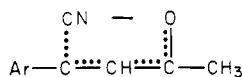


The plots of $\log k_{ap}$ are linear over a wide range of σ values¹³ (Figure 2).

The observed reaction constant is

$$\rho = +1.26 \pm 0.05 \quad (r^2 = 0.994)$$

Owing to the fact that the negative charge is delocalized over five atoms in the transition state (see I) and that the



enolate moiety is not directly located on the aromatic ring, the relatively high value of ρ implies a sizable charge redistribution. This result does not disagree with the hypothesis of a productlike transition state, which was put forward^{2,4} on the basis of the Hammond postulate, in connection with stereochemical problems.

This reaction constant agrees well with the mean ρ value (1.35 ± 0.23 , $r^2 = 0.86$) found by Currie et al.¹⁴ in a very intricate system in which hydrocyanation on benzalmonitriles occurred together with concomitant hydrolysis of the substrates.

In spite of the low degree of accuracy¹⁵ expected for comparison of ρ values between different reactions, it is worth comparing the present value (1.26) for conjugate hydrocyanation with that reported¹⁶ for the cyanohydrin formation from substituted benzaldehydes in 60% acetonitrile: 1.66. In the latter reaction, the negative charge in the transition state is less delocalized and much nearer to the aromatic ring. Also in that case, a late transition state appears from the Hammett correlation and the kinetic isotope effect.

Conclusion

The present study confirms the expected bimolecular nature of the conjugate hydrocyanation reaction, while explaining the unexpected pseudo-first-order rate law, and demonstrates clearly that a late and highly ordered transition state is involved.

Experimental Section

Materials. Dimethylformamide was purified by standard methods.¹⁷ 1-Cholesten-3-one was prepared by following a published procedure.¹⁸ The substituted 4-phenyl-3-buten-2-ones were obtained according to the classical Claisen-Schmidt reaction¹⁹ from commercially available benzaldehydes and acetone. These enones were purified by running them several times through column chromatography on silica gel in order to obtain both the highest melting point and the highest UV extinction coefficient.

The UV kinetic measurements were performed at the following wavelengths (substituent, λ_{max} in nm, ϵ): H, 286, 22610; *p*-MeO, 318, 25950; *p*-Me₂N, 375, 30150; *m*-MeO, 287, 18842; *p*-Cl, 295, 23166; *p*-*i*-Pr, 300, 24844; *p*-CN, 286, 29945; 1-cholesten-3-one, 237, 10634. Each ϵ value is the average of five measures; the error

on ϵ is about 1%. The spectra were obtained in 95% ethanol.

General Procedure for the Preparation of the Cyano Ketones. The enone (1 mmol) was dissolved in DMF-Water (9:1 v/v) (40 mL) containing KCN (130 mg) and NH₄Cl (80 mg); the solution was heated at 100 °C for 4 h. A standard workup (extraction by ether) gave a crude product which was purified by column chromatography (SiO₂; pentane-ether). Pure products were obtained in about 90% yields.

These reference cyano ketones exhibited no absorption at the UV wavelength used for the titration. The β -cyano derivatives of the substituted butenones showed the following ¹H NMR data (CDCl₃ solution, JEOL C 60 HL spectrometer) for the chemical shifts (δ) for COCH₃ (s), CH(CN) (t, $J = 7$ Hz), CH₂ (dd, $J = 7$, and 16 Hz): H (mp 45 °C) 2.17, 4.35, 2.98, 3.22; *p*-MeO (mp 40 °C) 2.13, 4.25, 2.83, 3.20; *p*-Me₂N (mp 82 °C) 2.13, 4.23, 2.93, 3.10; *m*-MeO (liquid) 2.17, 4.28, 2.92, 3.16; *p*-Cl (mp 92 °C) 2.17, 4.30, 2.94, 3.18; *p*-*i*-Pr (mp 77 °C) 2.15, 4.28, 2.90, 3.16; *p*-CN (mp 102 °C) 2.20, 4.43, 2.95, 3.21.

Elemental analysis of the aforementioned cyano ketones were performed by the Analysis Department of the P. and M. Curie University, and their results were within the accepted limits ($\pm 0.4\%$).

Kinetic Measurements. Kinetics were studied by following our original procedure⁴ with a Beckmann DK 2A spectrometer. The data were analysed by a linear least-squares treatment: (a) the correlation coefficients r^2 for the rate constants measurements were always higher than 0.990; (b) the precision on the activation parameters was obtained by calculation of the standard deviation. The rate constants were not corrected for solvent expansion.

The rate data on which Figure 2 is based are the following: (10^{-4} s⁻¹) 1-, 0.32; 2, 1.86; 3, 3.09; 4, 4.30; 5, 4.46; 6, 8.58; 7, 25.0.

Registry No. 4-[*p*-(Dimethylamino)phenyl]-3-buten-2-one, 5432-53-1; 4-(*p*-methoxyphenyl)-3-buten-2-one, 943-88-4; 4-(*p*-isopropylphenyl)-3-buten-2-one, 74389-78-9; 4-phenyl-3-buten-2-one, 122-57-6; 4-(*m*-methoxyphenyl)-3-buten-2-one, 20766-31-8; 4-(*p*-chlorophenyl)-3-buten-2-one, 3160-40-5; 4-(*p*-cyanophenyl)-3-buten-2-one, 51220-06-5; 1-cholesten-3-one, 50557-39-6; potassium cyanide, 151-50-8; ammonium chloride, 12125-02-9; α -phenyl-4-oxopentanitrile, 82323-82-8; α -(4-methoxyphenyl)-4-oxopentanitrile, 82323-83-9; α -[4-(dimethylamino)phenyl]-4-oxopentanitrile, 82323-84-0; α -(3-methoxyphenyl)-4-oxopentanitrile, 82323-85-1; α -(4-chlorophenyl)-4-oxopentanitrile, 82323-86-2; α -(4-isopropylphenyl)-4-oxopentanitrile, 82323-87-3; α -(4-cyanophenyl)-4-oxopentanitrile, 82323-88-4.

Preparation of "Tied-Back" Functionalizable Derivatives of Tetra-*tert*-butylethylene¹

E. R. Cullen,^{2a} F. S. Guziec, Jr.,^{*2b} and C. J. Murphy^{2a}

Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003, and Department of Chemistry, Tufts University, Medford, Massachusetts 02155

Received December 8, 1981

Investigations into the chemistry of strained organic molecules continue to generate new ideas on the nature of chemical bonding and reactivity.³ Recent research has led to the preparation of a variety of molecular structures which cannot fail to astonish chemists familiar with the "normal" constraints of molecular geometries. Among these structures are very sterically crowded olefins containing torsionally distorted bonds. The ultimate synthetic

(13) The σ values were taken from the following: Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; p 66.

(14) Pritchard, R. B.; Lough, C. E.; Reesor, J. B.; Holmes, H. L.; Currie, D. J. *Can. J. Chem.* 1967, 45, 775.

(15) McLennan, D. J. *Tetrahedron* 1978, 34, 2331.

(16) Young, P. R.; McMahon, P. E. *J. Am. Chem. Soc.* 1979, 101, 4678. See also: Ching, W. M.; Kallen, R. G. *Ibid.* 1978, 100, 6119.

(17) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 432.

(18) Johnson, H. E.; Crosby, D. J. *J. Org. Chem.* 1962, 27, 2205.

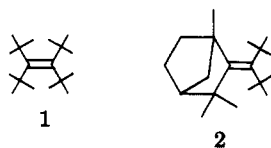
(19) Johnston, R. L.; Jones, L. A. *J. Chem. Eng. Data* 1971, 16, 112.

(1) Presented in part at the 2nd Chemical Conference of the North American Continent, Las Vegas, NV, Aug 1980.

(2) (a) Visiting Graduate Students, New Mexico State University, 1981-1982. (b) Present address: New Mexico State University.

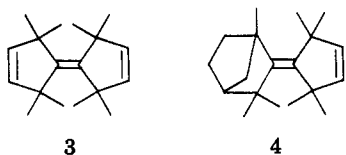
(3) For recent reviews, see: (a) Leibman, J. F.; Greenberg, A. *Chem. Rev.* 1976, 76, 311. (b) Greenberg, A.; Leibman, J. F.; "Strained Organic Molecules"; Academic Press: New York, 1978. (c) Tidwell, T. T. *Tetrahedron* 1978, 1855. (d) Martin, S. F. *Ibid.* 1980, 419.

goal in this area is the extremely hindered tetra-*tert*-butylethylene (1).⁴⁻¹⁰ Another important synthetic target is the less strained 2-(di-*tert*-butylmethylene)fenchane (2).

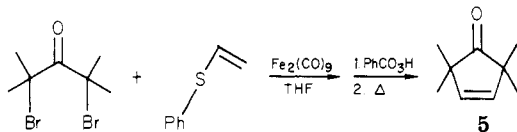


While these molecules remain elusive, a number of approaches to derivatives of 1 have been reported, using twofold extrusion reactions.⁹⁻¹¹ Recent work of Krebs and co-workers prompts us to report our research in this area.¹²

Two "tied-back" derivatives of 1 appeared to be useful starting points for the preparation of 1 and 2—bi-3,3,5,5-tetramethylcyclopenten-4-ylidene (3) and 2-(3,3,5,5-tetramethylcyclopenten-4-ylidene)fenchane (4). Oxidative cleavage of the much less hindered cyclopentene double bond in these compounds followed by reduction to the hydrocarbon would provide a route to the parent alkenes.

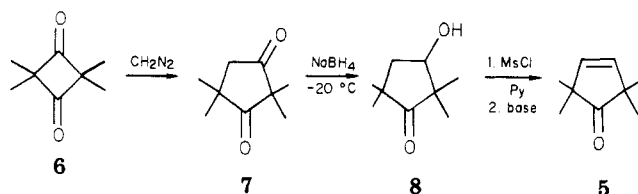


The apparently simple starting material for these preparations, 2,2,5,5-tetramethylcyclopentenone (5), had not been previously reported in the literature and could not be directly obtained by alkylation reactions. Initially 5 was prepared in 15% yield by the nonacarbonyldiiron-catalyzed reaction of 2,4-dibromo-2,4-dimethylpentanone and phenyl vinyl sulfide, followed by oxidation and pyrolysis of the intermediate substituted cyclopentanone.



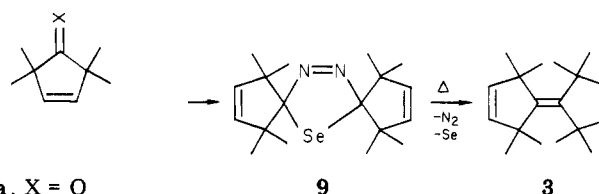
A much more useful preparation of 5 relies on the diazomethane ring expansion of the readily available 2,2,4,4-tetramethylcyclobutanedione (6).^{13,14} Regioselective reduction of the less hindered carbonyl of the resulting 2,2,5,5-tetramethyl-1,3-cyclopentanedione (7) using sodium borohydride at -20 °C afforded crystalline hydroxy ketone 8 in 85% isolated yield. Mesylation and elimination using the sodium salt of diethylene glycol afforded the extremely volatile 2,2,5,5-tetramethylcyclopentenone (5a) in 74% yield. All attempts to carry out the elimination using other

bases in the usual solvents for such a reaction were hampered by the difficulty of removing these solvents in workup without significant losses of 5.



Ketone 5a could be converted into the hydrazone 5b (75% yield) and phosphoranylidenehydrazone 5c (80% yield) by using standard procedures.¹⁰ Pyrolysis of 5c at 185 °C afforded the very volatile orange diazo compound 5d in 65% yield. Pyrolysis of 5c at 185 °C in the presence of selenium powder afforded the deep-blue crystalline selone 5e in 66% yield.

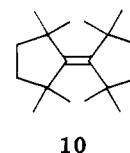
Treatment of diazo compound 5d with selone 5e in dry tetrahydrofuran at room temperature and removal of solvent under reduced pressure afforded crude crystalline selenadiazoline 9, which upon pyrolysis at 185 °C followed



- 5a, X = O
 b, X = NNH₂
 c, X = NN=PPh₃
 d, X = N₂
 e, X = Se

by flash chromatography¹⁵ and sublimation afforded pure bi-3,3,5,5-tetramethylcyclopenten-4-ylidene (3) in 40% yield. Olefin 3 could be more easily prepared by heating phosphoranylidenehydrazone 5c with selone 5e at 185 °C. Flash chromatography and sublimation afforded the pure crystalline olefin 3 in 65% yield. Alternatively, pyrolysis of 5c with excess selenium powder at 185 °C and similar workup also afforded 3, again in 65% yield.

The less hindered double bonds of olefin 3 could be selectively reduced by hydrogen over platinum rapidly at room temperature, affording the known bi-2,2,5,5-tetramethylcyclopentylidene (10)⁹ in 88% yield. Olefin 3 rapidly decolorizes bromine with evolution of hydrogen bromide but is inert to alkaline permanganate even at elevated temperatures.

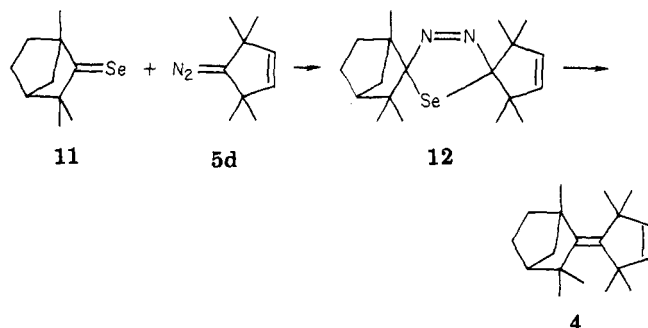


The unsymmetrical olefin 4 could be prepared in a similar manner. Treatment of diazo compound 5d in carbon tetrachloride with an equivalent of selenofenchone (11) afforded crystalline selenadiazoline 12 in excellent yield. Pyrolysis of 12 at 130 °C afforded a mixture containing 3, 4, and bifenchylidene⁷ in a ratio of 1:2:1. Careful flash chromatography¹⁵ and Kugelrohr distillation afforded pure crystalline 2-(3,3,5,5-tetramethylcyclopenten-4-ylidene)fenchane (4) in 42% yield.

Detailed investigations into the chemistry of olefins 3 and 4 and attempts at converting these compounds into

- (4) Abruscato, G. J.; Tidwell, T. T. *J. Org. Chem.* 1972, 37, 4151.
 (5) Boerma, J. A., Thesis, University of Groningen, 1972.
 (6) Barton, D. H. R.; Guziec, F. S., Jr.; Shahak, I. *J. Chem. Soc., Perkin Trans. 1* 1974, 1794.
 (7) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* 1976, 2079.
 (8) Olah, G. A.; Surya Prakash, G. K. *J. Org. Chem.* 1977, 42, 580.
 (9) Krebs, A.; Ruger, W. *Tetrahedron Lett.* 1979, 1305.
 (10) (a) Guziec, F. S., Jr.; Murphy, C. J. *J. Org. Chem.* 1980, 45, 2890.
 (b) Cullen, E. R.; Guziec, F. S., Jr.; Hollander, M. I.; Murphy, C. J. *Tetrahedron Lett.* 1981, 4563.
 (11) (a) Bushby, R. J.; Pollard, M. D.; McDonald, W. S. *Tetrahedron Lett.* 1978, 3851. (b) Bushby, R. J.; Pollard, M. D. *J. Chem. Soc., Perkin Trans. 1* 1979, 2401.
 (12) Krebs, A.; Ruger, W.; Nickel, W. U. *Tetrahedron Lett.* 1981, 4937.
 (13) Hanford, W. E.; Sauer, J. C. *Org. React.* 1946, 3, 108.
 (14) Krapcho, A. P.; Rao, D. R.; Silvon, M. P.; Abegaz, B. *J. Org. Chem.* 1971, 36, 3885.

- (15) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* 1978, 43, 2923.



1 and 2 are currently in progress.

Experimental Section

General Methods. GLC analyses were performed with a Varian Aerograph A90-P3 gas chromatograph with a stainless-steel column filled with 5% SE-30 on Chromosorb W-HP. ^1H NMR spectra were recorded with a JEOLCO PS 100 spectrometer; ^{13}C NMR spectra were recorded with a Varian XL 200 spectrometer. In both cases tetramethylsilane was used as an internal standard. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU-GL. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Baron Analytical, Orange, CN. Tetrahydrofuran was dried by distillation from benzophenone-sodium. Diethylene glycol and hydrocarbon solvents were distilled from calcium hydride. Benzene was dried over sodium wire. Triethylamine was distilled from barium oxide. Solvents were removed by using a rotary evaporator under reduced pressure. Extracts were dried by washing first with saturated brine, and the organic phase was treated with anhydrous sodium sulfate.

2,2,5,5-Tetramethyl-1,3-cyclopentanedione (7). Dione 7 was prepared by a modification of the literature procedure.¹⁴ 2,2,4,4-Tetramethylcyclobutanedione (6; 5.6 g, 40 mmol) in ether (20 mL) was treated with excess diazomethane (~3.0 g) prepared from Diazald in ethanolic ether (~250 mL). The mixture was connected to a bubbler containing ethanolic oxalic acid. After 4 days at room temperature excess diazomethane was destroyed by addition of small quantities of oxalic acid until gas evolution ceased. The solution was washed consecutively with dilute HCl, saturated NaHCO_3 , and water and dried. Concentration and recrystallization from pentane afforded dione 7: 5.2 g, 85% yield; mp 22–23 °C (lit.¹⁴ mp 22–23 °C).

3-Hydroxy-2,2,5,5-tetramethylcyclopentanone (8). To 2,2,5,5-tetramethyl-1,3-cyclopentanedione (7; 14.6 g, 95 mmol) in ethanol (200 mL) was added sodium borohydride (1.0 g) in small portions at –20 °C. The mixture was stirred at –20 °C for 3 h, allowed to come to room temperature, and treated with excess dilute HCl. After concentration to about 25% volume, the mixture was extracted with ethyl acetate (3 × 25 mL), and the combined organic extracts were washed with dilute HCl and saturated NaHCO_3 and dried. Concentration and crystallization from chloroform-hexanes, followed by recrystallization from ethyl acetate-hexanes, afforded the hydroxy ketone 8 as colorless crystals: 12.5 g, 85% yield; mp 74.5–76 °C; IR (KBr) 3495, 1733 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.10 (1 H, m), 2.82 (1 H, br), 2.24–1.72 (2 H, m), 1.17 (3 H, s), 1.08 (3 H, s), 1.03 (3 H, s), 1.01 (3 H, s); MS, m/e 156 (M^+). Anal. Calcd for $\text{C}_9\text{H}_{18}\text{O}_2$: C, 69.23; H, 10.35. Found: C, 69.19; H, 10.32.

2,2,5,5-Tetramethylcyclopentenone (5a). (a) Methanesulfonyl chloride (15 mL) was added dropwise over 15 min to a stirred, cooled (0 °C) solution of hydroxy ketone 8 (13.4 g, 86 mmol) in dry pyridine (100 mL), protected by a drying tube. After 2.5 h at 0 °C, the mixture was filtered through a plug of glass wool and added to ice-water (~20 mL) and extracted with ether (3 × 20 mL). The combined organic phases were washed consecutively with dilute HCl, saturated NaHCO_3 , and water and then dried. Concentration afforded 18.5 g of the crude mesylate as a pale-yellow oil in 92% yield.

Sodium metal (7.0 g) was added to dry diethylene glycol (250 mL) in small portions and the mixture heated to reflux overnight, protected from moisture. After cooling, the crude mesylate (37.0

g) was added in one portion and the mixture heated to 130–160 °C under reduced pressure (20 torr), collecting volatiles in a dry ice-acetone cooled trap. This crude product was taken up in ether, washed with water, and dried. Removal of solvent at 0 °C under reduced pressure afforded 17.5 g of ketone 5a: 80% yield; mp 44 °C subl; IR (CHCl_3) 1753, 1733 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.90 (2 H, s), 1.10 (12 H, s); MS, m/e 138 (M^+), 123 ($\text{M}^+ - \text{CH}_3$), 110 ($\text{M}^+ - \text{CO}$). Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}$: C, 78.2; H, 10.2. Found: C, 78.3; H, 10.2.

(b) Under argon, phenyl vinyl sulfide¹⁶ (2.00 g, 15 mmol) and 2,4-dibromo-2,4-dimethylpentanone (1.38 g, 5 mmol) in benzene (5 mL) were added over 10 min with stirring to a warm solution (45 °C) of $\text{Fe}_2(\text{CO})_9$ (2.0 g, 55 mmol) in benzene (15 mL). The mixture was stirred for 1 h at 45 °C and allowed to cool to room temperature overnight. Ethyl acetate (10 mL) was added and the solution washed with 1 M NaHCO_3 (2 × 25 mL) and then dried in the usual way. Removal of solvent under reduced pressure afforded the crude sulfide as a yellow oil. The oil was dissolved in CH_2Cl_2 (5 mL) and added to a solution of NaIO_4 (3.0 g) in methanol (80 mL), and the mixture was stirred for 36 h. The mixture was filtered by suction and the resulting cake washed with CH_2Cl_2 (50 mL). The organic phase was washed with water and dried. Concentration afforded the crude sulfoxide as a brownish oil.

Solvent removal and pyrolysis at 170 °C (10 mmHg) with collection in a dry ice-acetone trap afforded crude ketone. Extraction, concentration, and sublimation (as in part a) afforded pure 5a: 100 mg, 15% yield.

2,2,5,5-Tetramethylcyclopentenone Hydrazone (5b). Ketone 5a (8.7 g, 63 mmol), hydrazine hydrate (10 g, 300 mmol), and ethanol (1 mL) in diethylene glycol (15 mL) were heated to reflux with stirring for 5 days. The cooled solution was poured into water (80 mL) and extracted with ether (3 × 25 mL). The organic phase was washed with water (2 × 10 mL) and dried. Removal of solvent under reduced pressure at 10 °C and crystallization from hexanes yielded the hydrazone: 7.2 g, 75% yield; mp 76–78 °C; IR (CCl_4) 3400, 3300, 1660 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.54 (1 H, d), 5.33 (1 H, d), 4.60 (2 H, s), 1.38 (6 H, s), 1.16 (6 H, s); MS, m/e 152 (M^+), 137 ($\text{M}^+ - \text{CH}_3$). Anal. Calcd for $\text{C}_9\text{H}_{18}\text{N}_2$: C, 71.0; H, 10.6; N, 18.4. Found: C, 71.0; H, 10.6; N, 18.5.

2,2,4,4-Tetramethylcyclopentenone (Triphenylphosphoranylidene)hydrazone (5c). Bromine (0.80 g, 5 mmol) in dry benzene (5 mL) was added over 30 min to a stirred, cooled solution of triphenylphosphine (13.0 g, 5 mmol) in dry benzene (12 mL). After the mixture was stirred for 30 min, hydrazone 5b (0.77 g, 5 mmol) and triethylamine (1.30 g, 13 mmol) in dry benzene (1.5 mL) were added over 30 min. After 8 h at room temperature, the mixture was filtered and evaporated at reduced pressure and the resulting yellow solid was crystallized from chloroform-hexanes to yield 5c: 1.68 g, 80% yield; mp 113.5–114.5 °C; IR (KBr) 1482, 1437, 1345 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.9–7.3 (15 H, complex), 5.51 (1 H, s), 5.49 (1 H, s), 1.58 (6 H, s), 1.07 (6 H, s). Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{P}$: C, 78.8; H, 7.1; N, 6.7. Found: C, 78.6; H, 7.1; N, 6.8.

4-Diazo-3,3,5,5-tetramethylcyclopentene (5d). The phosphoranylidenehydrazone 5c (2.58 g, 6.3 mmol) was heated for 2 h at 185 °C under reduced pressure (0.5 torr) with volatile material being collected into a dry ice-acetone trap. The volatile red-orange liquid was redistilled at 30 °C (20 torr) to provide essentially pure diazo compound (0.59 g, 65% yield): IR (CCl_4) 2040, 1640 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.33 (2 H, s), 1.24 (12 H, s).

2,2,5,5-Tetramethylcyclopenteneselone (5e). The phosphoranylidenehydrazone 5c (8.24 g, 20 mmol) and selenium powder (4.50 g, 56 mmol) were heated at 185 °C under reduced pressure (1 torr), with stirring, and volatile material was collected in a dry ice-acetone trap. Sublimation (40 °C, 20 torr) afforded the blue selone 5e: 2.64 g, 66% yield; mp 84–86 °C; IR (CCl_4) 1470, 1460 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.07 (2 H, s), 1.28 (12 H, s); MS, m/e 122 ($\text{M}^+ - \text{Se}$); UV-vis (cyclohexane) λ_{max} 656 nm (ϵ 31), 626 (ϵ 26). Anal. Calcd for $\text{C}_9\text{H}_{14}\text{Se}$: C, 53.76; H, 6.96; Se, 39.27. Found: C, 54.01; H, 6.92; Se, 39.38.

(16) Cooke, F.; Moerck, R.; Schwindeman, J.; Magnus, P. *J. Org. Chem.* 1980, 45, 1046.

Bi-3,3,5,5-tetramethylcyclopenten-4-ylidene (3). (a) To a solution of the diazo compound **5d** (0.60 g, 4 mmol) in dry tetrahydrofuran at room temperature was added dropwise with stirring under argon a solution of selone **5e** (~4 mmol) in dry tetrahydrofuran (5 mL) until the red color disappeared and a pale-green color persisted. Removal of solvent under reduced pressure and recrystallization from ether (-20 °C) yielded the light-sensitive selenadiazoline **9**: 1.1 g, 77% yield; mp 115–120 °C dec; IR (CCl₄) 1585, 1580 cm⁻¹; UV (cyclohexane) λ_{max} 301 nm (ε 2000); ¹H NMR (CDCl₃) δ 5.70 (4 H, s), 1.26 (12 H, s), 0.90 (12 H, s).

The crude selenadiazoline **9** (1.0 g, 3 mmol) was pyrolyzed at 185 °C for 8 h. Flash chromatography¹⁵ (hexanes) followed by solvent removal and sublimation yielded the olefin **3**: 0.30 g, 40% yield; mp 108–109 °C; IR (KBr) 3058, 1475, 1360 cm⁻¹; ¹H NMR (CDCl₃) δ 5.13 (4 H, s), 1.42 (12 H, s); ¹³C NMR (CDCl₃) δ 151.2, 138.1, 52.0, 31.0; MS, *m/e* 244 (M⁺), 229 (M⁺ - CH₃). Anal. Calcd for C₁₈H₂₆: C, 88.3; H, 11.6. Found: C, 88.4; H, 11.5.

(b) The phosphoranylidenehydrazone **5c** (3.64 g, 8.8 mmol) and selone (**2.0 g**, 25 mmol) were heated at 185 °C with stirring under argon for 24 h. The cooled mixture was extracted with ether (2 × 20 mL) and filtered through Celite. Concentration, followed by flash chromatography (hexanes), yielded olefin **3** (1.41 g, 65%), identical with that described in part a.

(c) The selone **5e** (1.40 g, 7.0 mmol) and the phosphoranylidenehydrazone **5c** (2.20 g, 55 mmol) were heated to 200 °C under nitrogen overnight. Removal of volatiles, followed by flash chromatography and recrystallization from ethanol, afforded the olefin **3** (0.87 g, 65% yield), identical with that described in part a.

Reactions of 3. (a) Bromine (40 mg, 0.25 mmol) in CDCl₃ (0.5 mL) was added dropwise at room temperature to a solution of olefin **3** (30 mg, 0.13 mmol) in CDCl₃. An exothermic reaction immediately occurred with liberation of an acidic gas. ¹H NMR showed a complex spectrum and TLC (silica gel, hexanes) showed a minimum of four components in the mixture.

(b) A solution of potassium permanganate (153 mg, 1 mmol) and sodium hydroxide (200 mg, 10 mmol) in 40% aqueous *tert*-butyl alcohol (15 mL) was added to a solution of olefin **3** (367 mg, 1.5 mmol) in *tert*-butyl alcohol (10 mL). The mixture was heated, with stirring, to 75 °C for 2 days. Filtration through Celite and extraction with ether yielded starting olefin **3** (327 mg, 89% recovery). Similar results were obtained with methylcyclohexane as solvent.

(c) A solution of potassium permanganate (10 mg), potassium periodate (460 mg, 2 mmol), anhydrous magnesium sulfate (120 mg, 2 mmol), and olefin **3** (240 mg, 1 mmol) in 40% aqueous *tert*-butyl alcohol (10 mL) was stirred at room temperature for 3 days. Filtration through Celite, followed by extraction with ether, afforded unreacted olefin **3** (180 mg, 70% recovery) as well as 50 mg of a mixture of more polar compounds.

(d) A solution of olefin **3** (198 mg, 0.8 mmol), potassium permanganate (830 mg, 5.3 mmol), and dicyclohexyl-18-crown-6 (5 mg) in benzene¹⁷ (10 mL) was stirred at room temperature for 2 weeks. Filtration through Celite followed by extraction with ether afforded the unreacted olefin **3** (174 mg, 88% recovery). Similar negative results were obtained with benzyltriethylammonium chloride in benzene with aqueous alkaline permanganate¹⁸ and also with benzyltriethylammonium permanganate¹⁹ in benzene.

Bi-2,2,5,5-tetramethylcyclopentylidene (10). Bi-3,3,5,5-tetramethylcyclopenten-4-ylidene (**3**; 35.7 mg) in ethanol (2 mL) was hydrogenated over platinum black (5 mg) until no further hydrogen was taken up (6.73 mL, ~1.5 h). The mixture was filtered through Celite and concentrated. Chromatography on silica gel (1 g; pentane) and recrystallization from ethanol afforded 31.3 mg of **10**: 88% yield; mp 103–104 °C (lit.⁹ mp 104–105 °C); ¹H NMR (CDCl₃) δ 1.51 (8 H, s), 1.34 (24 H, s); and other spectra identical with those reported for **10**.

2-(3,3,5,5-Tetramethylcyclopenten-4-ylidene)fenchane (4). (-)-Selenofenchone (0.97 g, 4.51 mmol) was slowly added at room temperature to a stirred solution of crude diazo compound **5d** (0.68

g, 4.51 mmol). The progress of the reaction can be monitored by the disappearance of the orange color of **5d**, the solution becoming lemon yellow with light-yellow crystals precipitating. The mixture was concentrated with a stream of nitrogen and the crude selenadiazoline dried at room temperature under vacuum (1 torr) affording lemon-yellow crystals: 1.64 g, 99% yield. Recrystallization from ether at -20 °C afforded the crystalline light-sensitive selenadiazoline **12**: mp 131–132 °C; IR (CCl₄) 1630, 1595, 1470, 1455, 900 cm⁻¹; NMR (CCl₄) δ 5.63 (2 H, s), 2.76 (1 H, brd), 2.00–0.54 (27 H, complex).

Crude selenadiazoline **12** (1.40 g, 3.84 mmol) was heated at 135 °C under positive nitrogen pressure for 2 days, and the temperature then was raised to 170 °C for 4 h. After being cooled, the reaction mixture was dissolved in dichloromethane, filtered, and concentrated. Flash chromatography,¹⁵ followed by Kugelrohr distillation [65 °C (0.1 torr)], afforded olefin **4** as colorless crystals: 417 mg, 42% yield; mp 70–73 °C; IR (CHCl₃) 3040, 3015, 1390, 1365 cm⁻¹; NMR (CDCl₃) δ 5.15 (2 H, AB q), 2.05–0.9 (28 H, complex); MS, *m/e* 258 (M⁺), 243 (M⁺ - CH₃). Anal. Calcd for C₁₉H₃₀: C, 88.30; H, 11.70. Found: C, 88.17; H, 11.61.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Chemistry Department of New Mexico State University for partial support of this research. We thank Professor Adolf Krebs for providing a preprint of closely related work and Professor Paul Vouros for providing low-resolution mass spectra.

Registry No. **3**, 78305-12-1; **4**, 82338-35-0; **5a**, 81396-36-3; **5b**, 81396-37-4; **5c**, 82338-36-1; **5d**, 81396-38-5; **5e**, 79958-61-5; **6**, 933-52-8; **7**, 31934-42-6; **8**, 81396-35-2; **8 mesylate**, 82338-37-2; **9**, 82338-38-3; **10**, 71691-01-5; **11**, 61849-83-0; **12**, 82338-39-4; diazomethane, 334-88-3; phenylvinyl sulfide, 1822-73-7; 2,4-dibromo-2,4-dimethylpentanone, 17346-16-6.

Synthesis of 6-Thiaellipticine and Related Compounds via Heterocyclic *o*-Quinodimethane Intermediates

Shinzo Kano, Naoki Mochizuki, Satoshi Hibino, and Shiroshi Shibuya*

Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

Received March 2, 1982

Indole-2,3-quinodimethane intermediates derived from 2-ethyl-3-[α-(3-pyridyl)vinyl]indole (**1**)¹ and 3-ethyl-2-[α-(4-pyridyl)vinyl]indole (**2**)² by way of thermal suprafacial [1,5] sigmatropic hydrogen shift have been applied to the synthesis of the antitumor carbazole alkaloid ellipticine (**3**)^{1,2} (Scheme I). We have now used this approach for the synthesis of 6-thiaellipticine^{3,4} and congeners. It is known that olefins are provided on pyrolysis of tertiary alcohols by direct elimination of water.⁵ In conjunction with a synthesis of 6-thiaellipticine and related compounds, we examined the thermal decomposition of a series of alcohols in the expectation that dehydration followed by

(1) Bergman, J.; Carlsson, R. *Tetrahedron Lett.* 1977, 4663.

(2) Kano, S.; Sugino, E.; Shibuya, S.; Hibino, S. *J. Org. Chem.* 1981, 46, 2979.

(3) Fujiwara, A. N.; Acton, E. M.; Goodman, L. *J. Heterocyclic Chem.* 1968, 5, 853.

(4) Elmes, B. C.; Swan, J. M. *Aust. J. Chem.* 1969, 22, 1963.

(5) (a) Maccoll, A. In "The Chemistry of Alkenes"; Patai, S., Ed.; Wiley: New York, 1964; p 222. (b) Knozinger, H. In "The Chemistry of the Hydroxyl Group"; Patai, S., Ed.; Wiley: New York, 1971; Part 2, p 662.

(17) Sam, D. J.; Simmons, H. E. *J. Am. Chem. Soc.* 1972, 94, 4024.

(18) Weber, W. P.; Shepard, J. P. *Tetrahedron Lett.* 1972, 4907.

(19) Sala, T.; Sargent, M. V. *J. Chem. Soc., Chem. Commun.* 1978, 253.