dilithio-3-MC (7) yielded[12] 42% of 6,12b-dicarboxy-6,12b-dihydro-3-methylcholanthrene (9) on carbonation, while disodio-3-MC (8) gave 59% of a monocarboxylic acid of unknown[13] structure.

On the basis of these data we hoped monomethylation of 8 would yield the desired 6,12-dihydro-3,6-dimethylcholanthrene (10). We now report the formation of 10 from 3 in 61% yield[14] and dehydrogenation of 10 with sulfur to pure 3,6-DMC (4) in 71.5% yield. The assigned structures 4 and 10 were confirmed by oxidation of 4 to 5-(6-methyl-1,2-benz[a]anthraquinoyl)acetic acid[8] (12).

Experimental Section[15]

6,12b-Dihydro-3,6-dimethylcholanthrene (10). To the stirred solution at room temperature of 8 prepared[8] from 2.5 g (9.3 mmol) of 3[16] in 400 mL of ether (dried by distillation from BuMgBr): benzene (1:1) was added 2 g (14.1 mmol) of methyl iodide. After 5 min the reaction mixture was quenched with a milliliter of methanol and filtered through a pad of silica gel. After evaporation of the solvent the residue was triturated twice with 10 mL each of hot acetone and the remainder was crystallized from 1-propanol to yield 0.89 g of 10 as long white needles, mp 167.5–168.5 °C. The purest 10 melted at 172–173 °C after several recrystallizations. Lower melting fractions[17] gave NMR spectra that were indistinguishable from that of pure 10. The total yield of stereoisomeric forms of 10 was 61%. Data for 10: mp 168 °C; UV (hexane) λ_{max} at 227, 231, 256 (sh), 264, 274, 283, 292, 306, 313, 321 nm; NMR ($CDCl_3$) δ 1.46 (d, 3, 6-CH_3), 2.26 (s, 3, 3-CH_3), 2.0–3.2 (m, 4, 1- and 2-CH_2), 4.0–5.0 (m, 2-, 6-, and 12b-CH), 6.8–8.3 (m, 8, aromatic); mass spectrum, m/e 284 (M^+).

3,6-Dimethylcholanthrene (4). A mixture of 1.422 g of 10 (mp 165–167.5 °C) and 0.175 g sulfur was initially melted at 170 °C and maintained at 160–165 °C for 1 h. The crude product in a small amount of benzene mixed with 5 g of picric acid in hot alcohol (100 mL) gave 2.42 g of 3,6-dimethylcholanthrene picrate, as dark reddish-black needles, mp 147.5–149 °C. One recrystallization from 90 mL of alcohol gave 2.13 g of pure picrate, mp 148.5–149.5 °C. On chromatography over basic alumina (benzene) 1.01 g (71%) of pure 3,6-DMC (4) was obtained as light-yellow needles (mp 135–136 °C[18]) after crystallization from 1-propanol. Data for 4: UV (hexane λ_{max} 267, 277, 288, 299, 336, 350, 367, 386 nm; NMR ($CDCl_3$) δ 2.3 (s, 3, 3-CH_3), 3.13 (s, 3, 6-CH_3), 2.8–3.5 (br m, 4, 1- and 2-CH_2), 7.0–8.8 (m, 8, aromatic); mass spectrum, m/e 282 (M^+). Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.38; H, 6.51.

5-(6-Methyl-1,2-benz[a]anthraquinoyl)acetic Acid[8] (12). A mixture of 40 mg of 4 and 200 mg of sodium dichromate in 4 mL of acetic acid was held at reflux for 0.5 h and then diluted with dilute H_2SO_4. The IR spectrum of the precipitated yellow solid (32 mg, mp 250–260 dec) was superimposable with that of 5-(6-methyl-1,2-benz[a]anthraquinoyl)acetic acid (12) obtained[8] by oxidation of 3: IR (KBr) 1700, 1665, 1590, 1462, 1430, 1300, 1063, 848, 785, 762 cm^{-1}.

Registry No. 3, 56-49-5; 4, 85923-37-1; 4 picrate, 85923-38-2; 10 (isomer 1), 85923-39-3; 10 (isomer 2), 85923-40-6; 12, 85923-41-7.

(13) We believe this acid has the structure 11, since monomethylation of 8 gives the 6-methyl derivative.

(14) The yield of 10 and the number of coproducts formed varied with the amount of methyl iodide used. A slight excess of methyl iodide (1.5 equiv) enhanced the isolated yield of 10 by depressing the amount of 6,12b-dihydro-3-methylcholanthrene (seen by NMR of mother liquor) formed, while a large excess (>2 equiv) resulted in the formation of small quantities of two different isomers of trimethylcholanthrene (M^+ at m/e 296) of unknown structure.

(15) All melting points are uncorrected. Analysis was done by the Galbraith Laboratories, Inc., Knoxville, TN.

(16) A commercial sample from Baker. 3-MC was also synthesized from 7-(4-methylhydrindyl) 1-naphthyl ketone as per L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **58**, 2482 (1936).

(17) Stereoisomeric with crystals, mp 172–173 °C; for a discussion on formation of stereoisomers in similar reductive methylations, see ref 9.

(18) On slow heating 3,6-DMC melts in a range of 133–136 °C primarily due to air oxidation as determined by the TLC of the dark-colored melt. When the melting point was taken in an evacuated tube, the melting point was 135–136 °C and no dark spot was obtained in the TLC.

1,4- and 1,5-Diketones via Palladium-Catalyzed Allylation of Potassium Enoxyborates[1]

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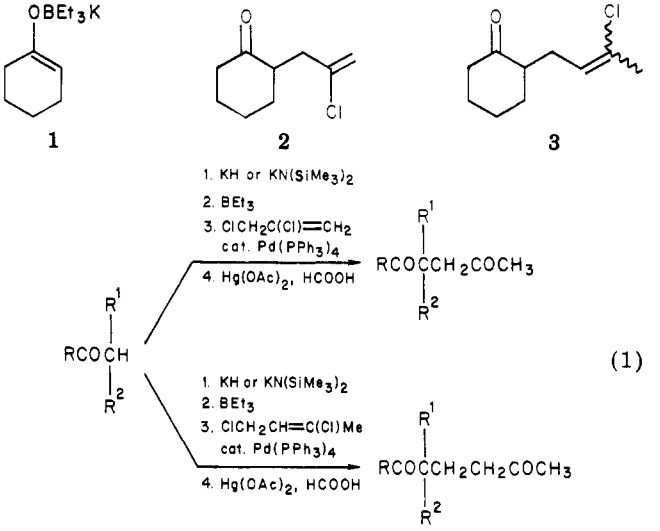
Received October 26, 1982

We have recently reported a Pd-catalyzed, highly regio- and stereoselective allylation of enoxyborates derived from ketones.[2] One particularly attractive feature of potential significance is that Pd catalysts significantly enhance the reactivity of otherwise relatively unreactive allylic electrophiles containing electron-withdrawing substituents. This presumably is because the oxidative addition reaction between allylic electrophiles and Pd complexes is accelerated by electron-withdrawing groups. Thus, for example, 2,3-dichloropropene and 1,3-dichloro-2-butene, both of which react only sluggishly with enolates, undergo a rapid and selective allylation with potassium cyclohexenoxytriethylborate (1) in the presence of 5 mol % of $Pd(PPh_3)_4$ to give 2 and 3 in 92% and 86% yields, respectively.

In view of the significance of γ- and δ-chloro-γ,δ-unsaturated ketones as precursors to 1,4- and 1,5-diketones, respectively, we investigated the generality and regiospecificity of the Pd-catalyzed reaction of potassium enoxyborates with 2,3-dichloropropene and 1,3-dichloro-2-butene. As the results summarized in Table I indicate, the reaction indeed appears to be not only general with respect to the structure of ketones but also highly regiospecific. Coupled with a recently developed procedure for converting alkenyl chlorides into ketones,[3] the herein-described method offers a satisfactory, potentially general, and regiospecific route to 1,4- and 1,5-diketones (eq 1).



(1)

R = alkyl; R^1,R^2 = H or alkyl

The following observations are noteworthy. First, all five cyclic and acyclic potassium enoxytriethylborates tested

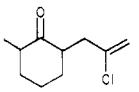
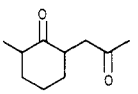
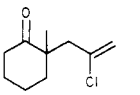
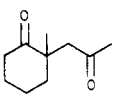
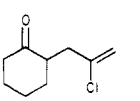
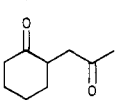
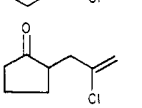
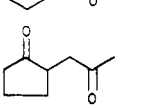
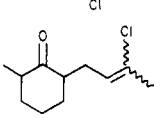
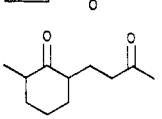
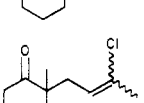
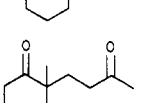
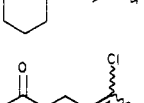
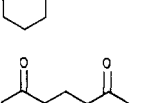
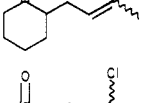
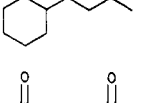
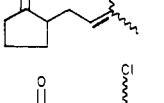
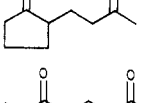
(1) Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis. 32. Part 31. Negishi, E.; Van Horn, D. E.; Yoshida, T.; Rand, C. L. *Organometallics* **1983**, *2*, 563.

(2) Negishi, E.; Matsushita, H.; Chatterjee, S.; John, R. A. *J. Org. Chem.* **1982**, *47*, 3188.

(3) (a) Julia, M.; Blasioli, C. *Bull. Soc. Chim. Fr.* **1976**, 1941. (b) Yoshioka, H.; Takasaki, K.; Kobayashi, M.; Matsumoto, T. *Tetrahedron Lett.* **1979**, 3489.

0022-3263/83/1948-2427$01.50/0

Table I. Chloroallylated Ketones and 1,4- and 1,5-Diketones via Palladium-Catalyzed Allylation[a]

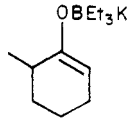
ketone	base	allyl chloride[b]	chloroallylated ketone	yield,[c] %	diketone	yield,[c] %
2-methylcyclohexanone	$KN(SiMe_3)_2$	A		81 (92)		82[d]
2-methylcyclohexanone	KH	A		77 (82)		74[e]
cyclohexanone	KH	A		86 (92)		78
cyclopentanone	KH	A		72 (85)		76
2-methylcyclohexanone	$KN(SiMe_3)_2$	B		72 (74)		81[f]
2-methylcyclohexanone	KH	B		74 (90)		83[g]
cyclohexanone	KH	B		78 (86)		74
cyclopentanone	KH	B		72 (81)		75
3-pentanone	KH	B		86 (91)		73

[a] The preparation of the regiodefined potassium enoxyborates was carried out at −78 °C in THF. The other enoxyborates may be prepared at room temperature. The Pd-catalyzed allylation was carried out at room temperature in THF with 5 mol % of $Pd(PPh_3)_4$ as a catalyst. The reaction time varied from 3 to 24 h. The hydrolysis of chloroallylated ketones was carried out at room temperature in 88% HCOOH with 1.2 equiv of $Hg(OAc)_2$. [b] A = 2,3-dichloropropene. B = 1,3-dichloro-2-butene. [c] Isolated yield. The number in parentheses is the GLC yield. [d] A 90:10 mixture of the 2,6- and 2,2-isomers. The cis-to-trans ratio of the 2,6-isomers is 10:90. [e] An 87:13 mixture of the 2,2- and 2,6-isomers. [f] A 95:5 mixture of the 2,6- and 2,2-isomers. The cis-to-trans ratio of the 2,6-isomers is 40:60. [g] An 89:11 mixture of the 2,2- and 2,6-isomers.

in this study gave the desired alkenyl chlorides in >70% isolated yields (>80% GLC yields), based on the starting ketones, indicating that the reaction may be of considerable generality with respect to the structure of ketones.

Second, no difficulty was encountered in converting the alkenyl chloride intermediates into 1,4- and 1,5-diketones in 73–83% isolated yields by the $Hg(OAc)_2$–HCOOH procedure originally developed by Julia[3a] and applied to the cases of chloroallylated ketones by Matsumoto.[3b] This procedure appears to be free of any noticeable complications, such as formation of 2-methyl-4,5,6,7-tetrahydrobenzo[*b*]furan from **2** reported by Martin.[4] In view of the ready availability of both $Hg(OAc)_2$ and 88% HCOOH as well as the uniformly high product yields, we prefer this procedure to the others, such as those involving $Hg(OOCCF_3)_2$–CH_3NO_2,[3b] $Hg(OAc)_2$–CF_3COOH,[4] HgX_2–H_2O, where X = ClO_4, $0.5SO_4$, NO_3, BF_4,[5] and $TiCl_4$–EtSH–H_2O.[6]

Third, the regioselectivity observed in the reaction of **4** or **5** with 2,3-dichloropropene or 1,3-dichloro-2-butene was 87–95% on the basis of ^1H and ^{13}C NMR examination. Since we have recently found that the regioselectivity in the conversion of 2-methylcyclohexanone into **4** or **5** is 95–98%,[7] the observed regioselectivity suggests that the regiospecificity in the allylation step must be in the 90–100% range.



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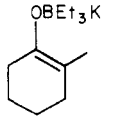

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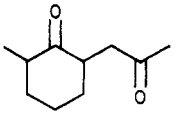

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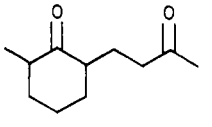

7

Fourth, the cis-to-trans ratios for the stereoisomers of **6** and **7** were 10:90 and 40:60, respectively, on the basis of ^1H and ^{13}C NMR examination (see Experimental Section). The predominant formation of the trans isomers is in

(4) Martin, S. F.; Chou, T. S. *Tetrahedron Lett.* **1978**, 1943.
(5) Arzoumanian, H.; Metzger, J. *J. Organomet. Chem.* **1973**, *57*, C1.
(6) Mukaiyama, T.; Imamoto, T.; Kobayashi, S. *Chem. Lett.* **1973**, 261.
(7) Chatterjee, S.; Negishi, E. *Tetrahedron Lett.* **1983**, *24*, 1341.

contrast with the predominant formation of the cis ring isomers observed in the reaction of **4** or **5** with geranyl or neryl acetate.[2]

α-(3-Chloro-2-butenyl) ketones have been prepared by the conventional Wichterle procedure involving the reaction of alkali-metal enolates with 1,3-dichloro-2-butene.[8] While the regioselectivity in the preparation of α-(3-chloro-2-butenyl) ketones corresponding to "thermodynamic" enolates can be reasonable (~80%), that corresponding to "kinetic" enolates tends to be low. Furthermore, the product yields have seldom been very high. The situation with respect to the reaction of alkali-metal enolates with 2,3-dichloropropene is even more frustrating, the product yields having been disappointingly low. The Pd-catalyzed chloroallylation herein described provides a convenient solution to the above-mentioned difficulties. Furthermore, the commercial availability of KH, BEt_3, 2,3-dichloropropene, 1,3-dichloro-2-butene, $Pd(PPh_3)_4$, and $Hg(OAc)_2$ as well as the operational simplicity make it an attractive alternative to some other recent solutions such as the reaction of alkali-metal enamides with 3-chloro-2-(trimethylsiloxy)-2-propene[9] and that of silyl enol ethers with 2-nitropropene promoted by $SnCl_4$.[10]

Experimental Section

All palladium-catalyzed reactions were run under an atmosphere of nitrogen. Tetrakis(triphenylphosphine)palladium was prepared as described in the literature.[11] The starting ketones, bis(trimethylsilyl)amine, triethylborane in THF, and 2,3-dichloropropene were obtained from Aldrich Chemical Co. and used without purification. 1,3-Dichloro-2-butene was obtained as a mixture of cis/trans isomers from Tokyo Kasei Kogyo Co. and used without purification. Mercuric acetate and 88% HCOOH were obtained from Fisher Scientific Co. and used as received. Tetrahydrofuran obtained from Aldrich was purified by distillation from Na and benzophenone. Potassium hydride (24.6% in oil) was obtained from Alfa Products and used as described in the literature.[12]

Conversion of Ketones into Chloroallylated Ketones via Allylation of Potassium Enoxytriethylborates Catalyzed by Tetrakis(triphenylphosphine)palladium. The following procedure for the conversion of 2-methylcyclohexanone into 2-methyl-2-(2-chloro-2-propenyl)cyclohexanone is representative. Potassium hydride (0.82 g, 20 mmol) was separated from mineral oil by washing it with pentane[12] and placed in a flask with a magnetic stirring bar, a septum inlet, and an outlet led to a mercury bubbler. To this were added at room temperature 40 mL of THF and 2-methylcyclohexanone (2.26 g, 20 mmol). Evolution of hydrogen subsided within 30 min, at which time 22 mL of a 1 M solution of triethylborane in THF was added to the mixture. A clear solution thus formed was added to a mixture of 2,3-dichloropropene (2.44 g, 22 mmol) and $Pd(PPh_3)_4$[11] (1.15 g, 1 mmol) in 20 mL of THF. The reaction mixture was stirred for 12 h at room temperature and was treated with 50 mL of 3 N HCl. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was treated with saturated $NaHCO_3$ and dried over $MgSO_4$. Distillative workup gave 2.88 g (77% yield) of 2-methyl-2-(2-chloro-2-propenyl)cyclohexanone:[3b] bp 80–82 °C (0.08 mmHg). Examination of the crude, isolated sample by ^1H and ^{13}C NMR indicated that it was a 87:13 mixture of the 2,2- and 2,6-isomers, the cis/trans ratio of the latter being 4/9. The 2,2-isomer yielded the following spectral data: IR (neat) 1705 (s), 1630 (s), 885 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.17 (s, 3 H), 1.3–2.0 (m, 6 H), 2.3–2.6 (m, 2 H), 2.63 (d, J = 13.5 Hz, 1 H), 2.81 (d, J = 13.5 Hz, 1 H), 5.15 (s, 1 H), 5.26 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.22, 22.80, 27.56, 38.79, 39.28, 46.61, 48.38, 116.31, 138.95, 213.83.

Conversion of 2-Methylcyclohexanone into 6-Chloroallylated Derivatives. The "kinetic" potassium enolate of 2-methylcyclohexanone was generated by treating at −78 °C the ketone with 1 equiv of $KN(SiMe_3)_2$, generated by the reaction of KH with 1.2 equiv of $HN(SiMe_3)_2$ in THF, according to a literature procedure.[12] Addition of BEt_3 was also carried out at −78 °C. The resultant potassium enoxytriethylborate was warmed to room temperature and reacted with an appropriate allylic chloride as described above.

Conversion of Chloroallylated Ketones into 1,4- or 1,5-Diketones. The following procedure for the preparation of 2-methyl-2-(2-oxopropyl)cyclohexanone is patterned after that reported in the literature[3] and is representative of all cases reported here.

2-Methyl-2-(2-chloro-2-propenyl)cyclohexanone (2.31 g, 12 mmol) was treated at room temperature with $Hg(OAc)_2$ (4.14 g, 13 mmol) in 20 mL of 88% HCOOH for 3 h. The resultant mixture was filtered, and most of HCOOH was removed by evaporation. The residue was dissolved in ether treated with saturated $NaHCO_3$ and dried over $MgSO_4$. Distillation gave 1.48 g (74% yield) of 2-methyl-2-(2-oxopropyl)cyclohexanone:[3] bp 69–71 °C (0.05 mmHg); IR (neat) 1705 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.15 (s, 3 H), 1.3–2.25 (m with a singlet at 2.10, 9 H), 2.25–2.5 (m, 2 H), 2.53 (d, J = 17 Hz, 1 H), 2.88 (d, J = 17 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.29, 24.06, 26.34, 30.85, 37.80, 38.41, 47.02, 51.59, 206.56, 213.83.

2-Methyl-6-(2-chloro-2-propenyl)cyclohexanone:[3] IR (neat) 1710 (s), 1630 (m), 875 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.01 (d, J = 7 Hz, 3 H), 1.1–3.1 (m, 10 H), 5.18 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.50, 25.33, 34.15, 37.29, 39.06, 45.65, 47.78, 113.99, 140.85, 212.57.

***trans*-2-Methyl-6-(2-oxopropyl)cyclohexanone:**[3] IR (neat) 1700 (s), 1355 (m), 1170 (m), 1130 (m), 1000 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.96 (d, J = 7 Hz, 3 H), 1.1–3.2 (m with a singlet at 2.17, 13 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.44, 25.37, 30.45, 34.84, 37.10, 43.22, 45.22, 46.56, 207.46, 212.71. In addition to these major signals for the trans isomer and a set of minor signals for the 2,2-regioisomer, another set of minor signals for the cis isomer was present. Those assignable to the cis isomer appear at 16.78, 20.29, 31.31, 33.27, 33.38, 44.12 ppm. Although the ^1H NMR signal for the 2-Me group of one stereoisomer is not readily discernible, the shift value of 0.96 ppm for the major isomer is within the range of 0.99 ± 0.03 ppm[2] for structurally related trans isomers. This assignment is further supported by the relative ^{13}C NMR shift values for the 2-Me group of the cis and trans isomers, i.e., 16.78 and 14.44 ppm, respectively. The relative intensities of these signals indicate that the trans-to-cis ratio is ca. 90:10.

2-(2-Chloro-2-propenyl)cyclohexanone:[3] IR (neat) 1710 (s), 1635 (s), 1130 (s), 880 (s), cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.1–3.05 (m, 11 H), 5.20 (br s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.19, 27.99, 33.10, 39.11, 42.11, 47.77, 113.98, 140.81, 210.88.

2-(2-Oxopropyl)cyclohexanone:[3,4] IR (neat) 1710 (s), 1355 (s), 1165 (s), 1130 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.1–3.15 (m with a singlet at 2.20); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.32, 27.89, 30.45, 34.05, 41.87, 43.21, 46.50, 207.25, 211.38.

2-(2-Chloro-2-propenyl)cyclopentanone:[13] IR (neat) 1740 (s), 1638 (m), 1160 (m), 890 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.7–3.0 (m, 9 H), 5.02 (s, 1 H), 5.10 (s, 1 H).

2-(2-Oxopropyl)cyclopentanone:[14] IR (neat) 1730 (s), 1360 (s), 1175 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.0–3.0 (m with a singlet at 2.15).

2-Methyl-6-(3-chloro-2-butenyl)cyclohexanone:[8] IR (neat) 1710 (s), 1445 (m), 1375 (m), 1125 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.99 (d, J = 7 Hz, 3 H), 1.1–2.7 (m with a singlet at 2.06, 13 H), 5.50 (t, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.52, 25.52, 26.19, 28.86, 34.91, 37.35, 45.59, 50.35, 123.95, 131.03, 213.35. In addition to this set of 11 major signals, other minor signals

(8) (a) Wichterle, O.; Prochezka, J.; Hofmann, J. *Collect. Czech. Chem. Commun.* **1948**, *13*, 300. (b) Marshall, J. A.; Schaeffer, D. J. *J. Org. Chem.* **1965**, *30*, 3642.
(9) Hosomi, A.; Shirahata, A.; Araki, Y.; Sakurai, H. *J. Org. Chem.* **1981**, *46*, 4631.
(10) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679.
(11) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(12) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.
(13) Lansbury, P. T.; Morkulich, P. M.; Gallagher, P. E. *Tetrahedron Lett.* **1973**, 65.
(14) Mattay, J. *Tetrahedron Lett.* **1980**, 2309.

were also present. However, no attempts were made to assign these minor signals. The stereo- and regiochemistry was established by examining 2-methyl-6-(3-oxobutyl)cyclohexanone, as described below.

***trans*-2-Methyl-6-(3-oxobutyl)cyclohexanone:**[8] IR (neat) 1710 (s), 1360 (s), 1160 (s), 1125 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.00 (d, J = 7 Hz, 3 H), 1.1–2.9 (m with a singlet at 2.14, 15 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.51, 23.79, 25.61, 29.84, 35.63, 37.53, 41.51, 45.77, 49.92, 209.03, 213.98. In addition to the above set of signals for the trans 2,6-isomer, those assignable to the cis 2,6-isomer and the 2,2-isomer were also present. Those assignable to the cis 2,6-isomer appear at 15.56, 20.51, 24.83, 30.02, 33.01, 35.09, 41.44, 42.77, 48.26, 208.25, 216.47 ppm. ^1H NMR signal for the 2-Me group of the cis 2,6-isomer appears at 1.06 ppm. The ratio of the 2,6-isomers to the 2,2-isomer was 95:5 and that of the trans 2,6-isomer to its cis isomer was 60:40.

2-Methyl-2-(3-chloro-2-butenyl)cyclohexanone:[8] IR (neat) 1705 (s), 1665 (m), 1450 (m), 1375 (m), 1125 (m), 1065 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.00 (s, 3 H), 1.0–2.5 (m with peaks at 1.67, 2.00, and 2.23, 13 H), 5.40 (t, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.26, 22.61, 26.08, 27.44, 36.82, 38.38, 38.76, 48.44, 121.73, 131.82, 213.79.

2-Methyl-2-(3-oxobutyl)cyclohexanone:[8] IR (neat) 1710 (s), 1450 (m), 1370 (m), 1170 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.07 (s, 3 H), 1.1–3.0 (m with a singlet at 2.17, 15 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.01, 22.64, 27.44, 31.17, 38.44, 38.81, 39.50, 48.26, 209.86, 215.90.

2-(3-Chloro-2-butenyl)cyclohexanone:[3-5] IR (neat) 1710 (s), 1670 (m), 1450 (s), 1130 (m), 1060 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.0–2.8 (m with a singlet at 2.06, 14 H), 5.50 (t, J = 7 Hz, 1 H).

2-(3-Oxobutyl)cyclohexanone:[3-5] IR (neat) 1710 (s), 1450 (m), 1355 (m), 1165 (m), 1130 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.1–2.6 (m with a singlet at 2.12).

2-(3-Chloro-2-butenyl)cyclopentanone:[15] IR (neat) 1730 (s), 1640 (m), 1150 (m), cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.0–2.8 (m with a peak at 1.90, 12 H), 5.44 (t, J = 7 Hz, 1 H).

2-(3-Oxobutyl)cyclopentanone:[16] IR (neat) 1730 (s), 1450 (m), 1410 (m), 1360 (m), 1175 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.0–3.0 (m with a singlet at 2.15).

4-Methyl-7-chloro-6-octen-3-one: IR (neat) 1710 (s), 1455 (m), 1380 (m), 1100 (m), 1020 (m), 975 (m), 800 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.4 (m with peaks at 0.93, 1.13, and 1.16, 6 H), 1.6–3.0 (m with a singlet at 2.10, 8 H), 5.47 (t, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 7.66, 16.09, 26.06, 31.80, 33.99, 45.29, 122.80, 131.77, 213.75.

5-Methyl-2,6-octanedione: IR (neat) 1710 (s), 1460 (m), 1410 (m), 1360 (m), 1165 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.05 (t, J = 7 Hz, 3 H), 1.10 (d, J = 7 Hz, 3 H), 1.5–2.1 (m, 2 H), 2.15 (s, 3 H), 2.2–2.8 (m, 5 H).

Acknowledgments are made to the National Science Foundation and the National Institutes of Health for support of this research. Some experimental data provided by Drs. H. Matsushita and R. A. John were useful in carrying out this study.

Registry No. **2**, 17392-07-3; **3**, 939-60-6; *cis*-**6**, 60450-46-6; *trans*-**6**, 60416-04-8; *cis*-**7**, 85893-55-6; *trans*-**7**, 85893-56-7; $Pd(PPh_3)_4$, 14221-01-3; BEt_3, 97-94-9; 2-methylcyclohexanone, 583-60-8; 2,3-dichloropropene, 78-88-6; 2-methyl-2-(2-chloro-2-propenyl)cyclohexanone, 72009-03-1; *cis*-2-methyl-6-(2-chloro-2-propenyl)cyclohexanone, 85893-57-8; *trans*-2-methyl-6-(2-chloro-2-propenyl)cyclohexanone, 85893-58-9; 2-methyl-2-(2-oxopropyl)cyclohexanone, 27943-50-6; 2-(2-oxopropyl)cyclohexanone, 6126-53-0; 2-(2-chloro-2-propenyl)cyclopentanone, 41100-30-5; 2-(2-oxopropyl)cyclopentanone, 60415-94-3; *cis*-2-methyl-6-(3-chloro-2-butenyl)cyclohexanone, 85893-59-0; *trans*-2-methyl-6-(3-chloro-2-butenyl)cyclohexanone, 85893-60-3; 2-methyl-2-(3-chloro-2-butenyl)cyclohexanone, 4071-75-4; 2-methyl-2-(3-oxobutyl)cyclohexanone, 4071-58-3; 2-(3-oxobutyl)-cyclohexanone, 26942-62-1; 2-(3-chloro-2-butenyl)cyclopentanone, 57428-31-6; 2-(3-oxobutyl)cyclopentanone, 1489-27-6; 4-methyl-7-chloro-6-octen-3-one, 85908-77-6; 5-methyl-2,6-octanedione, 30466-33-2; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; 3-pentanone, 96-22-0; 1,3-dichloro-2-butene, 926-57-8.

(15) Prelog, V.; Zimmerman, M. *Helv. Chim. Acta* **1949**, *32*, 2360.
(16) Gill, N. S.; James, K. B.; Lions, F.; Potts, K. T. *J. Am. Chem. Soc.* **1952**, *74*, 4923.

Evidence for Viscosity Effects on Disproportionation–Combination Ratios of *tert*-Butyl Radicals in Solution[1]

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Received December 20, 1982

Photolysis of di-*tert*-butyl ketone (2,2,4,4-tetramethyl-3-pentanone) in solution ultimately gives solvent-separated *tert*-butyl radicals (Scheme I).[2] In the absence of a scavenger these radicals form encounter pairs that quantitatively collapse to the disproportionation products 2-methylpropane (R(+H)) and 2-methylpropene (R(–H)), or the combination product 2,2,3,3-tetramethylbutane (R–R; Scheme I).[2,3] It has been shown that even in media of high viscosity, the *tert*-butyl radicals can be fully scavenged, indicating that loss of CO from the first-formed $Me_3CC(O)\cdot$ radical does not occur in the initial cage.[4] Cage disproportionation (k'_{-1}) yielding Me_3CCHO does compete with separative diffusion (k_D), but it is not a major process even at high viscosity.[2a]

Schuh and Fischer showed in *n*-alkane solvents that the encounter of two *tert*-butyl radicals (k_t) is governed by translational diffusion and that every such encounter leads to termination either by disproportionation (k_d) or combination (k_c).[3] Additionally, they documented both a temperature and solvent dependence for the k_d/k_c ratio.[2,3] They concluded that these dependences most likely were related to viscosity variation; however, they were unable to eliminate solvent internal pressure as the important variable.[2a,5]

For example, they varied solvent over a homologous series of *n*-alkanes from C_8 to C_{16} and found an increase in the k_d/k_c ratio. The same ratio decreased with increasing temperature. While this suggests that k_d/k_c depends directly on viscosity because η increases from C_8 to C_{16} and decreases with increasing temperature, internal pressure (P_i) also varies in the same way with solvent and temperature.[5]

We now report the effects of externally applied pressure on the k_d/k_c ratio. These data both support the proposed dependence on viscosity and provide evidence against an internal pressure dependence.

Results and Discussion

Degassed samples of 0.17 M di-*tert*-butyl ketone in *n*-octane were photolyzed at various pressures with use of a specially designed optical cell. The time of the photolyses were adjusted to provide less than 5% conversion of the ketone. The reaction products 2-methylpropane, 2-methylpropene, and 2,2,3,3-tetramethylbutane were immediately analyzed by GLC. The resulting concentrations are reported in Table I.

(1) High Pressures Studies. 27. Part 26: Neuman, R. C., Jr.; Sylwester, A. P. *J. Org. Chem.*, in press.
(2) (a) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463. (b) Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1976**, *8*, 341.
(3) Schuh, H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.
(4) Tanner, D. D.; Rahimi, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 225.
(5) See Neuman, R. C., Jr. *J. Org. Chem.* **1972**, *37*, 495.

0022-3263/83/1948-2430$01.50/0