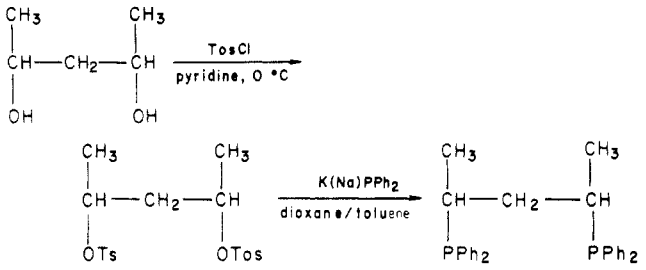

achieved with (benzoylamino)cinnamic acid as a substrate. Although this result is rather modest as compared to those reported for many other ditertiary phosphines,[6] it is significantly better than the only other value (12%) published[7] until now for a 1,3-diphosphine.

Experimental Section

(+)-(2*S*,4*S*)-2,4-Pentanediol. Raney nickel alloy (3.9 g) was added in small portions to a solution of 9 g NaOH in 40 mL water, and the suspension kept at 100 °C for 1 h. After the alkaline solution was decanted, the catalyst was washed 15 times with 40 mL of water. The so-obtained Raney Ni was treated at 100 °C for 1 h with a solution of 2 g of (*S,S*)-tartaric acid and 20 g of NaBr in 178 mL of water which had been adjusted to pH 3.2 with 1 M NaOH. The modifying solution was decanted and the procedure repeated two times. Finally, the catalyst was washed with 40 mL of water, 50 mL of methanol, and twice with 50 mL of THF.

The modified Raney Ni was weighed into a 100-mL autoclave with 22 mL of THF, 10.3 mL (0.1 mol) of acetylacetone, and 0.2 mL of acetic acid, and the autoclave was flushed several times with hydrogen and pressured to 100 bar. Hydrogenation was carried out at 100 °C with repeated repressuring from 80 to 100 bar (8–10 h). After H_2 consumption ceased, the pressure was blown off, the product and the catalyst were separated by filtration, and the solvent was evaporated in vacuo. The ratio of the diol diastereomers was determined by GLC (3% neopentyl glycol succinate on Chromosorb W-HP, 150 °C). The diastereomeric mixture was separated by recrystallizing it first at −50 °C and then at −5 °C from ether: Yield of the *S,S* enantiomer 4.7 g (0.044 mol, 44%); $[\alpha]^{20}_D$ +53.5° (*c* 1.89, EtOH); optical purity 99.6%.[4]

The (−)-(2*R*,4*R*)-2,4-pentanediol was prepared in the same way only by using (*R,R*)-tartaric acid for the modification of the catalyst: $[\alpha]^{20}_D$ −52.2° (*c* 2.56, EtOH); optical purity 97.2%; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.12 (d, $J_{H,H}$ = 6 Hz, CH_3), 1.46 (t, $J_{H,H}$ = 6 Hz, CH_2), 4.15 (sextet, $J_{H,H}$ = 6 Hz, CH), ^{13}C NMR ($CDCl_3$, 20 MHz) δ 23.4 (s, CH_3), 46.2 (s, CH_2), 64.9 (s, CH).

(+)-(2*S*,4*S*)-2,4-Bis[(diphenylphosphinyl)oxy]pentane (BDPOP). In a flask equipped with a magnetic stirrer, a thermometer, and a dropping funnel and flushed with Ar were dissolved 1.1 g (10.6 mmol) of (2*S*,4*S*)-pentanediol in 40 mL of absolute THF and 1.71 mL (21.2 mmol) of pyridine. The solution was cooled to 0 °C, and a solution of 3.80 mL (21.2 mmol) of Ph_2PCl in 25 mL of absolute THF was added slowly with stirring. Following the addition, the reaction mixture was left to warm to room temperature and stirred overnight. The pyridine hydrochloride was filtered off under Ar, the filtrate evaporated to dryness, and the residue dissolved in 20 mL of ether. When this solution was cooled to −5 °C, the product separated in the form of white crystals: yield 4.05 g (8.6 mmol, 81%); $[\alpha]^{20}_D$ +51.8° (*c* 2.18 $CHCl_3$); mp 86–89 °C.

The (−)-(2*R*,4*R*) enantiomer was prepared in the same way by starting from the (2*R*,4*R*)-diol: $[\alpha]^{20}_D$ −53.2 (*c* 3.48, $CHCl_3$); mp 86–89 °C; ^{1}H NMR ($CDCl_3$, 80 MHz) 1.15 (d, $J_{H,H}$ = 6 Hz, CH_3), 1.80 (t, $J_{H,H}$ = 6 Hz, CH_2), 4.15 (sextet, $J_{H,H}$ = 6 Hz, CH, J_{POCH} not detectable), 7.15 (m, C_6H_5); ^{13}C NMR ($CDCl_3$, 20 MHz) 22.1 (d, J_{POCC} = 4.6 Hz, CH_3), 47.6 (t, J_{POCC} = 1.6 Hz, CH_2), 73.7 (d, J_{POC} = 21.6 Hz, CH); ^{31}P NMR ($CDCl_3$, 32.1 MHz) + 106.1 ppm (chemical schift is given downfield from external 85% phosphoric acid); mass spectrum (75 eV), *m/e* (relative intensity) 472 (M^+, 10), 386 ($[(C_6H_5)_2POP(C_6H_5)_2]^+$, 10), 287 ($[M - P(C_6H_5)_2]^+$, 67), 271 ($[M - OP(C_6H_5)_2]^+$, 48), 262 ($[(C_6H_5)_3P]^+$, 93), 203 ($[(C_6H_5)_2POH_2]^+$, 95), 202 ($[(C_6H_5)_2POH]^+$, 43), 201 ($[(C_6H_5)_2PO]^+$, 100), 185 ($[(C_6H_5)_2P]^+$, 40), 183 ($[C_{12}H_8P]^+$, 36).

Asymmetric Hydrogenations. To a reaction vessel were added under hydrogen 11.6 mg (0.025 mmol) of $[(nor\text{-}C_7H_8)RhCl]_2$ and 26.0 mg (0.055 mmol) of BDPOP dissolved in a mixture of 5 mL of benzene and 2.5 mL of methanol. Et_3N (if used) was introduced into the hydrogenation flask by means of a syringe. After 40 min of prehydrogenation, 2.5 mmol prochiral olefin dissolved in 2.5 mL methanol was added to the solution. The reaction was followed by measuring H_2 absorption; 50% conversion was reached within 30–90 min. After H_2 uptake was complete (2–6 h) the reaction mixture was evaporated to dryness, and the following two procedures were used to isolate the hydrogenation product.

Method A. For *N*-acetylphenylalanine and *N*-benzoylphenylalanine the residue was dissolved in 20 mL of 10% aqueous sodium hydroxide and filtered, the filtrate acidified with 10% aqueous hydrochloric acid, and the product extracted with diethyl ether.

Method B. For *N*-acetylphenylalanine methyl ester the product was isolated by column chromatography on silica gel with ethyl acetate–hexane as the eluant.

The resulting ether or ethyl acetate–hexane solutions were evaporated in vacuo to give the product. The identities and chemical yields of these products were determined by proton NMR spectroscopy. The optical rotations of the products were measured on a Schmidt-Haensch LM visual polarimeter with approximately 0.01° precision. The optical yields were calculated by using reported[8,9] values for the optical rotations of the pure hydrogenation products.

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Registry No. I, 79499-46-0; II, 79499-47-1; (−)-(2*R*,4*R*)-2,4-pentanediol, 42075-32-1; (+)-(2*S*,4*S*)-2,4-pentanediol, 72345-23-4; 2-(acetylamino)-3-phenyl-2-propenoic acid, 5469-45-4; methyl 2-(acetylamino)-3-phenyl-2-propenoate, 52386-78-4; 2-(benzoylamino)-3-phenyl-2-propenoic acid, 1155-48-2; *N*-acetyl-L-phenylalanine, 2018-61-3; *N*-acetyl-D-phenylalanine, 10172-89-1; *N*-acetyl-L-phenylalanine methyl ester, 3618-96-0; *N*-acetyl-D-phenylalanine methyl ester, 21156-62-7; *N*-benzoyl-L-phenylalanine, 2566-22-5.

(6) L. Markó and J. Bakos, *Aspects Homogeneous Catal.*, 4, 145 (1981).
(7) H. B. Kagan, S. C. Fiaud, C. Hoornaert, D. Meyer, and S. C. Poulin, *Bull. Soc. Chim. Belg.*, 88, 923 (1979).
(8) R. Glaser and B. Vainas, *J. Organomet. Chem.*, 121, 249 (1976).
(9) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 99, 6262 (1977).

Synthesis and Diels–Alder Reactions of 1-Acylated 1,3-Cyclopentadienes[1]

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Acylcyclopentadienes are of potential interest for Diels–Alder reactions and as novel ligands for sandwich compounds and η-cyclopentadienyl compounds in general.[2] Hitherto only acetylcyclopentadiene (3) and formylcyclo-

(1) Reactive Iodine Compounds. 3. Part 2: Haase, K.; Hoffmann, H. M. R. *Angew. Chem.*, in press. This work was supported by the Fonds der Chemie.
(2) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196.

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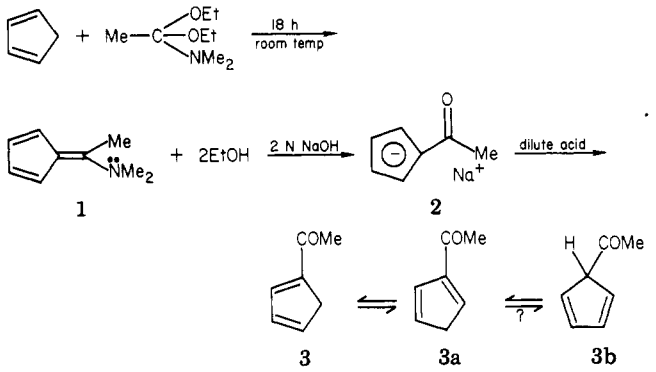
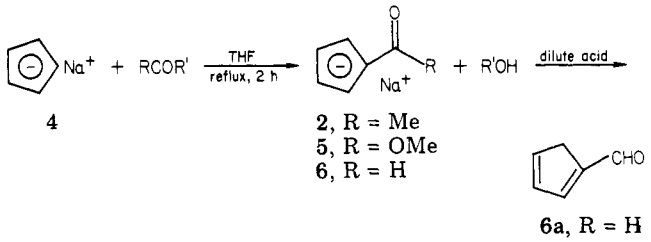
Scheme I. Acetylcyclopentadiene from 6-Amino-6-methylfulvene[3]



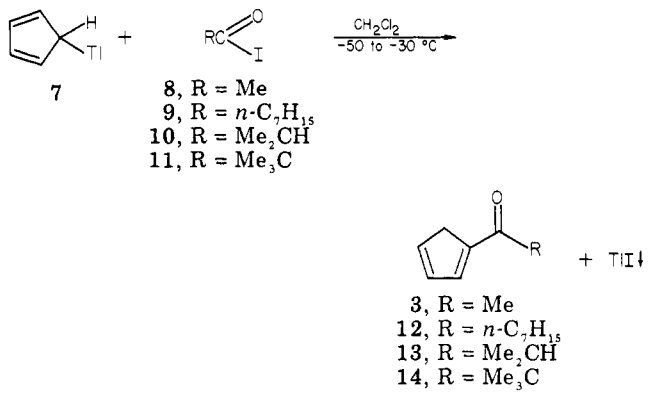
Scheme II. (Acetylcyclopentadienyl)sodium from Cyclopentadienylsodium and Methyl Acetate[2]



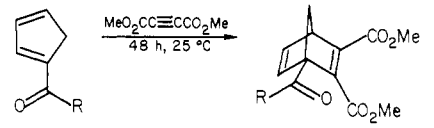
pentadiene (**6a**) have been prepared; several years ago Hafner showed[3] that alkaline hydrolysis 6-(dimethylamino)-6-methylfulvene[4] (**1**) yields the delocalized carbanion **2**, which on treatment with dilute acid gives acetylcyclopentadiene. This compound and also formylcyclopentadiene were initially formulated as a mixture of three valence isomers[3] (Scheme I). In following up Hafner's second route to formylcyclopentadiene **6a**,[3] Rausch and his co-workers reported recently that (acetylcyclopentadienyl)sodium (**2**) and the related anion **5** can be prepared by refluxing cyclopentadienylsodium (**4**) with methyl acetate and dimethyl carbonate, respectively, in tetrahydrofuran[2] (Scheme II). Earlier attempts to monoacetylate **4** with acetyl chloride instead of methyl acetate had failed, because acetyl chloride is too reactive as an acetylating agent and in a consecutive reaction combines with anion **2** to give diacetylated products of the fulvene type.[5]

We now describe a third and flexible route to acylcyclopentadienes which avoids diacylation by starting with a much less reactive cyclopentadienyl anion precursor but a very reactive acyl cation precursor. Specifically, the reaction of cyclopentadienylthallium (**7**) with acyl chlorides was tried but found to be too slow to be of any preparative use. In contrast, a slurry of **7** in dichloromethane or ether as the solvent reacted readily with representative acyl iodides (**8**–**11**) at −40 °C (Scheme III). The formation of acylcyclopentadienes was monitored by IR spectroscopy (characteristic band at 1650 cm^{-1}). Even the sterically hindered pivaloyl iodide (**11**) gave 1-pivaloylcyclopentadiene (**14**) as an aromatic-smelling liquid after the temperature had been allowed to reach 20 °C. Of the

Scheme III. 1-Acyl-1,3-cyclopentadienes from Cyclopentadienylthallium and Acyl Iodides

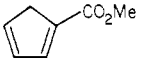


Scheme IV. Diels-Alder Adducts from 1-Acylated 1,3-Cyclopentadienes and Acetylenedicarboxylic Ester



acylcyclopentadienes which we have prepared, **14** was kinetically the most stable, dimerization occurring comparatively slowly.

For Diels–Alder reactions with an acetylenedicarboxylic ester as a dienophile, it is advantageous not to attempt isolation of the acylcyclopentadienes but to capture the diene in situ. The 1-acylcyclopentadienes **3**, **12**, and **13** gave the norbornadiene derivatives **15**–**17**, respectively, in 11–15% overall yield (Scheme IV), while the hindered 1-pivaloylcyclopentadiene (**18**) did not react with acetylenedicarboxylic ester. Presumably, the yield in the first stage of this sequence, i.e., formation of the 1-acyl-1,3-cyclopentadiene, is higher than that in the second stage, i.e., Diels–Alder reaction, in which an electron-deficient diene is matched with an electron-deficient dienophile. For comparison, Grunewald and Davis have reported recently[7] that 1-(methoxycarbonyl)-1,3-cyclopentadiene (**19**) is



19

formed in 33% yield on reaction of cyclopentadienyllithium and $ClCO_2Me$ below −50 °C.[8] In turn, **19** was trapped by Diels–Alder reaction with cyclopropene in 20–47% yield, i.e., only 7-15% overall yield.[9] Our attempts to trap acetylcyclopentadiene (**3**) with maleic anhydride and ynamines were not successful and were inconclusive, respectively.

1,5-Hydrogen Shifts in Acylcyclopentadienes and Formation of Dimers. Of the three valence isomers (**3**, **3a**, and **3b**) of acetylcyclopentadiene, only the 1-acetyl derivative **3** was discernible. In the NMR spectrum the singlet due to the acetyl protons at δ 2.37 stayed sharp

(3) Hafner, K.; Schulz, G.; Wagner, K. *Justus Liebigs Ann. Chem.* **1964**, *678*, 39. For a modification of this view see: Kaplan, L.; Wendling, L. A.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1971**, *93*, 3819. Krämer, H. J. Diploma Thesis, Technische Hochschule, Darmstadt, Germany, 1973.

(4) Meerwein, H.; Florian, W.; Schön, N.; Stopp, G. *Justus Liebigs Ann. Chem.* **1961**, *641*, 1.

(5) Riemschneider, R.; Krüger, M. *Monatsh. Chem.* **1959**, *90*, 573. See also: Webster, D. W. *J. Am. Chem. Soc.* **1966**, *88*, 3046. Mansson, J. E.; Nilsson, M.; Wennerström, O. *Acta Chem. Scand., Ser. B* **1977**, *B37*, 47. Linn, W.J.; Sharkey, W. H. *J. Am. Chem. Soc.* **1957**, *79*, 4970.

(6) Hoffmann, H. M. R.; Haase, K. *Synthesis* **1981**, 715.

(7) Grunewald, G. L; Davis, D. P. *J. Org. Chem.* **1978**, *43*, 3074.

(8) A less reactive electrophile, e.g., dimethyl carbonate,[2] should be advantageous for the preparation of **19**, because dialkoxycarbonylation is less likely.

(9) Chenier, P. J.; Kiland, P. J.; Schmitt, G. D.; VanderWegen, P. G. *J. Org. Chem.* **1980**, *45*, 5413.

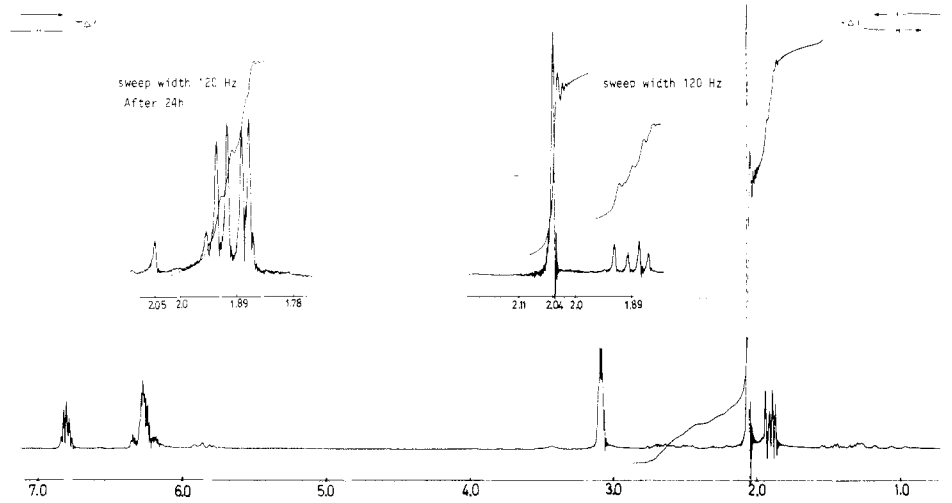


Figure 1. ^{1}H NMR spectrum of acetylcyclopentadiene (solvent C_6D_6).

Table I. Characteristic 90-MHz ^{1}H NMR Data ($CDCl_3$, δ) of Diels-Alder Adducts 15-17

cycloadduct	methylene protons	CO_2Me signals	bridgehead protons	olefinic protons
15	2.37, 2.57 (ABX pattern, $^2J_{A,B}$ = 6.5 Hz, $^3J_{A,X}$ = $^3J_{B,X}$ = 1.5 Hz)	3.77 (s, 3 H), 3.80 (s, 3 H)	4.00-4.11 (m, 1 H)	6.93-7.12 (m, 2 H)
16	2.37, 2.55 (ABX pattern, $^2J_{A,B}$ = 6.5 Hz, $^3J_{A,X}$ = $^3J_{A,B}$ = 1.5 Hz)	3.77 (s, 3 H), 3.80 (s, 3 H)	4.01-4.12 (m, 1 H)	6.93-7.12 (m, 2 H)
17	2.43, 2.60 (ABX pattern, $^2J_{A,B}$ = 6.5 Hz, $^3J_{A,X}$ = $^3J_{B,X}$ = 1.5 Hz)	3.77 (s, 3 H), 3.80 (s, 3 H)	4.02-4.12 (m, 1 H)	6.95-7.13 (m, 2 H)

down to −100 °C (solvent CD_2Cl_2). If any **3a** (or **3b**) had been present, 5% or more would have been detected. We have also repeated the alkaline hydrolysis of **1**[3] and found, after acidification, extraction into pentane, and distillation, just one valence isomer which was assigned structure **3**. However, even when the distillation was carried out quickly and the ^{1}H NMR spectrum was recorded without delay, further signals due to two dimers appeared and increased in intensity until all monomeric **3** had disappeared. The sample shown in Figure 1 consisted of 79% monomer [acetyl singlet at δ 2.04, solvent C_6D_6, and two dimers (two pairs of singlets, 12% and 9%)]. After 24 h a trace of monomer remained discernible, and the bulk of the product consisted of at least *two* dimers. The dimers could be cracked at 160 °C with recovery of monomeric **3**. Interestingly, dimerization of the monomer so obtained gave a more complex ^{1}H NMR spectrum than that in Figure 1, suggesting formation of further Diels–Alder dimers. In existing preferentially as 1-substituted valence isomers, acylcyclopentadienes resemble (methoxycarbonyl)cyclopentadiene (the monomeric Thiele ester), which has been formulated as **19** at room temperature.[7,9] However, the structure of the dimeric Thiele esters is more complicated and is a longstanding problem. While the 2-substituted valence isomer is not discernible as a monomer, a major dimer has been shown to arise by combination of the 2-substituted valence tautomer, serving as the diene, and the 1-substituted tautomer, serving as the dienophile.[10a] However, this is probably not the only dimeric Thiele ester formed, as has sometimes been assumed. The structure of other dimers[10b] remains to be elucidated. At elevated temperature 2-(methoxycarbonyl)-1,3-cyclopentadiene has recently been trapped as the minor valence tautomer by maleic anhydride[11a] and also by less reactive dienophiles.[11b]

Conclusions. Since we have prepared a large class of acyl iodides,[6] our approach to 1-acyl-1,3-cyclopentadienes is general. At present, the great tendency of most acylcyclopentadienes to dimerize limits the choice of partners for Diels–Alder reactions. Nonetheless, the crossed Diels–Alder adducts **15–17**, which have now been obtained, are norbornadienes selectively functionalized at the bridgehead carbon.

Experimental Section

Preparation and Diels–Alder Reaction of Acylcyclopentadienes. Typical Procedure. Acetyl iodide (1.70 g, 10 mmol) in absolute CH_2Cl_2 (50 mL) is mixed with cyclopentadienylthallium[12] (2.69 g, 10 mmol) under an atmosphere of dry nitrogen at −30 °C, the resulting suspension being stirred, while the reaction is monitored by TLC and IR. After 3 h dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) is added. The mixture is kept for 2.5 h at −30 to −40 °C and finally allowed to reach room temperature. After 2 h at 25 °C, TLC showed no more change (acylcyclopentadienes **12** and **13** are allowed to react with dimethyl acetylenedicarboxylate for 2 days at room temperature). The mixture is filtered through a short column of silica gel, and the solvent is evaporated under reduced pressure, while the remaining dimethyl acetylenedicarboxylate is removed in a Kugelrohr apparatus (45 °C, ca. 0.2 torr). The residue (1.11 g) is submitted to preparative thick-layer chromatography, giving 1-acetyl-2,3-bis(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene (**15**): 64 mg (15%); mp 51–52 °C (after recrystallization from a little ether at −78 °C overnight); IR (CCl_4) 1718, 1730 (sh), 1670, 1628, 1436, 1250 (br), 1109, 718 cm^{-1}; ^{1}H NMR, Table I.

Acetylcyclopentadiene (3) from 6-(Dimethylamino)-6-methylfulvene (1).[3] (i) Preparation of 1.[4] Dimethylacetamide dimethyl acetal (8.8 g, 60 mmol), obtained as a 90–95% solution in methanol from Fluka AG, and freshly distilled cyclopentadiene (3.96 g, 60 mmol) were mixed and kept overnight under dry

(10) (a) Dunn, G. L.; Donohue, J. K. *Tetrahedron Lett.* **1968**, 3485. Cf. also: Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976; pp 136, 167. (b) Peters, D. *J. Chem. Soc.* **1959**, 1761 and references cited therein. See also: Finnegan, R. A.; McNees, R. S. *J. Org. Chem.* **1964**, *29*, 3234.

(11) (a) See footnote 9 of ref 7. (b) Nallet, J. P.; Arnaud, C.; Huet, J. *Tetrahedron Lett.* **1979**, 2583.

(12) Meister, H. *Angew. Chem.* **1957**, *69*, 533.

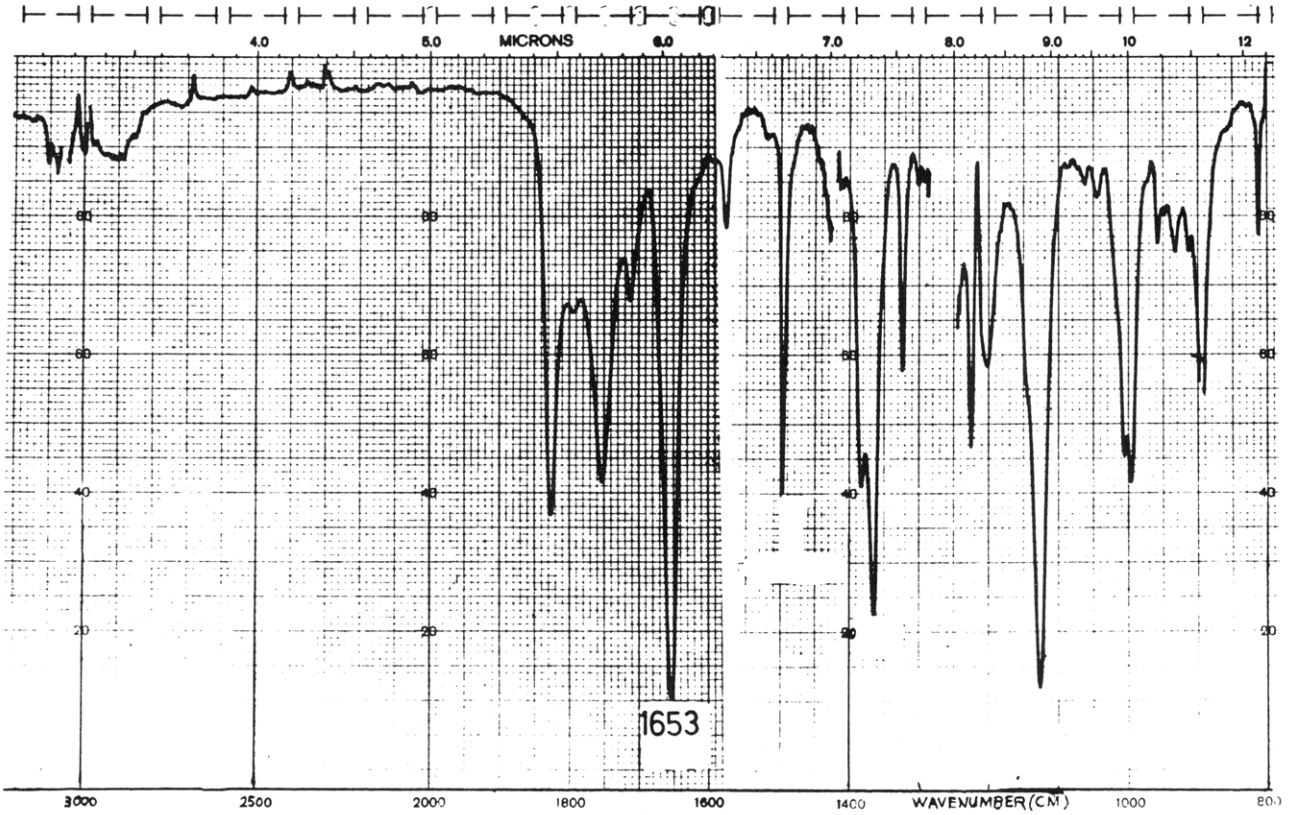


Figure 2. IR spectrum of **3** prepared from the reaction of **7** and **8** (solvent CH_2Cl_2). The sample contains some acetic anhydride from hydrolysis of **8**.

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 ^1H 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 ^1H 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 ^1H 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

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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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