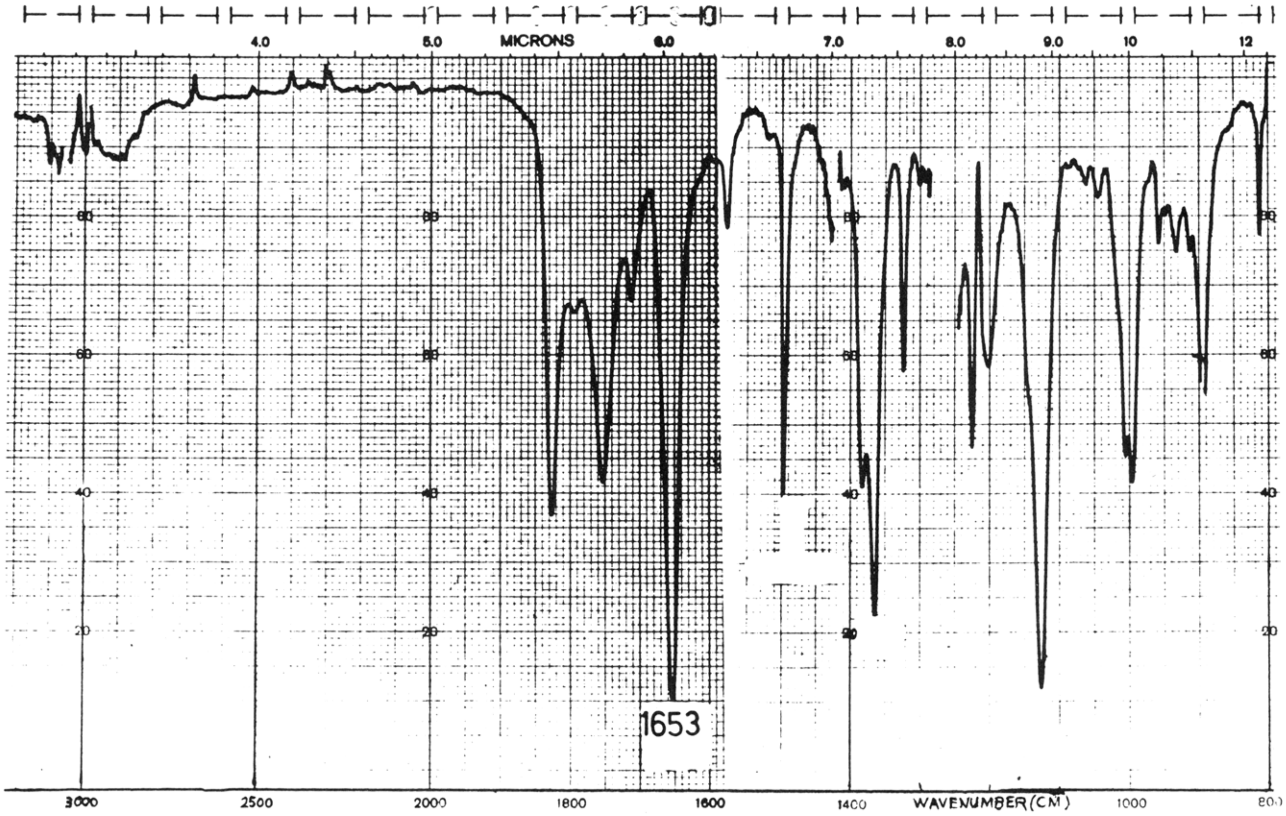

Figure 2. IR spectrum of **3** prepared from the reaction of **7** and **8** (solvent CH_2Cl_2). The sample contains some acetic anhydride from hydrolysis of **8**.

Table II. Refractive Index of "Acetylcyclopentadiene"

time, h	0	0.5	0.75	1	1.75	4	18
n^{22}_D	1.5258	1.5304	1.5319	1.5321	1.5333	1.5332	1.5355

nitrogen. The resulting brownish yellow crystals were suction filtered and washed with a little cold ether: yield of **1** 5.4 g (66.7%); light yellow crystals; mp 88–89 °C.

(ii) Preparation of 3. Compound 1 (5.4 g, 40 mmol) was boiled with an aqueous solution (100 mL) of 2 N NaOH under a stream of nitrogen until no more dimethylamine was evolved (3–4 h). The resulting solution was cooled to −15 °C and neutralized with 2 N H_2SO_4 (100 mL), the color changing from brown to light yellow at the endpoint. The product, which smells like benzaldehyde, was extracted with pentane and the resulting organic phase washed with cold water and dried ($CaCl_2$). After removal of the pentane, the residue was examined by ^{1}H NMR and distilled (Kugelrohr, 40 °C, 0.1 mm), giving several fractions of acetylcyclopentadiene (3.1 g, 72% altogether; cf. Figure 1). The residue from the distillation, i.e., dimeric acetylcyclopentadiene, was heated to 160 °C (water pump vacuum), giving a further fraction of monomeric acetylcyclopentadiene: 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.32 (q, 2 H), 6.55–6.69 (m, 1 H), 6.72–6.85 (m, 1 H), 7.35 (m, 1 H); the spectrum was also recorded in CD_2Cl_2 (no splitting of acetyl singlet down to −100 °C) and in C_6D_6 as solvents (Figure 1); ^{13}C NMR ($CDCl_3$) 26.5 (CH_3), 40.2 (CH_2), 132.6, 141.5, 143.8, 147.0 (quaternary C), 194.4 (C=O).

A sample of the product, which was left overnight at room temperature to dimerize, showed IR peaks at 1671 and 1701 cm^{-1}. These peaks were previously assigned to monomeric acetylcyclopentadiene.[3] An IR spectrum recorded on the dichloromethane solution from the reaction of **7** and **8** after 2.5 h at −30 °C showed a sharp carbonyl band at 1653 cm^{-1} (Figure 2). Table II shows the changing refractive index n_D of acetylcyclopentadiene, which was allowed to stand at room temperature. Since acetylcyclopentadiene dimerizes so quickly, it is unlikely that the value of n^{22}_D of 1.5258 corresponds to that of the pure monomer. In any event, the value of n^{21}_D of 1.5358 in the literature[3] must be assigned to the dimer(s).

1-Pivaloylcyclopentadiene (14). A suspension of cyclopentadienylthallium[12] (2.69 g, 10 mmol) and pivaloyl iodide[6] (2.12 g, 10 mmol) in ether (80 mL) was stirred for 4 h at −20 °C. The stirred suspension was allowed to reach 18 °C overnight, filtered through silica gel, and shaken with an aqueous solution (50 mL) of 2 N NaOH at room temperature. The ether phase which turned light yellow, was shaken with dilute sulfuric acid, washed, and dried ($CaCl_2$). After removal of the solvent the crude product was distilled (Kugelrohr), giving **14** (0.36 g, 24%) as a light yellow, aromatic-smelling liquid. A good deal of the product could not be collected, because it polymerized (dimerized?): 90 MHz ^{1}H NMR (C_6D_6) δ 1.21 (s, 9 H), 3.20–3.28 (d, 2 H), 6.22–6.33 (m, 2 H), 6.91–7.02 (m, 1 H); IR (CCl_4) 1650 cm^{-1}. For comparison, the IR carbonyl band of octanoylcyclopentadiene (**12**) appeared at 1653 cm^{-1}.

Registry No. 1, 14469-77-3; **3**, 60032-12-4; **7**, 34822-90-7; **8**, 507-02-8; **9**, 78209-74-2; **10**, 65269-91-2; **11**, 61915-52-4; **12**, 79517-44-5; **13**, 79517-45-6; **14**, 79517-46-7; **15**, 79517-47-8; **16**, 79517-48-9; **17**, 79534-11-5; dimethyl acetylenedicarboxylate, 762-42-5.

Effects of Para OCF_3 and SCF_3 Substitution on Excited States of Phenyl Ketones

Peter J. Wagner* and Michael J. Thomas

Chemistry Department, Michigan State University, East Lansing, Michigan 48824

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We have pointed out in previous publications that benzene ring substitutents do not have parallel effects on ground-state and on excited-state chemistry.[1,2] The re-

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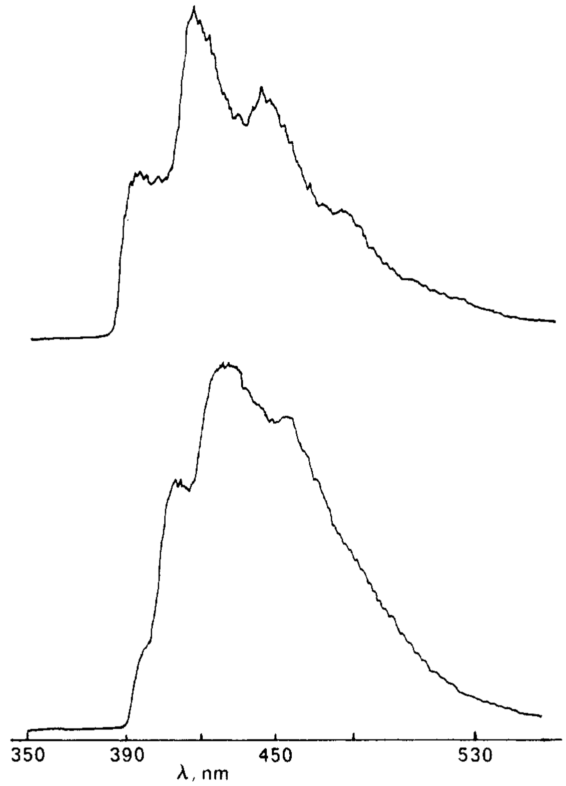


Figure 1. Phosphorescence spectra at 77 K in MCIP glasses of 1-OCF_3 (top) and 2-SCF_3 (bottom).

versal of meta-para conjugating propensities has been well established for some time.[3] However, differences in the conjugative effects of individual substituents are not so widely appreciated. One particular example which we have already noted is the greater electron-donating ability of thiomethoxy relative to methoxy itself in the π,π^* states of phenyl ketones.[1] In the ground state, methoxy is the far better donor.[4]

Substitution of fluorine for the hydrogens of methoxy and thiomethoxy makes them both strong electron-withdrawing groups in the ground state.[4] We decided to determine to what extent fluorines affect the excited-state conjugating ability of these substituents. To that end we have investigated the electronic spectroscopy and photochemistry of some *p*-trifluoromethoxy and *p*-trifluorothiomethoxy phenyl ketones. The results indicate that fluorination inductively stabilizes n,π^* states, as expected, and destabilizes π,π^* states, completely cancelling the donor properties of methoxy and halving those of thiomethoxy.

Both *p*-(trifluoromethoxy)valerophenone (1-OCF_3) and *p*-(trifluorothiomethoxy)-γ-methylvalerophenone (2-SCF_3) were prepared by addition of the appropriate alkylmagnesium bromide to the aromatic nitrile. Figure 1 shows the phosphorescence spectra of both ketones at 77 K in hydrocarbon glasses. That of 1-OCF_3 differs little from that of valerophenone itself (1-H), displaying the characteristic vibrational structure of n,π^* emission and a slightly lower energy 0,0 band. That of 2-SCF_3 is less structured, as commonly observed when π,π^* emission predominates,[5] and strongly resembles the spectrum of 1-OCH_3.[1] From this comparison we conclude that the two fluorinated ketones have lowest triplet states of different configuration.

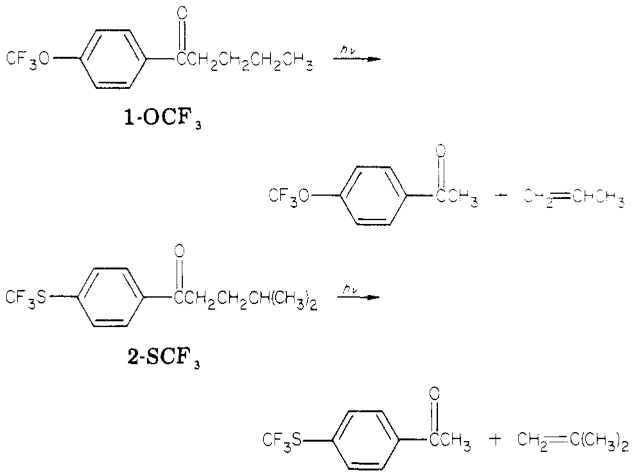
Table I. Spectroscopic Properties of Phenyl Ketones

ketone	^1L_a λ_{max}, nm (ϵ)[a]	Phos 0,0, nm (kcal/mol)[b]
1-H	238 (14 000)	386 (74.3) (n,π^*)
1-OCH_3	264 (17 000)	403 (71.0) (π,π^*)
1-OCF_3	239 (10 400)	392 (73.0) (n,π^*)
1-SCH_3	304 (23 000)	446 (64.2) (π,π^*)
2-SCF_3	272 (8400)	410 (69.8) (π,π^*)

[a] In heptane. [b] In 4:1 methylcyclohexane/isopentane.

UV spectra of ketones confirm this conclusion. The lowest π,π^* triplet of simply substituted benzenes is derived from the ^1L_a state[5,6] and responds to substituents in a parallel but attenuated fashion.[1,2] Table I compares ^1L_a λ_{max} values and the phospohorescence 0,0 bands for the fluorinated and unfluorinated ketones. The ^1L_a band for 1-OCF_3 occurs at almost the same energy as in 1-H itself. Therefore the π,π^* triplet of 1-OCF_3 would be expected to remain above the n,π^* triplet as in 1-H.[1] The ^1L_a band of 2-SCF_3 occurs 15 kcal/mol lower than in 1-H. Therefore we expect a 5–6 kcal/mol lowering of the π,π^* triplet energy[1] and a likely inversion of lowest triplets.

Both fluorinated ketones undergo facile Norrish type II photoelimination[7] upon 313- or 365-nm irradiation, producing the substituted acetophenone and propylene or isobutylene. Material balances are excellent. Small GC peaks with the expected retention times for cyclobutanols are also detected.



1-OCF_3

2-SCF_3

The reaction of 1-OCF_3 is readily quenched by conjugated dienes. That of 2-SCF_3 is not; but it is readily quenched by naphthalene. As expected, both ketones react from their triplet states. Table II lists quantum yields, Stern-Volmer quenching slopes,[9] and triplet lifetimes for the two ketones and compares them to those already reported for the unfluorinated ketones. The triplet reactivity of 1-OCF_3 is indistinguishable from that of 1-H, showing a high quantum yield and the same rate constant. This observation confirms the n,π^* nature of the lowest triplet, since the γ-hydrogen abstraction which leads to type II elimination[7,8] occurs exclusively in n,π^* triplets and is

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[1] Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

[2] Wagner, P. J.; Thomas, J. J.; Harris, E. *J. Am. Chem. Soc.* **1976**, *98*, 7675.

[3] (a) Havinga, E.; de Jongh, R. O.; Dorst, W. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 378. (b) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915. (c) Zimmerman, H. E.; Somasekhara, S. *Ibid.* **1963**, *85*, 922.

[4] Kosower, E. M., "An Introduction to Physical Organic Chemistry"; Wiley: New York, 1968; p 49.

[5] Mc Glynn, S. P.; Azumi, T.; Kinoshita, M. "Molecular Spectroscopy of the Triplet State"; Prentice-Hall: Englewood Cliffs, NJ, 1969.

[6] Kearns, D. R. *J. Chem. Phys.* **1962**, *36*, 1608.

[7] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

[8] Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.

[9] Wagner, P. J. In "Creation and Detection of the Excited State"; Lamola, A., Ed.; Marcel Dekker: New York, 1971; Vol 1A, p 182.

Table II. Photokinetic Data for Para-Substituted Phenyl Ketones[a]

ketone	Φ_{II}[b]	Φ_{CB}[c]	Φ_{-K}	Φ_{II}^{max}[d]	$k_q\tau$, M^{-1}[e]	$10^{-7}(1/\tau)$, s^{-1}[f]
1-H[g]	0.33	0.07		1.0	40	12.5
1-OCH_3[h]	0.14	0.03		0.26	2300	0.22
1-OCF_3	0.30	0.06	0.36	1.0	40 ± 4	12.5
2-H[g]	0.25	0.03		1.0	10	50
1-SCH_3[h]	0	0		0		
2-SCF_3	0.16	0.01	0.16	0.54	20.5 ± 1	25

[a] 0.03–0.05 M ketone in degassed benzene solution irradiated at 313 nm. [b] Acetophenone formation. [c] Cyclobutanol formation. [d] Total product in 5 M *t*-BuOH for 1 and 0.5 M pyridine for 2. [e] 2,5-Dimethyl-2,4-hexadiene quencher for 1, naphthalene for 2. [f] $k_q = 5 \times 10^9\ M^{-1}\ s^{-1}$. [g] From ref 17. [h] From ref 1.

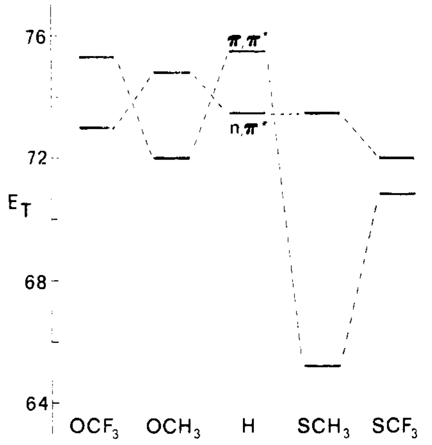

Figure 2. Estimated excitation energies of n, π* and π,π* triplets of phenyl alkyl ketones in benzene solution as a function of para substituents.

much slower when π,π* triplets are lowest.[1,2,10]

The triplet decay rate of **2**-SCF_3 is half that of the unsubstituted **2**-H, much faster than in the unfluorinated ketone. Since the maximum quantum yield from **2**-SCF_3 is only 54%, we deduce that half of the triplet decay represents something other than γ-hydrogen abstraction and therefore than hydrogen abstraction by triplet **2**-SCF_3 is only one-fourth as fast as in triplet 2-H. Furthermore, substituents with σ values as large as SCF_3 (0.64)[4] are known to double the rate of hydrogen abstraction by n,π* triplets.[1] Therefore the observed rate of hydrogen abstraction by triplet **2**-SCF_3 is only one-eighth what would be expected for its n,π* triplet. Such substituent-induced decreases in reactivity are known to signify π,π* lowest triplets.[1,10] The decrease normally measures the equilibrium fractional population of the reactive n,π* triplet.[1] In this case the factor of $^1/_8$ indicates a 1.3 kcal/mol separation between the two lowest triplets of **2**-SCF_3.

Figure 2 summarizes the various substituent effects on triplet energies as deduced from the spectroscopy and the photoreactivity. The data for CH_3O and the methodology employed are already published.[2] Fluorination produces opposite effects on the two triplets. It effectively cancels the electron-donating conjugative stabilization of the π,π* triplet afforded by methoxy. The slight inductive destabilization of the n,π* triplet by methoxy ($\sigma = -0.27$)[4] is replaced by a slight stabilization ($\sigma_{OCF_3} = 0.28$).[4] As usual, substituent effects on n,π* triplets follow Hammett σ values closely.[11,12]

The n,π* energy for SCH_3-substituted ketones cannot be measured. The zero σ value for SCH_3[4] suggests a negligible change from the unsubstituted ketone. As expected from its large σ, SCF_3 stabilizes the n,π* triplet by some 1.5 kcal/mol. It also stabilizes the π,π* triplet but only half as much as does SCH_3. SCF_3 is thus similar to Cl[1] and to CN[13] in stabilizing both triplets, n,π* by its electron-withdrawing inductive effect and π,π* by (diminished) electron-donating conjugation. Since SCF_3 and OCH_3 have similar effects on π,π* energies, the 100-fold difference in their effects on triplet reactivities reflects largely their opposite effects on n,π* energies.

We suspect that **2**-SCF_3 undergoes a small amount of S–CF_3 bond homolysis because of the poor quenching ability of dienes. This behavior is symptomatic of radical-initiated destruction of the quencher.[14] Such homolysis probably is not a major reaction of **2**-SCF_3 because of the excellent material balance observed and therefore cannot be entirely responsible for the low quantum yields. These we must blame on either impurity quenching or on self-quenching.

Experimental Section

Preparation of 1-OCF_3. Butyl Grignard reagent was prepared by adding 5 g of *n*-butyl bromide to 1 g of Mg turnings in 30 mL of ether. To this was added 4.5 g of *p*-(trifluoromethoxy)benzonitrile (Pierce). The solution was allowed to stir at room temperature overnight and was then added to an ice–HCl mixture. Normal workup[15] and distillation provided 4.8 g of **1**-OCF_3: bp 106–107 °C (4.5 torr); ^1H NMR (CCl_4) δ 0.95 (t, 3 H, *J* = 8.5 Hz), 1.1–2.0 (m, 4 H), 2.87 (t, 2 H, *J* = 6 Hz), 7.20 (d, 2 H, *J* = 8.5 Hz), 7.93 (d, 2 H, *J* = 8.5 Hz); mass spectrum, *m/e* 246, 217, 204, 189 (base), 161.

Preparation of 2-SCF_3. Isovaleryl Grignard reagent was prepared by adding 6 g of 1-bromo-3-methylbutane to 1 g of Mg in 35 mL of ether. To this was added 4.4 g of *p*-(trifluorothiomethoxy)benzonitrile (Pierce). The solution was refluxed for 3 h. Normal acid hydrolysis and workup provided 3.8 g of **2**-SCF_3: bp 140 °C (5.5 torr); ^1H NMR (CCl_4) δ 0.95 (d, 6 H, *J* = 5 Hz), 1.3–1.7 (m, 3 H), 2.83 (t, 2 H, *J* = 7 Hz), 7.53 (d, 2 H, *J* = 8 Hz), 7.80 (d, 2 H, *J* = 8 Hz); mass spectrum, *m/e* 276, 261, 257, 233, 220, (base), 205 (base), 177,151.

Spectroscopy. UV spectra were recorded on a Unicam SP800 and phosphorescence spectra on an Aminco-Bowman spectrofluorimeter with a mechanical chopper.

Photokinetic Studies. Samples were prepared as in our earlier studies in carefully purified benzene.[1] After being degassed and sealed, they were irradiated on a "merry-go-round" apparatus.[16] An alkaline potassium chromate filter solution isolated the 313-nm region of a Hanovia 450-W mercury arc and a set of Corning No. 7-83 filters isolated the 366-nm region. Product formation and ketone disappearance relative to known concentrations of alkane internal standards were measured by GC analysis on a 6 ft × $^1/_8$ in column packed with 4% QF-1 and 1% Carbowax 20M. Analyses were performed on Varian 1200 chromatographs with FID detectors. Propylene and isobutylene were identified by their

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[10] Yang, N. C.; Dusenbery, R. *J. Am. Chem. Soc.* **1968**, *90*, 5899.

[11] Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301.

[12] Loutfy, R. O; Loutfy, R. *Tetrehedron* **1973**, *29*, 2251.

[13] Wagner, P. J.; Siebert, E. *J. Am. Chem. Soc.*, in press.

[14] (a) Wagner, P. J.; McGrath, J. M.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 6883. (b) Turro, N. J.; McDaniel, D. M. *Mol. Photochem.* **1970**, *2*, 39.

[15] Hauser, C. R.; Humphlett, W. J.; Weiss, M. J. *J. Am. Chem. Soc.* **1948**, *70*, 426.

[16] Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.

characteristic retention times. The acetophenones were not actually isolated; GC product peacks with the expected retention times were assumed to correspond to these products which necessarily accompany the alkenes. Light intensity for quantum yield measurements was measured by parallel irradiation of 0.1 M valerophenone actinometers[17] and equalled 0.064 einstein L^{-1} h^{-1}.

Acknowledgment. This work was supported by NSF Grants No. CHE-76-11892 and -79-10831. M.J.T. thanks the Institute of General Medical Sciences of the NIH for a postdoctoral fellowship (No. CM57549-01).

Registry No. 1-OCF$_3$, 79619-25-3; 1-H, 1009-14-9; 1-OCH$_3$, 1671-76-7; 1-SCH$_3$, 42916-75-6; **2**-SCF$_3$, 79631-89-3; *p*-(trifluoromethoxy)benzonitrile, 332-25-2; *p*-(trifluorothiomethoxy)benzonitrile, 332-26-3.

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[17] Wagner, P. J.; Kemmpainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.

4,7,7-Trimethyl-*cis*-bicyclo[3.3.0]oct-3-en-2-one: A Potentially Useful Synthon for Triquinane Natural Products

Leo A. Paquette,* Eugene Farkas,[1] and Robert Galemmo

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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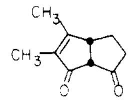
The rapidly growing number of structurally interesting and biologically active polyquinane (polycyclopentanoid) natural products[2] has prompted considerable interest in new methodology for the construction of condensed five-membered ring systems. Because the availability of functionalized bicyclo[3.3.0]octane building blocks could greatly facilitate the elaboration of more complex target molecules, the design of expedient synthetic routes to such intermediates has been actively pursued. The recent reports detailing pathways to **1**[3] and **2**[4] are exemplary. Herein we describe the preparation of title ketone **3** by a new scheme which begins with 4,4-dimethylcyclohexanone (**6**), a readily available substance.[5] The relationship of **3** to senoxydene (**4**),[6] hirsutene (**5**),[7] and their more structurally embellished congeners such as pentalenolactone E[8] and coriolin[9] is apparent.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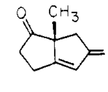
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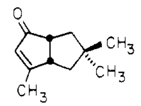
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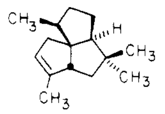
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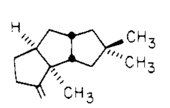
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With but one exception,[10] previous methods of five-ring annulation do not lead to fused cyclopent-3-en-2-ones.[2] In addition, it is doubtful that 3,3-dimethylcyclopentanone could be transformed regiospecifically into the desired synthon.[11] These considerations prompted us to examine the base-promoted ring contraction of a suitably substituted cyclohexanone derivative in the hope that the pendant groups could subsequently be crafted into the cyclopentenone moiety.

Carbomethoxylation of **6** with dimethyl carbonate and a mixture of sodium and potassium hydrides[12] produced **7** in 89% yield (Scheme I). Although new techniques are available for the preparation of 2-isopropylidenecycloalkanones,[13] our experience has been that the procedure originally described for the synthesis of pulegone[14] is both operationally simpler and more efficient in this instance. Thus, ketalization of **7** and treatment with methylmagnesium iodide led in excellent yield to the crystalline tertiary carbinol **8**. This intermediate underwent direct conversion to **9** (82.5% yield) when heated in aqueous acidic methanol.

The salient feature of the impending ring contraction was the Favorskii rearrangement. Extensive studies have been made of the bromination and base-induced isomerization of pulegone.[15,16] However, the reaction of **9** with Br$_2$ in acetic acid proved sluggish and rather unpredictable; significant amounts of unreacted starting material were invariably recovered. A substantial improvement was made upon adaptation of the conditions of Marx and Norman[17] which involve slow addition of the halogen to a cold (−10 °C), buffered (NaHCO$_3$) ethereal solution of the α,β-unsaturated ketone. The dibromide was then directly added to methanolic sodium methoxide solution and left to stir at room temperature overnight. In a typical experiment, a 2:1 ratio of **10** and **9** was obtained and efficiently separated by high-pressure liquid chromatography (Waters Prep 500).

The conversion of **10** to bicyclic lactone **11**, achieved simply by heating with hydrochloric acid in aqueous methanol, afforded colorless crystalline product in 82% yield. In agreement with Eaton's general findings,[18] **11** was conveniently isomerized to **3** upon heating (50 °C) in 8% phosphorus pentoxide–methanesulfonic acid solution. Interestingly, no evidence for the presence of the internal conjugated enone was detected under these cyclization conditions.

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[1] On sabbatical leave from the Eli Lilly Research Laboratories, Indianapolis, IN.

[2] Paquette, L. A. *Fortschr. Chem. Forsch.* **1979**, *79*, 43.

[3] Quesada, M. L.; Schlessinger, R. H.; Parsons, W. H. *J. Org. Chem.* **1978**, *43*, 3968.

[4] Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699.

[5] A one-pot synthesis of 4,4-dimethyl-2-cyclohexen-1-one has been reported [Flaugh, M. E.; Crowell, T. A.; Farlow, D. S. *J. Org. Chem.* **1980**, *45*, 5399]. Catalytic hydrogenation over Pd/C as previously described [Bordwell, F. G.; Wellman, K. M. *J. Org. Chem.* **1963**, *28*, 1350] proceeds in high yield.

[6] Bohlmann, F.; Zdero, C. *Phytochemistry* **1979**, *18*, 1747.

[7] (a) Nozoe, S.; Furukawa, J.; Sankawa, U.; Shibata, S. *Tetrahedron Lett.* **1976**, 195. (b) Tatsuta, K.; Akimoto, K.; Kinoshita, M. *J. Am. Chem. Soc.* **1979**, *101*, 6116. (c) Hudlicky, T.; Kutchan, T. M.; Wilson, S. R.; Mao, D. T. **Ibid. 1980**, **102**, 6351. (d) Greene, A. E. *Tetrahedron Lett.* **1980**, 3059.

[8] Cane, D. E.; Rossi, T. *Tetrahedron Lett.* **1979**, 2973; Paquette, L. A.; Schostarez, H.; Annis, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 6526.

[9] (a) Shuji, T.; Naganawa, H.; Iinuma, H.; Takita, T.; Maeda, K.; Umezawa, H. *Tetrahedron Lett.* **1971**, 1955. (b) Nakamura, H.; Takita, T.; Umezawa H.; Mamoru, K.; Yuga, N.; Iitaka, Y. *J. Antibiot.* **1974**, *27*, 301. (c) Tatsuta, K.; Akimota, K.; Kinoshita, M. *Ibid.* **1980**, *23*, 100. (d) Danishefsky, S.; Zamboni, R.; Kahn, M.; Etheredge, S. J. *J. Am. Chem. soc.* **1980**, *102*, 2097. (e) Shibasaki, M.; Iseki, K.; Ikegami, S. *Tetrahedron Lett.* **1980**, 3587.

[10] Stevens, K. E.; Paquette, L. A. *Tetrahedron Lett.*, in press.

[11] Bay, A. L., unpublished results.

[12] Ruest, L.; Blouin, G.; Deslongchamps, P. *Synth. Commun.* **1976**, *6*, 169.

[13] (a) Corey, E. J.; Chen, R. H. K. *Tetrahedron Lett.* **1973**, 3817. (b) Majetich, G.; Grieco, P. A.; Nishizawa, M. *J. Org. Chem.* **1977**, *42*, 2327.

[14] Black, C.; Buchanan, G. L.; Jarvie, A. W. *J. Chem. Soc.* **1956**, 2971.

[15] Achmad, S. A.; Cavill, G. W. K. *Aust. J. Chem.* **1963**, *16*, 858; **1965**, *18*, 1989.

[16] Wolinsky, J.; Chan, D. *J. Org. Chem.* **1965**, *30*, 41.

[17] Marx, J. N.; Norman, L. R. *J. Org. Chem.* **1975**, *40*, 1602.

[18] Eaton, P. E.; Carlson, G. R.; Lee, J. T. *J. Org. Chem.* **1973**, *38*, 4071.