2-phenyl-2-indanols. Table I lists several of the compounds together with excited-state kinetics data. All starting ketones were synthesized by standard methods; product structures were determined by isolation and standard spectroscopic analysis. In all cases, the yield of indanol was within experimental error of 100% for 313-nm irradiation of 0.1 M ketone solutions. Quantum efficiencies are quite high,

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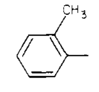
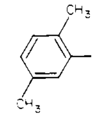
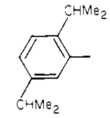
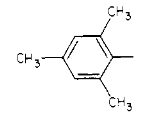
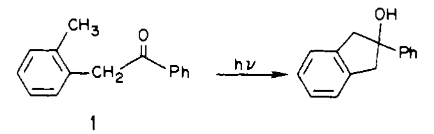
Table I. Photokinetics for Photocyclization of α-Arylacetophenones[a]

aryl group	Φ_{cyc} [b]	$k_q\tau$, M^{-1} [c]	k_H, 10^8, s^{-1} [d]
	1.0	31	1.6
	0.62	19	2.6
	0.44	4.6	15
	0.42	3.4	11

[a] 0.10 M in degassed benzene, irradiated at 313 nm and 25 °C to <5% conversion. [b] Determined with valerophenone actinometry. [c] 2,5-Dimethyl-2,4-hexadiene quencher. [d] $k_H = 1/\tau$, calculated from $k_q = 5 \times 10^9$ M^{-1} s^{-1}.

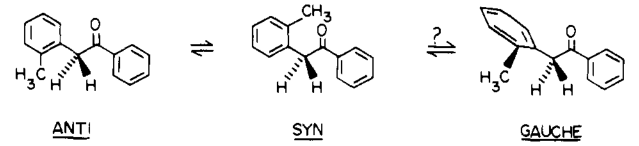
and triplet lifetimes determined by Stern–Volmer quenching studies are quite short.



1

This α-tolyl ketone system is a simple homologue of the widely studied *o*-alkylphenyl ketones.[6,7] In this latter case we originally showed[7] that there are two kinetically distinct triplets corresponding to syn and anti conformers with respect to rotation about the aryl–carbonyl bond. Moreover, the rate-determining step for internal γ-hydrogen abstraction by the anti triplet is the anti → syn bond rotation. We were particularly interested to see whether similar conformational effects might manifest themselves in δ-hydrogen abstraction.

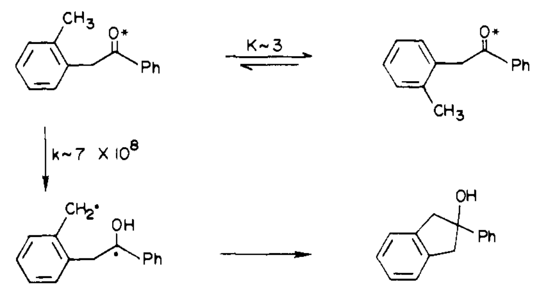
There are probably only three important conformations in α-(*o*-tolyl)acetophenone, syn, gauche, and anti with respect to



rotation around the tolyl–methylene bond, with only the syn being able to undergo δ-hydrogen abstraction. In general, the largest α-substituent preferentially eclipses the carbonyl group,[8] as has been found specifically for α-phenylacetaldehyde.[9] In our case this preference would be reinforced by the ortho hydrogens of the phenone benzene ring hindering any conformations with the α-tolyl ring twisted very far from the eclipsed geometry. Our results suggest that there is very little of the gauche conformer.

We assume that the reaction proceeds via a 1,5-biradical and that $1/\tau$ is determined by the rate for δ-hydrogen abstraction. The large quantum yields and triplet decay rates indicate that the reactive syn conformer is readily accessible and that the excited conformers attain equilibrium before reaction. The only alternative kinetic possibilities are total lack of conformational interchange (ground-state control)[10] or rate-determining bond rotation for reaction by the unreactive conformers.[7,11] The high quantum yields rule out ground-state control, since the unreactive anti conformer should be favored over the syn in both ground and excited states, so that quantum yields would have to be appreciably lower than 0.5 and certainly could not approach unity.

Scheme I



If hydrogen abstraction from the initially excited unreactive conformers were limited by the rate of rotation to the reactive syn conformer, there would be two kinetically distinct triplets, and the predominant one would display a lifetime independent of C–H bond strength. We find no evidence for more than one triplet. Moreover, the significantly greater hydrogen abstraction rate constants for ketones bearing tertiary instead of primary hydrogens indicate that hydrogen abstraction itself is rate determining. The lack of rotation control in this situation indicates that rotation about the phenyl–CH_2 bond is more rapid than hydrogen abstraction. Such is normally the case in acyclic systems; it is only when the carbonyl is conjugated to the phenyl ring that excitation affects the rate of rotation of the phenyl group.

Of particular note is the difference between the xylyl and the mesityl ketones. It is known that alkyl ring substitution slightly enhances rates of benzylic hydrogen abstraction.[12] We see this small effect here in comparing the xylyl- and tolylacetophenones. However, the 7-fold rate enhancement for the mesitylacetophenone then is too large for an inductive effect and must reflect the impossibility of any unreactive anti conformers. Correcting for a small inductive effect, we estimate a conformational factor of ~4. This number indicates that there is 3 times as much anti conformer as the sum of the other two in triplet **1**. The actual anti/syn ratio in **1** cannot be too different from the syn/anti ratio of 4 in *o*-methylacetophenone,[7] so we conclude minimal population of any gauche conformer in **1** (see Scheme I).

The above considerations suggest a rate constant for δ-hydrogen abstraction by the equilibrating syn and gauche conformers of triplet **1** of 7×10^8 s^{-1}. In the syn conformer of *o*-methylacetophenone, the rate constant for γ-hydrogen abstraction has been measured as 3×10^9 s^{-1}, some 4 times higher. These two systems represent a fairly good comparison of intrinsic δ/γ relative reactivities, since we have found separately that α-phenyl[13] and *o*-methyl[7] groups each cut triplet ketone reactivity by factors of 2–3. There has always been doubt as to how to partition the ~20-fold[15] rate difference between γ- and δ-hydrogen abstraction in freely rotating acyclic systems into enthalpic and entropic contributions. The 4-fold difference we estimate for two systems with presumably only one major conformation each suggests that enthalpic factors (seven-membered transition state) are comparable in magnitude to entropic factors. Of course, this conclusion rests on the previous conclusion that there is little gauche conformation in **1**.

The large cyclization quantum efficiencies are noteworthy in themselves, since the 1,5-biradicals formed from some acyclic

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ketones cyclize quite inefficiently.[14] We presume that the quantum yields below unity reflect some biradical disproportionation[15] and not direct triplet radiationless decay, which for phenyl ketones is too slow to compete with these measured lifetimes.[16]

We are extending this study to ketones other than phenones. We have confirmed the report[17] that type I cleavage is too rapid in *o*-tolylacetone for cyclization to compete. Such unfortunately would be expected for alkyl benzyl ketones.[18] We are currently investigating furyl ketones, with the expectation that the furan ring of the resulting 2-indanols will allow further functional group manipulations.

Acknowledgment. This work was supported by NSF Grants CHE-79-10831 and CHE-82-02404, for which we are very grateful. M.A.M. thanks Michigan State University for an L. L. Quill Fellowship.

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Resonance Raman Spectra of the Ground and Excited States of Specifically Deuterated Tris(2,2′-bipyridine)ruthenium(II)

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We report the resonance Raman (rR) spectra of a specifically deuterated analogue of the title complex in both its ground and lowest electronic excited states. The sensitivity of vibrational frequencies to deuterium substitution permits a more reliable correlation of ground- and excited-state frequencies and provides insight into the nature of the vibrational modes in each state. These results are of interest in light of the recent reports by Woodruff and Dallinger and co-workers[2] and Forster and Hester,[3] in which such a correlation was invoked as evidence for the localized excited-state model.

The preparation of the deuterated complex, Ru(bpy-*3,3′-d*$_2$)$_3^{2+}$, was recently reported[4] although detailed reaction conditions were not given. We have found that other positions are susceptible to deuterium exchange and that conditions must be carefully controlled to ensure specific deuteration at the 3,3′-ring positions. The complex was purified by chromatography on Sephadex LH-20 with ethanol eluant and was shown by ^{1}H NMR to be 95% deuterated at the 3,3′-positions with negligible exchange occurring at other sites. The electronic absorption spectrum is identical with that of the natural abundance compound.

Ground state rR spectra were obtained at 4579 Å by using a continuous wave argon ion laser and a Spex 1403 monochromator equipped with photon-counting detection. Excited-state spectra were obtained by employing the 354.7-nm third harmonic line of a Nd:YAG laser as both the pulse and probe beams (7 ns/pulse, 18-Hz pulse rate, 3 mJ/pulse). A triplemate (Spex Industries) monochromator was used to disperse the scattered radiation onto a PAR OMA-II multichannel detector. Toluene was used for wavelength calibration. For both the ground- and excited-state spectra, ~1 mM solutions were circulated through capillary tubes and 90° scattering geometry was employed.

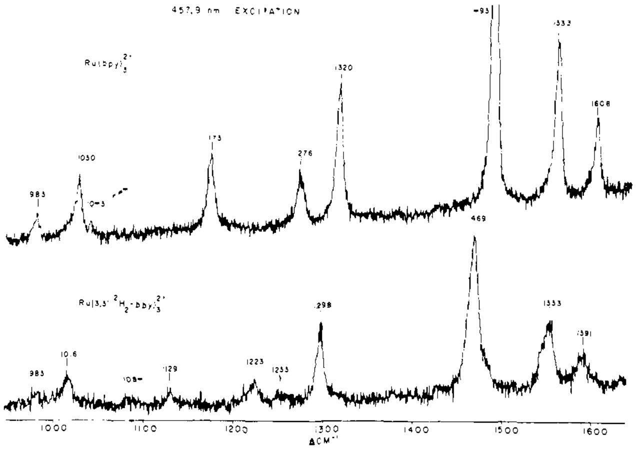

Figure 1. Ground-state resonance Raman spectra of Ru(bpy)$_3^{2+}$ (top) and Ru(bpy-*3,3′-d*$_2$)$_3^{2+}$ (bottom) in H$_2$O. In both cases, the excitation source was the 457.9-nm line of a continuous wave Ar$^+$ laser. The peaks at 983 cm^{-1} are due to the 0.5 M SO$_4^{2-}$ added internal reference.

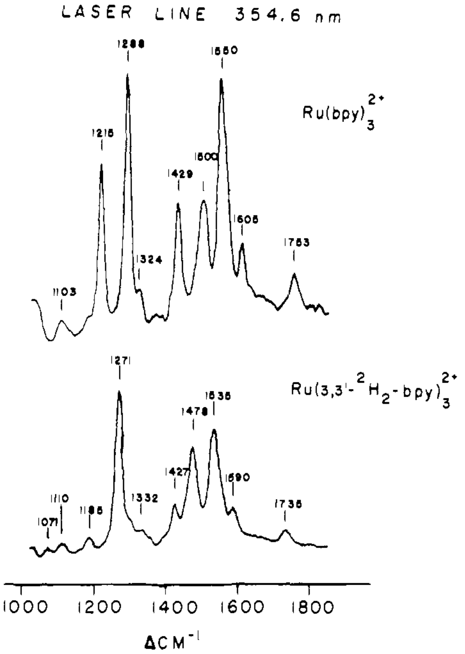

Figure 2. Excited-state resonance Raman spectra of Ru(bpy)$_3^{2+}$ (top) and Ru(bpy-*3,3′-d*$_2$)$_3^{2+}$ (bottom) in H$_2$O. The 354.7-nm third harmonic of a Nd:YAG laser served as both the pulse and probe beams (7 ns/pulse, 18-Hz pulse rate, 3 mJ–pulse).

The ground- and excited-state rR spectra of the deuterated and parent compounds are given in Figures 1 and 2, respectively. The observed frequencies and proposed correlation of bands are given in Table I.

Eleven totally symmetric modes are expected to appear in the ground-state rR spectrum between 1600 and 1000 cm^{-1} with the remaining five modes (excluding four C–H stretches) occurring below 800 cm^{-1}.[5,6] Indeed, consideration of the data presented here, along with those previously reported by using excitation at 400 and 350 nm,[2,3] reveals that at least 11 bands are observed between 1620 and 1000 cm^{-1}.

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