(w), 549 (m). The mass spectrum matched that reported by Beringer et al.[1]

Anal. Calcd for $C_{28}H_{20}I_2{\cdot}H_2O$: C, 53.53; H, 3.53; total I, 40.40, ionizable I, 20.20. Found: C, 53.51; H, 3.47; total I, 40.44, ionizable I, 20.10.

In one reaction in which rigorously dried acetone solvent was used and the NaI was dried before use, a material melting at 139 °C was obtained. The infrared spectrum of this compound (**1b**) was essentially identical with that of **1c** except the hydroxyl band at 3460 cm^{-1} was absent. After storage for 7 months in a screw-topped vial, the elemental analysis, melting behavior, and the infrared spectrum became identical with those of **1c**.

Preparation of 1c from 1a. **1a** was dissolved at room temperature in a minimum amount of methanol, and 1.0 molar NaI in methanol was added to precipitate **1c** as a monohydrate. The amber colored filtrate was bleached upon adding aqueous $Na_2S_2O_3$, indicating the presence of free iodine.

2,3,4,5-Tetraphenyliodolium Tetraphenylborate (1d). A solution of 0.1 g of **1a** in 1.0 mL of methanol was added to 2 mL of 1.0 M sodium tetraphenylborate in methanol. Yellow crystals of **1d** precipitated over a 1-h period. They were washed first with methanol and then several times with water: mp 125–135 °C dec; IR (KBr) 3055 (m), 3030 (m), 3000 (w), 1592 (w), 1576 (w), 1572 (w), 1477 (m), 1440 (s), 1422 (m), 1260 (w), 1170 (w), 1068 (w), 1025 (m), 996 (w), 913 (w), 840 (w), 782 (m), 750 (m), 728 (s), 695 (s), 610 (w), 602 (w), 548 (w).

Anal. Calcd for $C_{52}H_{40}BI$: C, 77.82; H, 5.02. Found: C, 78.04; H, 5.09.

2,3,4,5-Tetraphenyliodolium Hexachloroantimonate (1e). A solution of 0.20 g (0.40 mmol) of 1,1-dimethyl-2,3,4,5-tetraphenylstannole (**2**) in 3 mL of chloroform was added dropwise to a rapidly stirred solution of 0.09 g (0.40 mmol) of iodine trichloride and 0.12 g (0.40 mmol) of antimony pentachloride dissolved in 3 mL of chloroform at 0 °C under nitrogen. After concentration of the solution under vacuum and cooling in an ice bath, 0.056 g (17%) of an orange solid precipitated. This was recrystallized from a methylene chloride–hexane mixture to give **1e**: mp 121–122 °C dec; IR (KBr) 3050 (w), 1590 (w), 1575 (w), 1485 (m), 1445 (s), 1280 (w), 1220 (w), 1177 (m), 1168 (w), 1080 (w), 1030 (w), 1020 (w), 1005 (w), 955 (w), 926 (w), 878 (w), 790 (s), 765 (s), 740 (s), 710 (s), 697 (s), 680 (m); ^1H NMR (Me_2SO-d_6) δ 7.13 (s, 10 H), 7.44 (s, 10 H).

Anal. Calcd for $C_{28}H_{20}Cl_6ISb$: C, 41.12; H, 2.46; Cl, 26.01; I, 15.52. Found: C, 41.07, H, 2.44; Cl, 26.20; I, 15.57.

1e from 1c. A 0.1-g amount of **1c** was suspended in 2 mL of $CHCl_3$ and an excess of $SbCl_5$ was added, changing the color from yellow to deep red and forming an orange precipitate of **1e**, mp 110–114 °C dec. The IR spectrum was identical with that of **1e** prepared from stannole.

Isomerization of 1c to 1,4-Diiodo-1,2,3,4-tetraphenyl-(*Z*,*Z*)-butadiene (6). (a) Solid state: **1c** was heated in a sealed melting point capillary until the color of the solid changed from orange to light yellow (138–139 °C). A mixed melting point with authentic **6** and a comparison of the IR spectrum identified the product as **6**.

(b) Solution: A slurry of 0.1 g of **1c** in 5 mL of methylene chloride was stirred for several hours. The solid slowly dissolved, and evaporation of the solution under vacuum at room temperature yielded **6**, mp 194–204 °C. The IR spectrum was identical with that of authentic **6**, and a recrystallized sample gave no melting point depression when mixed with **6**: IR (KBr) 3075 (w), 3042 (w), 3020 (w), 1590 (w), 1568 (w), 1487 (m), 1436 (s), 1167 (w), 1150 (w), 1072 (m), 1067 (m), 1024 (m), 930 (m), 912 (w), 907 (w), 792 (m), 783 (m), 760 (s), 728 (s), 690 (s), 607 (m), 560 (m), 543 (m).

Reaction of 1e with Sodium Hydroxide. To a solution of 14.4 mg (0.0176 mmol) of **1e** in 4 mL of acetone was added 5.0 mL of 0.1 N (0.5 mmol) aqueous NaOH. The mixture was heated under reflux for several hours, whereupon 5.5 mg of brown solid separated and was filtered off. It was chromatographed on an EK silica gel thin-layer plate using 66/33 solution of hexane/methylene chloride. Five components were detected in the mixture: R_f values 0.62, 0.50, 0.34, 0.25, and 0.0. A mass spectrum was run on the major component, R_f 0.62, by introducing the impregnated silica gel into the spectrometer using the solids inlet probe; mass spectrum (70 eV), 520 (0.3) and 518 (0.8), $C_{28}H_{20}ICl$; 482 (21), $C_{28}H_{20}I$; 356 (100), $C_{28}H_{20}$; 178 (37), $C_{14}H_{10}$.

Reaction of 1e with Cyanide and Subsequent Hydrolysis. A solution of 20 mg (0.025 mmol) of **1e** and 6.5 mg (0.13 mmol) of sodium cyanide in 2 mL of acetone was heated under reflux for 19 h. Then 2 mL of water and 0.5 mL of 6 N sodium hydroxide were added, and the mixture was heated under reflux for 22 h more. When the mixture cooled, 2 mg of a brown solid precipitated, mp 158–165 °C, which was identified as impure tetraphenylfuran (lit. mp 175 °C) by its infrared and mass spectra. Acidification of the remaining solution produced no precipitate.

Thermal Analysis of 1c. The solid-state enthalpy of rearrangement was determined with a Du Pont 900 differential thermal analyzer using indium metal as a standard and a 5 deg/min heating rate. **1c** showed an irreversible −7.5 kcal/mol (exothermic) transition occurring at 140 °C.

Reaction of 6 with Antimony Pentachloride. Under a dry nitrogen atmosphere a solution of 0.50 g (1.7 mmol) of freshly distilled antimony pentachloride in 10 mL of dry carbon disulfide was added dropwise with stirring to 1.0 g (1.6 mmol) of **6** in 20 mL of dry carbon disulfide. The solution turned black and a brown precipitate formed. After the mixture was stirred for 15 min, the brown solid was filtered off, washed with CS_2, and dried under vacuum. The compound (**5**) decomposed near its melting point, thus resulting in melting point that varied between 100 and 117 °C, depending on the heating rate: IR (KBr) 3070 (w), 1595 (w), 1570 (w), 1482 (m), 1440 (s), 1280 (w), 1258 (w), 1167 (m), 1155 (w), 1090 (w), 1070 (m), 1020 (m), 995 (m), 942 (w), 912 (w), 862 (w), 778 (s, m), 748 (s, m), 722 (s), 690 (s), 680 (s), 548 (s), 540 (s); ^1H NMR (Me_2SO-d_6) same as **1e**.

Anal. Calcd for $C_{28}H_{20}Cl_6ISb$: C, 41.11; H, 2.47. Found: C, 40.94; H, 2.63.

Attempts to recrystallize the product from either chloroform or acetonitrile yielded **1e**.

Reaction of 5 with Cycloheptatriene. With vacuum line techniques, 0.2 mL (1.9 mmol) of cycloheptatriene and 2.0 mL of dry methylene chloride were distilled onto 123 mg (0.254 mmol) of **5** cooled in liquid nitrogen. When the mixture warmed to room temperature a precipitate formed. After the mixture was stirred for 1 h, all volatile material was distilled out at room temperature under high vacuum, and 15 mL of dry acetonitrile was distilled in. The resulting solution was filtered to remove a small amount of black insoluble material, and was concentrated to a volume of 5 mL. Cooling yielded 33 mg of tropylium hexachloroantimonate as yellow-brown needles. Concentration of the solution yielded another 4 mg of the same material, a total yield of 58%. The material turned dark at 191 °C but did not melt up to 350 °C.

Anal. Calcd for $C_7H_7Cl_6Sb$: C, 19.78; H, 1.66. Found: C, 19.97; H, 1.64.

Thin-layer chromatography of the mother liquor showed at least four other products from the reaction. These were not identified.

Registry No. 1a, 78479-56-8; **1c**, 34143-19-6; **1d**, 78479-57-9; **1e**, 78479-58-0; **2**, 20195-60-2; **3**, 29582-42-1; **5**, 78479-60-4; **6**, 78479-61-5; 1-chloro-4-iodo-1,2,3,4-tetraphenylbutadiene, 78479-62-6; cycloheptatriene, 544-25-2; tropylium·$SbCl_6^-$, 26810-97-9.

Reduction of [(Phenylthio)methyl]carbinyl Benzoate Esters to Alkenes with Titanium Metal

Steven C. Welch* and Jiann-Ping Loh

Department of Chemistry, University of Houston, Houston, Texas 77004

Received March 20, 1981

The methylene moiety contained within structures of the type C occurs quite often in terpenoid natural products. One elegant method for constructing this methylene structural unit is by the reductive elimination of the corresponding [(phenylthio)methyl]carbinyl benzoate esters

Scheme I

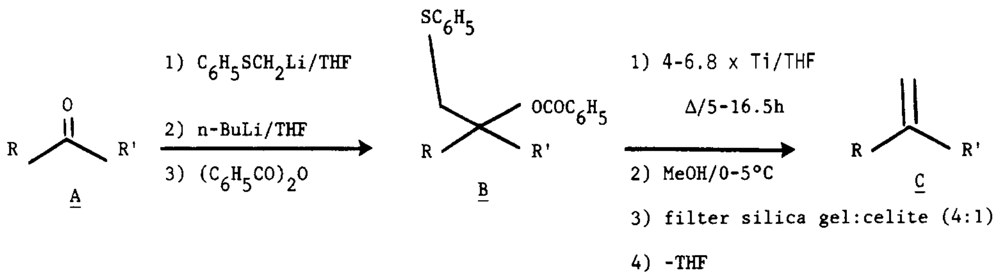
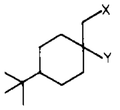
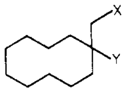
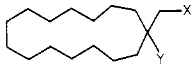
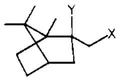
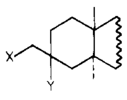
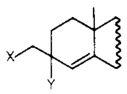
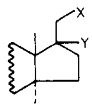


Table I[a,b]

no.	benzoate esters B	amt, mmol	molar ratio of Ti/B (mL of THF)	time of reflux, h	yield of alkenes C, %	ref
1		1.29	4.1 (25)	15	78	6
2		1.50	5.0 (25)	15	69	7
3		0.96	4.4 (25)	16.5	84	8
4		2.02	4.4 (20)	5	67	9
5		0.52	5.0 (12)	5	97	1b, 10
6		0.54	6.8 (14)	11	87	10
7		0.48	5.0 (14)	15	92	11

[a] X = SC_6H_5, Y = $OCOC_6H_5$. [b] All new compounds gave satisfactory elemental analyses.

B[1] which are readily derived from the respective ketones A[2] (Scheme I).

We recently reported that freshly prepared, highly activated titanium metal is a useful reagent for the reduction of substituted phosphate esters to alkenes and arenes in good yields.[3] We now report that titanium metal in refluxing tetrahydrofuran is a convenient alternative reducing agent for the reductive elimination of [(phenylthio)methyl]carbinyl benzoate esters B to alkenes C in high yields under aprotic conditions without any observed overreduction.

Highly activated titanium metal can be prepared from anhydrous titanium(III) chloride by treatment with either magnesium,[4] lithium,[5] or potassium[5] metals in dry tetrahydrofuran or 1,2-dimethoxyethane. The optimum conditions for the reductive elimination of [(phenylthio)methyl]carbinyl benzoate esters B to alkenes C utilizes 4.1–6.8 equiv of titanium metal (prepared by treatment of 4.1–6.8 equiv of titanium(III) chloride with 13.5–22.4 equiv of potassium metal in refluxing tetrahydrofuran under argon for 1 h) in refluxing tetrahydrofuran for 5–16.5 h. After cooling to 0–5 °C, the reaction mixture is quenched with absolute methanol, filtered through a short column of silica gel–Celite (4:1, respectively), concentrated in vacuo, and either distilled or crystallized to afford the respective alkenes C in high yield without the necessity of an aqueous extraction type of workup.

---

(1) (a) Sowerby, R. L.; Coates, R. M. *J. Am. Chem. Soc.*, **1972**, *94*, 4758–4759. (b) Mukaiyama, T.; Watanabe, Y.; Shiono, M. *Chem. Lett.* **1974**, 1523–1524. (c) Watanabe, Y.; Shiono, M.; Mukaiyama, T. *Ibid.* **1975**, 871–872.

(2) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097–4099.

(3) (a) Welch, S. C.; Walters, M. E. *J. Org. Chem.* **1978**, *43*, 4797–4799. (b) *Ibid.* **1978**, *43*, 2715–2717.

(4) (a) Brauer, G. "Handbook of Preparative Inorganic Chemistry", 2nd ed.; Academic Press: New York, 1965. (b) Kroll, W. *J. Less-Common Met.* **1965**, *8*, 361. (c) Kroll, W. *Trans. Electrochem. Soc.* **1940**, 78. (d) Hunter, M. A. *J. Am. Chem. Soc.* **1910**, *32*, 330–336. (e) Tyrlik, S.; Wolochowicz, I. *Bull. Soc. Chim. Fr.* **1973**, 2147–2148. (f) *J. Chem. Soc., Chem. Commun.* **1975**, 781–782. (g) Nelson, T. R.; Tufaniello, J. *J. Org. Chem.* **1975**, *40*, 3159–3160.

(5) (a) McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1976**, *41*, 896–897. (b) McMurry, J. E.; Krepski, L. R. *Ibid.* **1976**, *41*, 3929–3930. (c) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *Ibid.* **1978**, *43*, 3255–3266.

(6) Cross, B.; Whitham, G. H., *J. Chem. Soc.* **1960**, 3892–3895.

(7) Traynham, J. G.; Baird, W. C., Jr. *J. Org. Chem.* **1962**, *27*, 3189–3195.

(8) Ruzicka, L.; Jeger, O. *Chem. Abstr.* **1955**, *49*, 11008*ab*.

(9) (a) Zeiss, H. H.; Zwanzig, F. R. *J. Am. Chem. Soc.* **1957**, *79*, 1733–1738. (b) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128–1129.

(10) Sondheimer, F.; Mechoulan, R. *J. Am. Chem. Soc.* **1957**, *79*, 5029–5033.

(11) Kanojia, R.; Rovinsky, S.; Sheer, I. *Chem. Commun.* **1971**, 1581–1582.

Table I lists the starting [(phenylthio)methyl]carbinyl benzoate esters B, the molar ratio of titanium metal to B in tetrahydrofuran, the times for the reductions (5-16.5 h), and the respective yields of alkenes C (67-97%). The advantages of this new reduction technique are (a) ease of preparation of active titanium metal, (b) aprotic reaction conditions, (c) filtration and concentration type of workup, and (d) no observed overreduction even in the case of diene 6.

Experimental Section

Materials and Techniques. All boiling points were measured external to the bulb-to-bulb distillation pot in an Aldrich Kugelrohr apparatus (catalog No. Z10,046-3) and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 237B spectrometer using 0.10-mm NaCl solution cells or as thin films between NaCl plates. NMR spectra were measured on a Varian Associates Model T-60. Silica gel 60 (F-254, E. Merck No. 5765 and No. 7734, 70-230 mesh) were used for thin-layer and column chromatography and filtration, respectively. All elution solutions were prepared by volume. Ether (Et_2O) and tetrahydrofuran (THF) were purified by fresh distillation of anhydrous commercial solvents from $LiAlH_4$ under N_2 immediately before use in all reactions. Thioanisole (Aldrich, catalog No. T2,800-2) and benzoic anhydride were distilled just prior to use. *n*-Butyllithium was obtained as a 1.6 M solution in hexane from Aldrich (catalog No. 18, 617-1). Anhydrous titanium(III) chloride (catalog No. 77116) and potassium metal (catalog No. 306692) were purchased from Alfa Inorganics. The term petroleum ether refers to the Baker "Analyzed Reagent" (bp 30-60 °C). For all anhydrous reactions performed under an atmosphere of dry N_2 or Ar the equipment was dried in an oven at 120 °C for several hours and then allowed to cool in an atmosphere of dry N_2 or Ar. All liquid transfer were made with N_2- or Ar-filled syringes. All microanalyses were performed by Spang Microanalytical Laboratory.

General Method for the Preparation of [(Phenylthio)methyl]carbinyl Benzoate Esters. 1-(Benzoyloxy)-1-[(phenylthio)methyl]cyclopentadecane (3B). To a solution of freshly distilled thioanisole (2.8 mL, 24 mmol) in anhydrous THF (10 mL) was added slowly with stirring *n*-BuLi/hexane (15 mL, 1.6 M, 24 mmol) at 0 °C. The resulting solution was allowed to stir at room temperature for 23 h. Freshly distilled cyclopentadecanone (**3A**; 1.03 g, 4.6 mmol) was added at 0 °C, and then the resulting reaction mixture was stirred at room temperature for 15 h. The reaction mixture was then poured into H_2O (75 mL) and extracted with Et_2O (4 × 20 mL). The combined ethereal extracts were washed with 5% $HOAc/H_2O$ (2 × 20 mL) followed by 5% KOH/H_2O (2 × 20 mL) and then dried over anhydrous K_2CO_3. Concentration in vacuo and chromatography of the residue on silica gel (200 g) with 10% Et_2O/90% petroleum ether affords 1.55 g (96%) of the corresponding (phenylthio)methyl alcohol: IR (CCl_4) 3540 (OH), 1585 (aromatic cm^{-1}; NMR (CCl_4) δ 1.37 (br, 28 H, CH_2), 2.07 (s, 1 H, OH), 3.02 (s, 2 H, $CH_2SC_6H_5$), 7.05-7.55 (m, 5 H, SC_6H_5). Anal. Calcd for $C_{22}H_{36}OS$: C, 75.80; H, 10.41; S, 9.26. Found: C, 75.61; H, 10.29; S, 9.07.

To a solution of the above (phenylthio)methyl alcohol (1.52 g, 4.4 mmol) in anhydrous THF (15 mL) was added slowly *n*-BuLi/hexane (3.4 mL, 1.6 M, 5.2 mmol) at 0 °C. The resulting reaction mixture was allowed to warm to room temperature (4 h) and then recooled to 0 °C, and freshly distilled benzoic anhydride (1.18 g, 5.2 mmol) was added. The resulting reaction mixture was stirred at room temperature for 12 h and then poured into ice-water (60 mL). The mixture was extracted with ether (4 × 20 mL). The combined ethereal extracts were dried (Na_2SO_4). Concentration in vacuo and chromatography of the resulting residue over silica gel (350 g) with 3% Et_2O/97% petroleum ether produced 1.91 g (97%) [(phenylthio)methyl]carbinyl benzolate ester **3B**: bp 90 °C (0.9 mmHg); IR (CCl_4) 1720 (CO) cm^{-1}; NMR (CCl_4) δ 1.00-2.67 (m, 28 H, CH_2), 3.60 (s, 2 H, $CH_2SC_6H_5$), 6.93-8.00 (2 m, 10 H, aromatic). Anal. Calcd for $C_{29}H_{40}O_2S$: C, 76.94; H, 8.91; S, 7.08. Found: C, 76.71; H, 8.78; S, 7.05.

General Method for the Reduction of [(Phenylthio)methyl]carbinyl Benzoate Esters with Titanium Metal. Methylene Cyclopentadecane (3C). To a stirred suspension of anhydrous $TiCl_3$ (0.651 g, 4.2 mmol) in dry THF (20 mL) under Ar was added potassium metal (0.587 g, 15 mmol, cut in three pieces). The resulting mixture was stirred at reflux for 1 h. To the resulting black suspension of freshly prepared Ti metal was added a solution of [(phenylthio)methyl]carbinyl benzoate ester **3B** (0.433 g, 0.96 mmol) in THF (5 mL) and the resulting mixture was stirred at reflux under Ar for 16.5 h. The reaction was cooled to 0-5 °C, quenched with absolute methanol (2 mL), and filtered through a column of silica gel-Celite (4:1, respectively). Concentration in vacuo and filtering through a column of silica gel (100 g) eluted with petroleum ether and again concentration in vacuo gave 0.244 g (84%) of methylenecyclopentadecane (**3C**): bp 75 °C (0.9 mmHg); IR (CCl_4) 3070, 1640, 890 ($C{=}CH_2$) cm^{-1}; NMR (CCl_4) δ 1.20-2.65 (m, 28 H, CH_2), 4.70 (s, 2 H, $C{=}CH_2$).

Acknowledgment. We thank The Robert A. Welch Foundation (Grant No. E-518) for the funds to support this research program.

Registry No. 1, 78514-50-8; 2, 78514-51-9; 3, 78514-52-0; 4, 78514-53-1; 5, 78514-54-2; 6, 78514-55-3; 7, 78514-56-4; 4-*tert*-butylmethenylcyclohexane, 13294-73-0; methenylcyclodecane, 3817-57-0; methenylcyclopentadecane, 78514-57-5; 2-methylene bornane, 27538-47-2; 3-methylene-5α-androstane, 28113-74-8; 3-methylene-androst-4-ene, 78514-58-6; 17-methyleneandrost-4-ene, 78514-59-7; cyclopentadecanone, 502-72-7; 1-(phenylthiomethyl)cyclopentadecanol, 78514-60-0; titanium, 7440-32-6.

Ion Pairs of Benzylic Cations, a Theoretical Study

C. Decoret and J. Royer

Equipe de Recherche Associêe au CNRS, Universitê Claude Bernard, 69622 Villeurbanne, France

J. J. Dannenberg*

Department of Chemistry, City University of New York, Hunter College, New York, New York 10021

Received April 22, 1981

Our interest in the mechanism of nucleophilic displacement reactions and the structures of the intermediates that occur along these reaction paths has led us to propose that nucleophilic substitution in simple alkyl substrates proceeds via anion-stabilized and anion-cation-stabilized intermediates (ASI and ACSI) rather than true ion pairs. These suggestions were originally based upon molecular orbital studies of model systems,[1] although subsequent experimental studies[2] seem to be in accord with the basic ideas. Nevertheless, there remains a substantial body of evidence in favor of ion pairs as intermediates, particularly in substitutions of benzylic substrates.[3] The charge is much more effectively delocalized away from the α-carbon in a benzyl than in an alkyl cation. We, therefore, reasoned that an anion could interact with the delocalized charge to form an ion-pair intermediate that might be a true minimum on a potential energy surface. Such a species should require an activation energy to return to covalent material.

---

[1] J. J. Dannenberg, *J. Am. Chem. Soc.*, **98**, 6261 (1976).

[2] (a) M. Gillard, F. Metras, S. Tellier, and J. J. Dannenberg, *J. Org. Chem.*, **41**, 3920 (1976); (b) L. S. Miller, D. Zazzaron, J. J. Dannenberg, F. Metras, and M. Gillard, *ibid.*, **45**, 641 (1980); (c) M. Gillard, F. Metras, S. Tellier, and J. J. Dannenberg, submitted for publication.

[3] See for example: (a) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman Eds., Van Nostrand-Rheinhold, New York, 1979, ACS Monogr. No. 167, Chapter 2; (b) E. Grunwald, A. Heller, and F. S. Klein, *J. Chem. Soc.*, 2604 (1975).