A New, General Cyclopentenone Synthesis

Paolo Ceccherelli, Massimo Curini,* Maria Carla Marcotullio, and Ornelio Rosati

Istituto di Chimica Organica, Facoltà di Farmacia, Università degli Studi, 06100 Perugia, Italy

Ernest Wenkert*

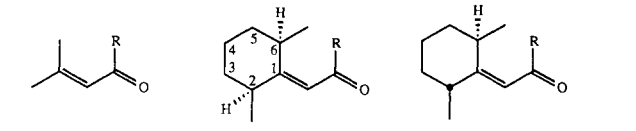
Department of Chemistry (D-006), University of California—San Diego, La Jolla, California 92093

Received May 25, 1989

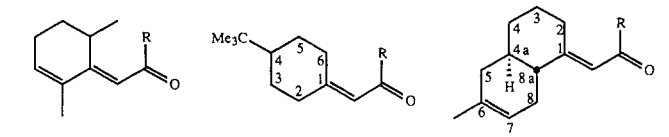
A new synthesis of cyclopentenones, involving an Rh(II)-catalyzed, intramolecular carbon–hydrogen insertion of diazomethyl ketones derived from α,β-unsaturated acids, is described.

After early, isolated observations of cycloalkanone production on thermal, metal-induced α-diazo ketone decomposition[1] there was introduced in 1968 a facile method of cyclopentanone synthesis, based on the decomposition of diazomethyl ketones under transition-metal catalysis leading to intramolecular carbon–hydrogen insertion of the resultant, transient α-acylcarbene–metal complexes.[2] Over the years this procedure of α-diazo ketone → cyclopentanone conversion has found wide use in organochemical synthesis.[3] As the following discussion will illustrate, the scope of this method of synthesis of cyclic compounds has been broadened by a study of the decomposition behavior of diazoketones derived from α,β-unsaturated acids.[4]

Preparation of α,β-Unsaturated Acids. Commercially available senecioic acid (**1a**) and acids **2a–6b** were utilized in the study. The latter five carboxylic acids were prepared in the following manner.



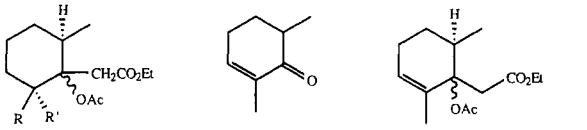
1 2 3



4 5 6

a, R = OH; b, R = Cl; c, R = CHN_2; d, R = OEt

Exposure of a cis–trans mixture of 2,6-dimethylcyclohexanone to a Reformatsky reaction and O-acylation of the resultant hydroxy esters with acetyl chloride and *N,N*-dimethylaniline led to diesters **7a** and **7b**. Ethoxide-induced elimination of acetic acid converted the two substances into olefinic esters **2d** and **3d**, respectively, whose alkaline hydrolysis produced acids **2a** and **3a**, respectively.



7a, R = Me, R' = H
b, R = H, R' = Me

8 9

The synthesis of acid **4a** emanated from 2,6-dimethyl-2-cyclohexenone (**8**),[5] prepared from 2,6-dimethylcyclohexanone by its transformation into the trimethylsilyl enol ether, halogenation thereof with *N*-bromosuccinimide and dehydrohalogenation of the resultant 2-bromo-2,6-di-

(1) (a) Greuter, F.; Kalvoda, J.; Jeger, O. *Proc. Chem. Soc., London* **1958**, 349. (b) Lansbury, P. T.; Colson, J. G. *Chem. Ind. (London)* **1962**, 821. (c) Yates, P.; Danishefsky, S. *J. Am. Chem. Soc.* **1962**, *84*, 879. (d) House, H. O.; Boots, S. G.; Jones, V. K. *J. Org. Chem.* **1965**, *30*, 2519. (e) Yates, P.; Crawford, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 1562.

(2) Wenkert, E.; Mylari, B. L.; Davis, L. L. *J. Am. Chem. Soc.* **1968**, *90*, 3870.

(3) (a) Regitz, M.; Rüter, J. *Chem. Ber.* **1969**, *102*, 3877. (b) Cambie, R. C.; Franich, R. A. *Chem. Commun.* **1969**, 725; *Aust. J. Chem.* **1971**, *24*, 117. (c) Chakrabarti, J. K.; Szinai, S. S.; Todd, A. *J. Chem. Soc. C* **1970**, 1303. (d) Kitadani, M.; Ito, K.; Yoshikoshi, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3431. (e) Ghatak, U. R.; Chakrabarty, S. *J. Am. Chem. Soc.* **1972**, *94*, 4756. Ghatak, U. R.; Alam, S. K.; Ray, J. K. *J. Org. Chem.* **1978**, *43*, 4598. (f) Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1973**, *38*, 1694. (g) Mane, R. B.; Krishna Rao, G. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1806. (h) Tresca, J. P.; Fourray, J. L.; Polonsky, J.; Wenkert, E. *Tetrahedron Lett.* **1973**, 895. (i) Burns, W.; McKervey, M. A.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1975**, 965. Burns, W.; McKervey, M. A.; Mitchell, T. R. B.; Rooney, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 906. (j) Chakrabarty, S.; Ray, J. K.; Mukherjee, D.; Ghatak, U. R. *Synth. Commun.* **1975**, *5*, 275. (k) Agosta, W. C.; Wolff, S. *J. Org. Chem.* **1975**, *40*, 1027. (l) Godleski, S. A.; Schleyer, P. v. R.; Osawa, E. *J. Chem. Soc., Chem. Commun.* **1976**, 38. Godleski, S. A.; Schleyer, P. v. R.; Osawa, E.; Inamoto, Y.; Fujikura, Y. *J. Org. Chem.* **1976**, *41*, 2596. (m) Vijayasarathy, P. S.; Krishna Rao, G. S. *Chem. Ind. (London)* **1976**, 161. (n) Ghatak, U. R.; Chakrabarty, S. *J. Org. Chem.* **1976**, *41*, 1089. (o) Kuwajima, I.; Iguchi, Y.; Iwasawa, H.; Sato, T. *Chem. Lett.* **1976**, 1271. (p) Ghatak, U. R.; Ray, J. K.; Chakrabarty, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1975. (q) Fărcaşiu, D.; Bohm, H.; Schleyer, P. v. R. *J. Org. Chem.* **1977**, *42*, 96. (r) Inamoto, Y.; Aigami, K.; Takaishi, N.; Fujikura, Y.; Tsuchihashi, K.; Ikeda, H. *J. Org. Chem.* **1977**, *42*, 3833. (s) Buckwalter, B. L.; Burfitt, I. R.; Felkin, H.; Joly-Goudket, M.; Naemura, K.; Solomon, M. F.; Wenkert, E.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 6445. (t) Wenkert, E.; Davis, L. L.; Mylarl, B. L.; Solomon, M. F.; da Silva, R. R.; Shulman, S.; Warnet, R. J.; Ceccherelli, P.; Curini, M.; Pellicciari, R. *J. Org. Chem.* **1982**, *47*, 3242. (u) Taber, D. F.; Petty, E. H. *J. Org. Chem.* **1982**, *47*, 4808. (v) Taber, D. F.; Raman, K. *J. Am. Chem. Soc.* **1983**, *105*, 5935. (w) Chakraborti, A. K.; Ray, J. K.; Kundu, K. K.; Chakrabarty, S.; Mukherjee, D.; Ghatak, U. R. *J. Chem. Soc., Perkin Trans. 1* **1984**, 261. (x) Taber, D. F.; Petty, E. H.; Raman, K. *J. Am. Chem. Soc.* **1985**, *107*, 196. (y) Sakai, K.; Fujimoto, T.; Yamashita, M.; Kondo, K. *Tetrahedron Lett.* **1985**, *26*, 2089. (z) Taber, D. F.; Ruckle, R. E., Jr. *Tetrahedron Lett.* **1985**, *26*, 3059. (a') Taber, D. F.; Schuchardt, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5289. (b') Taber, D. F.; Ruckle, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7686. (c') Taber, D. F.; Raman, K.; Gaul, M. D. *J. Org. Chem.* **1987**, *52*, 28. (d') Nakatani, K. *Tetrahedron Lett.* **1987**, *28*, 165. (e') Monteiro, H. J. *Tetrahedron Lett.* **1987**, *28*, 3459. (f') Corbel, B.; Hernot, D.; Haelters, J.-P.; Sturtz, G. *Tetrahedron Lett.* **1987**, *28*, 6605. (g') Stork, G.; Nakatani, K. *Tetrahedron Lett.* **1988**, *29*, 2283.

(4) Benzocycloalkanone formation on decomposition of *o*-alkylaryl diazomethyl ketones (i.e. diazo compounds derived from aromatic equivalents of the α,β-unsaturated acids) is precedented.[1b,3b] For the simplest example thereof (the i → ii transformation) see the Experimental Section.

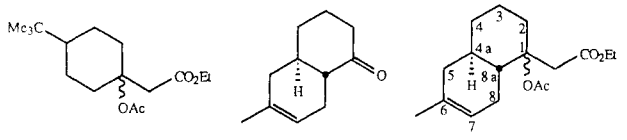
i ii

(5) (a) Trost, B. M.; Salzmann, T. N.; Hirol, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887. (b) Marino, J. P.; Jaên, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3165. (c) Cory, R. M.; Burton, L. P. J.; Chan, D. M. T.; McLaren, F. R.; Rastall, M. H.; Renneboog, R. M. *Can. J. Chem.* **1984**, *62*, 1908.

0022-3263/90/1955-0311$02.50/0

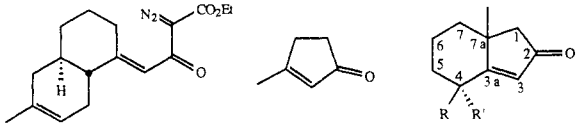
methylcyclohexanone with lithium carbonate in dimethylformamide. Once again, a Reformatsky reaction, followed by an O-acylation, yielded a β-acetoxy ester (**9**), whose β-elimination provided dienoic ester **4d**. Its diene stereochemistry was established by NOE difference ^{1}H NMR spectroscopy revealing the proximity of the olefinic methyl group to the olefinic α-keto hydrogen of ester **4d**. Alkaline hydrolysis of the ester gave acid **4a**.

A Reformatsky reaction on 4-*tert*-butylcyclohexanone and subsequent acetylation afforded diester **10**, whose base-induced elimination of acetic acid yielded olefinic ester **5d**. Alkaline hydrolysis of the latter led to acid **5a**. The same four-step procedure (via esters **12** and **6d**) caused the transformation of ketone **11**[6] into acid **6a**. The stereochemistry of the exocyclic double bond of dienes **6a** and **6d** was based on the assumption of the **12** → **6d** elimination proceeding in the direction of the sterically least encumbered product.



10 **11** **12**

Diazo Ketone Decompositions. Treatment of the sodium salts of acids **1a–6a** with oxalyl chloride produced acid chlorides **1b–6b**, whose exposure to diazomethane and triethylamine afforded diazo ketones **1c–6c**. Interaction of acyl chloride **6b** with ethyl diazoacetate produced α-diazo-β-keto ester **13**.[7] Decomposition of the α-diazocarbonyl compounds was accomplished in 47–65% yield by their slow addition to a stirring suspension of dirhodium tetraacetate[8] in methylene chloride.

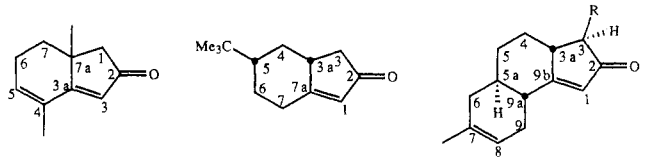


13 **14** **15a**, R = Me, R' = H; **b**, R = H, R' = Me

In this fashion diazo ketones **1c**, **2c**, and **3c** were transformed into cyclopentenones **14** (59%), **15a** (47%), and **15b**[9] (53%), respectively. The ^{13}C NMR spectral characteristics of isomers **15a** and **15b** differentiate the two substances. Thus, for example, the secondary methyl group and C(6) of ketone **15a** are shielded (vs **15b**), revealing the axiality of the methyl side chain, and the angular methyl function of the same compound is deshielded (vs **15b**), showing the δ-effect from the secondary methyl group.

Decomposition of diazo ketones **4c** and **5c** led to the formation of cyclopentenones **16** (53%) and **17** (57%), respectively. The stereochemistry assignment of the latter bicycle rests on interpretation of the ^{13}C NMR spectrum of the ketone. The carbon shifts of C(5) and C(6) reflect a chair-like cyclohexane holding an equatorial *tert*-butyl group, a condition compatible only with a H(3a)–H(5) cis relationship.

The diazo compounds **6c** and **13** were transformed into ketones **18a** (65%) and **18b** (55%), respectively. The



16 **17** **18a**, R = H; **b**, R = CO_2Et

stereochemistry assignment of ketones **18** is founded on the carbon shift similarity of relevant carbons with like centers in models **6d** and **17**. The ^{13}C NMR spectral characteristics of keto ester **18b** and its H(3)–H(3a) coupling constant of 3 Hz show its carboethoxy group to be oriented equatorially.

Conclusion

As in the case of the earlier cyclopentanone syntheses,[2,3] the carbenoid insertion process may involve carbon–hydrogen bonds at the site of methyl (e.g., **1c** decomposition), methylene (e.g., **5c** and **6c** decompositions), and methine (e.g., **2c**, **3c**, and **4c** decompositions) units. Despite the greater distance between the carbenoid center and the carbon–hydrogen inserting system than in cyclopentanone synthesis,[2,3] the cyclization takes place. However, the proximity constraint manifests itself in terms of high stereoselectivity (in cases of the carbon–hydrogen inserting unit being part of a ring system) by a strong preference of the carbenoid moiety for equatorial carbon–hydrogen bonds (as in the reactions of diazo compounds **5c**, **6c**, and **13**). In conformationally flexible, methine-inserting systems, as diazo ketones **2c**, **3c**, and **4c**, the methyl group at the reacting site must assume an axial orientation, in order to bare an equatorial hydrogen toward the carbenoid carbon.

The experimental results of the present study constitute the discovery of a simple method of synthesis of cyclopentenones, one capable of furnishing rapid access to substances of fair structure complexity (e.g., the angularly methylated bicycles **15** and **16**).

Experimental Section

Melting points were obtained on a Reichert micro hotstage and are uncorrected. Infrared spectra of chloroform solutions were observed on a Perkin-Elmer 1320 spectrophotometer. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Bruker AC 200 spectrometer operating at 200.1 and 50.3 MHz, respectively, in the Fourier transform mode. The carbon shifts are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyzer. Column chromatography was executed on 0.063–0.200 mesh Merck silica gel. All reactions were carried out under nitrogen, and all extracts were dried over Na_2SO_4.

2,6-Dimethyl-2-cyclohexenone (8). 2,6-Dimethylcyclohexanone (25.9 g, 0.20 mol) was added over a 0.5-h period to a stirring solution of 24.0 g (0.24 mol) of trimethylsilyl chloride and 27.5 g (0.26 mol) of triethylamine in 100 mL of anhydrous dimethylformamide, and the mixture was then refluxed for 48 h.[10] Hexane (200 mL) was added, and the mixture was washed with saturated sodium bicarbonate and 1.5 M hydrochloric acid solutions. Further washing with water was followed by evaporation of the organic solution. Distillation of the residue at 52–58 °C (10 Torr) yielded 30.5 g of colorless, liquid 2,6-dimethyl-1-[(trimethylsilyl)oxy]cyclohexene: ^{1}H NMR δ 0.19 (s, 9, $SiMe_3$), 1.04 (d, 3, J = 7 Hz, 6-Me), 1.2–2.1 (m, 7, CH, methylenes), 1.55 (s, 3, 2-Me).

N-Bromosuccinimide (20.5 g, 0.11 mol) was added in small portions to a stirring solution of 20.5 g (0.10 mol) of the silyl ether in 500 mL of tetrahydrofuran at 0 °C, and stirring was continued

(6) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056.
(7) Cf.: Wenkert, E.; Guo, M.; Pizzo, F.; Ramachandran, K. *Helv. Chim. Acta* **1987**, *70*, 1429.
(8) Hubert, A.; Noels, A. F.; Anciaux, A. J.; Teyssié, P. *Synthesis* **1976**, 600.
(9) Fukuyama, Y.; Tokoroyama, T.; Kubota, T. *Tetrahedron Lett.* **1973**, 4869.
(10) Cf.: Blanco, L.; Amice, P.; Conia, J. M. *Synthesis* **1976**, 194.

for 0.5 h.[10] A saturated $NaHCO_3$–NaCl solution (200 mL) was added, and the mixture was extracted with ether. The extract was washed with water, dried, and evaporated. The residue, 22.5 g of unstable, pale yellow, viscous liquid 2-bromo-2,6-dimethylcyclohexanone [^{1}H NMR δ 1.10 (d, 3, J = 6 Hz, 6-Me), 1.1–2.6 (m, 6, methylenes), 1.80 (s, 3, 2-Me), 3.40 (m, 1, H-6)], was used in the next reaction without purification.

A solution of 22.3 g of the bromo ketone in 50 mL of dimethylformamide was added dropwise over a 15-min period to a stirring suspension of 32.0 g (0.43 mol) of lithium carbonate in 150 mL of dimethylformamide, and the mixture was refluxed for 15 h. It then was filtered, and the precipitate was washed with ether. Water, 250 mL, was added to the combined filtrate and washings, and the mixture was extracted with ether. The extract was washed with water, dried, and evaporated. Chromatography of the residue and elution with 50:1 hexane–ethyl acetate gave 8.3 g (60% three-reaction yield) of colorless, liquid ketone 8;[5] ^{1}H NMR δ 1.14 (d, 3, J = 7 Hz, 6-Me), 1.6–2.5 (m, 5, CH, methylenes), 1.76 (br s, 3, 2-Me), 6.70 (m, 1, H-3); ^{13}C NMR δ 14.8 (6-Me), 15.6 (2-Me), 24.9 (C-4), 30.9 (C-5), 41.2 (C-6), 134.6 (C-2), 143.9 (C-3), 201.6 (C=O).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.31; H, 9.85.

General Procedure. Reformatsky Reaction.[11] A stirring mixture of 10 mmol of ketone, 12 mmol of ethyl bromoacetate, and 18 mmol of zinc dust in 40 mL of dry dioxane was placed into a sonication apparatus. After initiation of the sonication, 2 mmol of iodine was added, and the exothermic reaction was terminated after 0.3–3 h. The mixture was filtered through a Celite pad, and the filtrate was poured into 200 mL of ice water. The organic mixture was extracted with methylene chloride, and the extract was dried and evaporated. Chromatography of the residue and elution with 20:1 hexane–ethyl acetate yielded hydroxy ester which was acetylated as follows.

Diesters.[12] A solution of 10 mmol of hydroxy ester, 180 mmol of acetyl chloride, and 360 mmol of *N,N*-dimethylaniline in 100 mL of chloroform was refluxed for 12 h. The mixture was poured into 300 mL of ice water, and the organic layer was concentrated to a 10-mL volume. Ether (100 mL) was added, and the solution washed with 10% hydrochloric acid and water, dried, and evaporated. Chromatography of the residue and elution with 50:1 hexane–ethyl acetate led to the diester.

Ethyl (1ξ-acetoxy-2β,6β-dimethyl-1-cyclohexyl)acetate (7a): colorless liquid (51%); ^{1}H NMR δ 1.01 (d, 6, J = 6 Hz, 2-Me, 6-Me), 1.24 (t, 3, J = 7 Hz, ethyl Me), 1.3–2.1 (m, 8, methylenes, methines), 2.02 (s, 3, acetyl Me), 3.42 (s, 2, $COCH_2$), 4.11 (q, 2, J = 7 Hz, OCH_2).

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.58; H, 9.47.

Ethyl (1ξ-acetoxy-2β,6α-dimethyl-1-cyclohexyl)acetate (7b): colorless liquid (33%); ^{1}H NMR δ 0.92, 0.94 (d, 3 each, J = 6 Hz, methyls), 1.1–2.7 (m, 8, methylenes, methines), 1.24 (t, 3, J = 7 Hz, ethyl Me), 2.08 (s, 3, acetyl Me), 2.98 (br s, 2, $COCH_2$), 4.09 (q, 2, J = 7 Hz, OCH_2).

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.65; H, 9.39.

Ethyl (1ξ-acetoxy-2,6β-dimethyl-2-cyclohexen-1-yl)acetate (9):[13] colorless liquid (54%); ^{1}H NMR δ 1.06 (d, 3, J = 6 Hz, 6-Me), 1.12 (t, 3, J = 7 Hz, ethyl Me), 1.4–2.4 (m, 5, CH, methylenes), 1.68 (s, 3, 2-Me), 2.04 (s, 3, acetyl Me), 3.10 (br s, 2, $COCH_2$), 4.12 (q, 2, J = 7 Hz, OCH_2). The diester was used without purification in the next reaction.

Ethyl (1ξ-acetoxy-4β-*tert*-butyl-1-cyclohexyl)acetate (10): colorless liquid (90%); ^{1}H NMR δ 0.84 (s, 9, methyls), 1.0–2.5 (m, 9, CH, methylenes), 1.22 (t, 3, J = 7 Hz, ethyl Me), 1.98 (s, 3, acetyl Me), 3.00 (s, 2, $COCH_2$), 4.10 (q, 2, J = 7 Hz, OCH_2); ^{13}C NMR δ 14.3 (ethyl Me), 22.2 (acetyl Me), 23.9 (C-3, C-5), 27.6 (*t*-Bu methyls), 32.3 (*t*-Bu C), 35.7 (C-2, C-6), 37.0 (α-C), 47.4 (C-4), 60.0 (OCH_2), 81.7 (C-1), 169.8 (C=O), 170 (C=O).

Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.58; H, 9.92. Found: C, 67.48; H, 9.99.

(11) Cf.: Han, B.-H.; Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 5030.
(12) Cf.: Fung, K. H.; Schmalzl, K. J.; Mirrington, R. H. *Tetrahedron Lett.* **1969**, 5017.
(13) The acetylation had been carried out at 40 °C for 12 h.

Ethyl (1ξ-acetoxy-6-methyl-1,2,3,4,4aα,5,8,8aβ-octahydro-1-naphthyl)acetate (12): colorless liquid (82%); ^{1}H NMR δ 1.21 (t, 3, J = 7 Hz, ethyl Me), 1.2–3.0 (m, 12, methylenes, methines), 1.63 (br s, 3, 6-Me), 2.02 (s, 3, acetyl Me), 2.63, 2.85, 3.30, 3.52 (4-line AB, 2, $COCH_2$), 4.11 (q, 2, J = 7 Hz, OCH_2), 5.2–5.5 (m, 1, H-7).

Anal. Calcd for $C_{17}H_{28}O_4$: C, 69.36; H, 8.90. Found: C, 69.41; H, 8.82.

General Procedure. α,β-Unsaturated Esters.[12] A solution of 10 mmol of diester and 10 mmol of sodium ethoxide in 130 mL of anhydrous ethanol was kept at 40 °C for 12 h and then reduced to a 50-mL volume by vacuum distillation. It was poured into 150 mL of water and extracted with chloroform. The extract was washed with water, dried, and evaporated. Chromatography of the residue and elution with 50:1 hexane–ethyl acetate produced olefinic ester.

Ethyl (2β,6β-dimethyl-1-cyclohexylidene)acetate (2d): colorless liquid (90%); ^{1}H NMR δ 1.19, 1.21 (d, 3 each, J = 7 Hz, methyls), 1.2–1.9 (m, 6, methylenes), 1.26 (t, 3, J = 7 Hz, ethyl Me), 2.4–2.6 (m, 1, H-2), 3.8–3.9 (m, 1, H-6), 4.12 (q, 2, J = 7 Hz, OCH_2), 5.59 (s, 1, olefinic H); ^{13}C NMR δ 14.0 (ethyl Me), 15.5 (C-4), 20.9 (2-Me), 22.3 (6-Me), 30.3 (C-6), 31.7 (C-3 or C-5), 32.2 (C-5 or C-3), 38.4 (C-2), 59.0 (OCH_2), 114.5 (α-keto CH), 166.1 (C-1), 170.1 (C=O).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.46; H, 10.24.

Ethyl (2α,6β-dimethyl-1-cyclohexylidene)acetate (3d): colorless liquid (88%); ^{1}H NMR δ 1.08, 1.10 (d, 3 each, J = 7 Hz, methyls), 1.28 (t, 3, J = 7 Hz, ethyl Me), 1.3–2.0 (m, 6, methylenes), 2.3–2.6 (m, 1, H-2), 3.8–4.1 (m, 1, H-6), 4.15 (q, 2, J = 7 Hz, OCH_2), 5.51 (s, 1, olefinic H); ^{13}C NMR δ 14.1 (ethyl Me), 18.2 (2-Me or 6-Me), 18.5 (6-Me or 2-Me), 20.6 (C-4), 30.8 (C-6), 33.1 (C-5), 33.5 (C-2), 37.2 (C-3), 59.2 (OCH_2), 110.4 (α-keto CH), 169.0 (C-1), 170.5 (C=O).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.38; H, 10.34.

Ethyl (2,6-dimethyl-2-cyclohexen-1-ylidene)acetate (4d): colorless liquid (76%); ^{1}H NMR δ 1.06 (d, 3, J = 7 Hz, 6-Me), 1.25 (t, 3, J = 7 Hz, ethyl Me), 1.5–2.5 (m, 4, methylenes), 1.78 (br s, 3, 2-Me), 3.8–4.0 (m, 1, H-6), 4.12 (q, 2, J = 7 Hz, OCH_2), 5.62 (s, 1 olefinic α-keto H), 5.9–6.0 (m, 1, H-3); ^{13}C NMR δ 14.3 (ethyl Me), 18.0 (6-Me), 20.3 (2-Me), 21.6 (C-4), 28.0 (C-5), 28.7 (C-6), 59.5 (OCH_2), 111.6 (α-keto CH), 131.1 (C-2), 134.6 (C-3), 159.8 (C-1), 166.9 (C=O).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.10; H, 9.40.

Ethyl (4-*tert*-butylcyclohexylidene)acetate (5d): colorless liquid (64%); ^{1}H NMR δ 0.88 (s, 9, *t*-Bu methyls), 1.1–2.4 (m, 8, CH, methylenes), 1.28 (t, 3, J = 7 Hz, ethyl Me), 3.7–4.0 (m, 1, eq H-6), 4.08 (q, 2, J = 7 Hz, OCH_2), 5.56 (br s, 1, α-keto H); ^{13}C NMR δ 14.1 (ethyl Me), 27.4 (*t*-Bu methyls), 28.3 (C-6), 29.0 (C-5 or C-3), 29.3 (C-3 or C-5), 32.2 (*t*-Bu C), 37.7 (C-2), 47.7 (C-4), 59.1 (OCH_2), 112.7 (α-keto CH), 162.9 (C-1), 166.4 (C=O).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.96; H, 10.78. Found: C, 75.02; H, 10.71.

Ethyl (6-methyl-1,2,3,4,4aα,5,8,8aβ-octahydro-1-naphthylidene)acetate (6d): colorless liquid (94%); ^{1}H NMR δ 1.1–2.3 (m, 11, methylenes, methines), 1.28 (t, 3, J = 7 Hz, ethyl Me), 1.62 (br s, 3, 6-Me), 3.8–4.1 (m, 1, eq H-2), 4.15 (q, 2, J = 7 Hz, OCH_2), 5.3–5.6 (m, 1, H-7), 5.58 (br s, 1, α-keto H); ^{13}C NMR δ 14.1 (ethyl Me), 22.9 (6-Me), 26.8 (C-3 or C-8), 27.9 (C-8 or C-3), 30.3 (C-2), 34.0 (C-4), 39.1 (C-5), 40.3 (C-4a), 43.8 (C-8a), 59.2 (OCH_2), 112.2 (α-keto CH), 119.5 (C-7), 135.6 (C-6), 164.4 (C-1), 166.8 (C=O).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.89; H, 9.46. Found: C, 76.79; H, 9.52.

General Procedure. α,β-Unsaturated Acids. A solution of 10 mmol of α,β-unsaturated ester in 150 mL of 6% methanolic potassium hydroxide was kept at 40 °C for 12 h and then reduced to a 60-mL volume by vacuum distillation. It was poured into 140 mL of water and extracted with chloroform. The aqueous solution was acidified with 2% sulfuric acid and extracted with chloroform. The extract was washed with water, dried, and evaporated. Chromatography of the residue and elution with 25:1 chloroform–ethyl acetate afforded the α,β-unsaturated acid.

(2α,6β-Dimethyl-1-cyclohexylidene)acetic acid (2a): colorless, crystalline solid; mp 77–79 °C (C_6H_{14}–Et_2O) (83%); ^1H NMR δ 1.21 (d, 6, J = 7 Hz, methyls), 1.3–1.9 (m, 6, methylenes), 2.5–2.7 (m, 1, H-2), 3.8–4.0 (m, 1, H-6), 5.63 (s, 1, α-keto H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.40; H, 9.59. Found: C, 71.35; H, 9.64.

(2α,6β-Dimethyl-1-cyclohexylidene)acetic acid (3a): colorless, crystalline solid; mp 50–53 °C (C_6H_{14}–Et_2O) (78%); ^1H NMR δ 1.03, 1.13 (d, 3 each, J = 7 Hz, methyls), 1.4–2.0 (m, 6, methylenes), 2.4–2.6 (m, 1, H-2), 4.1–4.3 (m, 1, H-6), 5.51 (s, 1, α-keto H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.40; H, 9.59. Found: C, 71.36; H, 9.67.

(2,6-Dimethyl-2-cyclohexen-1-ylidene)acetic acid (4a): colorless, amorphous solid (80%); ^1H NMR δ 1.07 (d, 3, J = 7 Hz, 6-Me), 1.5–2.5 (m, 4, methylenes), 1.80 (s, 3, 2-Me), 3.8–4.1 (m, 1, H-6), 5.68 (s, 1, α-keto H), 6.0–6.1 (m, 1, H-3); ^{13}C NMR δ 18.0 (6-Me), 20.2 (2-Me), 21.6 (C-4), 27.9 (C-6), 28.6 (C-5), 111.1 (α-keto CH), 131.1 (C-2), 135.6 (C-3), 162.1 (C-1), 172.7 (C=O).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.18; H, 8.55.

(4-*tert*-Butylcyclohexylidene)acetic acid (5a): colorless, amorphous solid (84%); ^1H NMR δ 0.85 (s, 9, methyls), 1.2–2.4 (m, 8, CH, methylenes), 3.8–4.0 (m, 1, eq H-6), 5.54 (s, 1, α-keto H); ^{13}C NMR δ 27.4 (methyls), 28.4 (C-6), 29.4 (C-3 or C-5), 29.7 (C-5 or C-3), 32.3 (*t*-Bu C), 38.0 (C-2), 47.7 (C-4), 112.4 (α-keto CH), 166.3 (C-1), 172.6 (C=O).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.36; H, 10.32.

(6-Methyl-1,2,3,4,4aα,5,8,8aβ-octahydro-1-naphthylidene)acetic acid (6a): colorless, amorphous solid (92%); ^1H NMR δ (MeOH-d_4) 1.0–2.2 (m, 11, methylenes, methines), 1.62 (br s, 3, Me), 3.7–4.0 (m, 1, eq H-2), 5.2–5.4 (m, 1, H-7), 5.48 (br s, 1, α-keto H).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.70; H, 8.80. Found: C, 75.62; H, 8.85.

General Procedure. Preparation of Diazo Ketones. A solution of 10 mmol of α,β-unsaturated acid in 30 mL of methanol was neutralized by titration with a 0.1 N methanolic sodium methoxide solution to the phenolphthalein endpoint. The mixture was evaporated under vacuum, and the residue was dried at 10 Torr and 100 °C for 1 h. A suspension of the dry salt in 50 mL of anhydrous benzene was treated with 30 mmol of freshly distilled oxalyl chloride at 0 °C, and the mixture was stirred for 3 h. It then was filtered, and the filtrate was evaporated under vacuum. A solution of the residue in 100 mL of anhydrous ether was added dropwise over a 0.5-h period to a stirring solution of 13 mmol of diazomethane and 10 mmol of distilled triethylamine in 50 mL of dry ether at 0 °C, and the stirring was continued for 1–3 h. The mixture was filtered, and the filtrate was evaporated. Chromatography of the residue through a short column of neutral alumina (activity III) and elution with 25:1 hexane–ethyl acetate produced a diazo ketone, which was used in the next reaction without further purification.

***o*-(Diazoacetyl)toluene (i)**: rapidly decomposing, pale yellow, amorphous solid (68%); ^1H NMR δ 2.42 (s, 3, Me), 5.51 (s, 1, CHN_2), 7.0–7.4 (m, 4, aromatic Hs).

1-Diazo-4-methyl-3-penten-2-one (1c): yellow, amorphous solid (67%); ^1H NMR δ 1.86, 2.32 (s, 3 each, methyls), 5.20 (s, 1, H-1), 5.73 (br s, 1, H-3).

2-(Diazoacetonylidene)-1β,3β-dimethylcyclohexane (2c): yellow, viscous liquid (52%); ^1H NMR δ 1.18, 1.22 (d, 3 each, J = 7 Hz, methyls), 1.3–1.9 (m, 6, methylenes), 2.3–2.5 (m, 1, H of methine anti to C=O), 3.8–4.0 (m, 1, H of methine syn to C=O), 5.18 (s, 1, CHN_2), 5.64 (br s, 1, α-keto H).

2-(Diazoacetonylidene)-1α,3β-dimethylcyclohexane (3c): yellow, viscous liquid (54%); ^1H NMR δ 1.15, 1.17 (d, 3 each, J = 7 Hz, methyls), 1.5–2.0 (m, 6, methylenes), 2.4–2.6 (m, 1, H-1), 4.1–4.3 (m, 1, H-3), 5.30 (s, 1, CHN_2), 5.65 (br s, 1, α-keto H).

3-(Diazoacetonylidene)-2,4-dimethyl-1-cyclohexene (4c): yellow, amorphous solid (53%); ^1H NMR δ 1.12 (d, 3, J = 7 Hz, 4-Me), 1.5–2.5 (m, 4, methylenes), 1.80 (s, 3, 2-Me), 4.0–4.1 (m, 1, H-4), 5.30 (s, 1, CHN_2), 5.71 (s, 1, α-keto H), 6.0–6.2 (m, 1, H-1).

1-(Diazoacetonylidene)-4-*tert*-butylcyclohexane (5c): yellow, amorphous solid (67%); ^1H NMR δ 0.88 (s, 9, methyls), 1.1–2.4 (m, 8, CH, methylenes), 3.7–4.0 (m, 1, allyl eq H syn to C=O), 5.18 (s, 1, CHN_2), 5.64 (br s, 1, α-keto H).

1-(Diazoacetonylidene)-6-methyl-1,2,3,4,4aα,5,8,8aβ-octahydronaphthalene (6c): yellow, amorphous solid (50%); ^1H NMR δ 1.1–2.1 (m, 11, methylenes, methines), 1.63 (br s, 3, Me), 3.9–4.1 (m, 1, eq H-2), 5.22 (s, 1, CHN_2), 5.3–5.4 (m, 1, H-7), 5.53 (br s, 1, α-keto H).

Ethyl 2-Diazo-3-oxo-4-(6-methyl-1,2,3,4,4aα,5,8,8aβ-octahydro-1-naphthylidene)butanoate (13). A solution of acid chloride **6b** [from 800 mg (3.8 mmol) of acid **6a**] and 885 mg (7.8 mmol) of ethyl diazoacetate was kept at room temperature away from light for 96 h. Volatile materials were removed under 10 Torr vacuum at room temperature. Chromatography of the residual oil on neutral alumina (activity III) and elution with chloroform furnished 540 mg (46%) of yellow, amorphous diazo keto ester **13**: ^1H NMR δ 1.29 (t, 3, J = 7 Hz, ethyl Me), 1.3–2.2 (m, 11, methylenes, methines), 3.9–4.1 (m, 1, eq H-2), 4.15 (q, 2, J = 7 Hz, OCH_2), 5.3–5.5 (m, 1, H-7), 5.56 (br s, 1, α-keto H). The diazo compound was used in the next reaction without further purification.

General Procedure. Diazo Ketone Decompositions. A solution of 2 mmol of diazo ketone in 150 mL of methylene chloride was added dropwise over a 6-h period to a suspension of 0.04 mmol of dirhodium tetraacetate in 50 mL of methylene chloride. The mixture was evaporated under vacuum. Chromatography of the residue and elution with 30:1 hexane–ethyl acetate yielded the cyclopentenone.

Indanone (ii): colorless, crystalline solid; mp 38–40 °C (Et_2O) (60%); IR, ^1H NMR, and ^{13}C NMR spectrally identical with an authentic sample.

3-Methyl-2-cyclopentenone (14): colorless liquid (59%); ^1H NMR and ^{13}C NMR spectrally identical with an authentic sample.

1,4,5,6,7,7a-Hexahydro-4β,7aβ-dimethyl-2*H*-inden-2-one (15a): colorless, viscous liquid (47%); IR (C=O) 1680 (s), (C=C) 1605 (s) cm^{-1}; ^1H NMR δ 1.18 (d, 3, J = 7 Hz, 4-Me), 1.3–2.0 (m, 6, methylenes), 1.36 (s, 3, 7a-Me), 2.28 (s, 2, C-1 Hs), 3.0–3.2 (m, 1, H-4), 5.80 (s, 1, H-3); ^{13}C NMR δ 17.5 (C-6), 19.1 (4-Me), 26.9 (7a-Me), 33.3 (C-5), 33.9 (C-4), 40.6 (C-7), 43.5 (C-7a), 54.0 (C-1), 127.3 (C-3), 191.1 (C-3a), 207.4 (C-2).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.40; H, 9.87.

1,4,5,6,7,7a-Hexahydro-4α,7aβ-dimethyl-2*H*-inden-2-one (15b): colorless, viscous liquid (53%); IR (C=O) 1677 (s), (C=C) 1607 (s) cm^{-1}; ^1H NMR δ 1.0–2.1 (m, 6, methylenes), 1.18 (d, 3, J = 7 Hz, 4-Me), 1.28 (s, 3, 7a-Me), 2.18, 2.27, 2.30, 2.39 (4-line AB, 2, C-1 Hs), 2.5–2.7 (m, 1, H-4), 5.78 (br s, 1, H-3); ^{13}C NMR δ 18.2 (4-Me), 21.9 (C-6), 24.6 (7a-Me), 32.5 (C-4), 36.6 (C-5), 40.7 (C-7), 43.6 (C-7a), 52.5 (C-1), 124.0 (C-3), 192.7 (C-3a), 207.0 (C-2).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.52; H, 9.81.

1,6,7,7a-Tetrahydro-4,7a-dimethyl-2*H*-inden-2-one (16): colorless, viscous liquid (52%); IR (C=O) 1682 (s), (C=C) 1620 (m), 1580 (m) cm^{-1}; ^1H NMR δ 1.0–2.0 (m, 4, methylenes), 1.19 (s, 3, 7a-Me), 1.92 (br s, 3, 4-Me), 2.1–2.4 (m, 2, C-1 Hs), 5.80 (s, 1, H-3), 5.9–6.1 (m, 1, H-5); ^{13}C NMR δ 18.7 (4-Me), 24.1 (C-6), 25.3 (7a-Me), 33.8 (C-7), 40.5 (C-7a), 51.8 (C-1), 122.0 (C-3), 129.0 (C-4), 134.6 (C-5), 179.3 (C-3a), 207.5 (C-2).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.52; H, 8.64.

5-*tert*-Butyl-3,3a,4,5,6,7-hexahydro-2*H*-inden-2-one (17): colorless, amorphous solid (57%); ^1H NMR δ 0.91 (s, 9, methyls), 1.0–3.0 (m, 10, methylenes, methines), 5.83 (br s, 1, H-1); ^{13}C NMR δ 27.5 (methyls), 28.0 (C-6), 30.8 (C-4), 36.0 (C-7), 41.9 (C-3a), 42.6 (C-3), 47.1 (C-5), 126.3 (C-1), 184.5 (C-7a), 208.8 (C-2).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.15; H, 10.56.

Ketone 18a: colorless, viscous liquid (65%); ^1H NMR δ 1.0–2.9 (m, 13, methylenes, methines), 1.64 (br s, 3, Me), 5.3–5.5 (m, 1, H-8), 5.74 (br s, 1, H-1); ^{13}C NMR δ 23.1 (Me), 28.2 (C-9), 32.3 (C-4), 34.0 (C-5), 38.0 (C-6), 39.5 (C-3a, C-5a), 41.2 (C-9a), 42.0 (C-3), 119.2 (C-8), 124.8 (C-1), 133.0 (C-7), 187.0 (C-9b), 208.6 (C-2).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.13; H, 8.97. Found: C, 83.21; H, 8.90.

Keto ester 18b: colorless, crystalline solid; mp 93–95 °C (C_6H_{14}–Et_2O) (55%); IR (C=O) 1730 (s), 1698 (s), (C=C) 1608 (s) cm^{-1}; ^1H NMR δ 1.2–2.4 (m, 10, methylenes, methines), 1.28 (t, 3, J = 7 Hz, ethyl Me), 1.65 (br s, 3, 7-Me), 3.0–3.2 (m, 1, H-3a),

3.04 (d, 1, J = 3 Hz, H-3), 4.22 (q, 2, J = 7 Hz, OCH_2), 5.3–5.5 (m, 1, H-8), 5.78 (s, 1, H-1); ^{13}C NMR δ 14.0 (ethyl Me), 23.1 (7-Me), 28.3 (C-9), 32.1 (C-4), 33.1 (C-5), 38.0 (C-6), 39.2 (C-5a), 41.3 (C-9a), 46.3 (C-3a), 59.1 (C-3), 61.3 (OCH_2), 119.2 (C-8), 123.3 (C-1), 133.1 (C-7), 169.0 (ester C=O), 186.3 (C-9b), 200.9 (C-2).

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.43; H, 8.08. Found: C, 74.52; H, 8.01.

Acknowledgment. P.C., M.C., M.C.M., and O.R. are indebted to the Consiglio Nazionale delle Ricerche (Rome) and the Ministero della Pubblica Istruzione for financial support and to F. Castrica for technical assistance.

Registry No. **1a**, 541-47-9; **1c**, 29166-18-5; **2a**, 123992-56-3; **2c**, 123992-74-5; **2d**, 123992-70-1; **3a**, 123992-57-4; **3c**, 123992-75-6; **3d**, 123992-71-2; **4a**, 123992-58-5; **4c**, 123992-76-7; **4d**, 123992-72-3; **5a**, 13733-51-2; **5c**, 123992-77-8; **5d**, 13733-50-1; **6a**, 123992-59-6; **6b**, 123992-79-0; **6c**, 123992-78-9; **6d**, 123992-73-4; **7a**, 123992-60-9; **7b**, 123992-69-8; **8**, 40790-56-5; **9**, 123992-61-0; **10**, 123992-62-1; **11**, 83586-09-8; **12**, 123992-63-2; **13**, 123992-64-3; **14**, 2758-18-1; **15a**, 123992-65-4; **15b**, 76803-50-4; **16**, 123992-66-5; **17**, 123992-67-6; **18a**, 123992-68-7; **18b**, 123992-80-3; i, 41441-74-1; ii, 83-33-0; ethyl bromoacetate, 105-36-2; ethyl diazoacetate, 623-73-4; dirhodium tetraacetate, 15956-28-2; 4-*tert*-butylcyclohexanone, 98-53-3; 2,6-dimethylcyclohexanone, 2816-57-1; *cis*-2,6-dimethylcyclohexanone, 766-42-7; *trans*-2,6-dimethylcyclohexanone, 766-43-8; 2-bromo-2,6-dimethylcyclohexanone, 55234-03-2; 2,6-dimethyl-1-[(trimethylsilyl)oxy]cyclohexene, 63547-53-5.

Preparation of [Hydroxy(((+)-10-camphorsulfonyl)oxy)iodo]benzene and Its Reactivity toward Carbonyl Compounds†

Evangelia Hatzigrigoriou, Anastasios Varvoglis,* and Maria Bakola-Christianopoulou‡

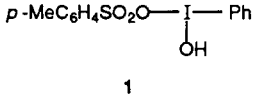
Laboratory of Organic Chemistry, University of Thessaloniki, 540 06 Thessaloniki, Greece

Received May 3, 1989

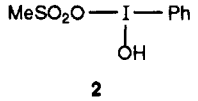
The title compound is prepared and used for the direct α-((10-camphorsulfonyl)oxylation) of various ketones and carbonyl compounds with an active methylene group. Its reaction with 2-butanone and 4-methyl-2-pentanone yields predominantly the corresponding 1-sulfonyloxy derivatives. The stereoselectivity of the reaction is studied by using benzoylacetone, ethyl benzoylacetate, and propiophenone. In some reactions 10-camphorsulfonyl peroxide is formed as a byproduct.

Organic hypervalent iodine reagents are useful in effecting direct α-functionalization of ketones and active methylene compounds. Groups attached through oxygen include hydroxy, methoxy or ethoxy,[1] acetoxy,[2] phosphoryloxy,[3] and sulfonyloxy;[4,5] also, azido[5] and saccharinyl[6] groups as well as fluorine[7] and chlorine[8] have been successfully introduced to ketones, β-diketones, and esters of β-keto acids.

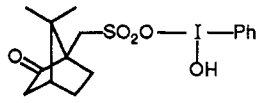
Presently there is considerable interest in various α-sulfonyloxy ketones because of their potential in organic synthesis[4] and their photochemical reactivity.[9] Approaches toward their preparation not requiring the availability of α-hydroxy ketones and involving enolic ketone derivatives have been summarized.[4] The direct introduction of a tosyloxy or a mesyloxy group to carbonyl compounds has been effected by using [hydroxy(tosyloxy)iodo]benzene[10] (1) or [hydroxy(mesyloxy)iodo]-



1



2



3

benzene[4,11] (2), respectively; the latter reagent can also be used as formed in situ from iodosylbenzene, $(PhIO)_n$, and methanesulfonic acid.[5] Both reagents 1 and 2 have been shown to react not only with carbonyl compounds but also with their trimethylsilyl enol ethers affording again α-sulfonyloxylated carbonyl compounds.[12] The synthetic utility of reagents 1 and 2 and also of some analogues of 1 in which the phenyl group has been changed to pentafluorophenyl or perfluoropropyl has been demonstrated further in their reactions with alkenes,[13–15] alkynes,[16–18] trimethylsilyl aromatics,[19,20] thiophenes,[21] alkenoic

* Author to whom correspondence should be addressed.
† Dedicated to the memory of Professor E. B. Merkushev.
‡ In part.

(1) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244.
(2) Mizukami, E.; Ando, M.; Tanaka, T.; Imamura, J. *Bull Chem. Soc. Jpn.* **1978**, *51*, 335.
(3) Koser, G. F.; Lodaya, J. S.; Ray, III, D. G.; Kokil, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 2987.
(4) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 210.
(5) Moriarty, R. M.; Vaid, R. K.; Ravikumar, V. T.; Vaid, B. K.; Hopkins, T. E. *Tetrahedron* **1988**, *44*, 1603.
(6) Papadopoulou, M.; Varvoglis, A. *J. Chem. Res., Synop.* **1984**, 166.
(7) Tsushima, T.; Kawada, K.; Tsuji, T. *Tetrahedron Lett.* **1982**, *23*, 1165.
(8) Dneprovskii, A. S.; Krainyuchenko, I. V.; Temnikova, T. I. *Zh. Org. Khim.* **1978**, *14*, 1514.
(9) Charlton, J. L.; Lai, H. K.; Lypka, G. N. *Can. J. Chem.* **1980**, *58*, 458.
(10) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.
(11) Zefirov, N. S.; Zhdankin, V. V.; Dankov, Yu. V.; Kozmin, A. S.; Chizhov, O. S. *Zh. Org. Khim.* **1985**, *21*, 2461.
(12) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Epa, W. R.; Prakash, I. *J. Org. Chem.* **1989**, *54*, 1101.
(13) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462.
(14) Zefirov, N. S.; Zhdankin, V. V.; Dankov, Yu. V.; Sorokin, V. D.; Semerikov, V. N.; Kozmin, A. S.; Caple, R.; Berglund, B. A. *Tetrahedron Lett.* **1986**, *27*, 3971.
(15) Moriarty, R. M.; Khosrowshahi, J. S.; Prakash, O. *Tetrahedron Lett.* **1985**, *26*, 2961.
(16) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700.
(17) Moriarty, R. M.; Vaid, R. K.; Duncan, M. P.; Vaid, B. K. *Tetrahedron Lett.* **1987**, *28*, 2845.
(18) Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228.
(19) Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, *45*, 1543.

0022-3263/90/1955-0315$02.50/0