Table I. Ethanolysis of 1

concn of 1, M	alcohol	catalyst	time to disappearance of 1
9.1×10^{-4}	abs C_2H_5OH	none	no change
4×10^{-3}	95% C_2H_5OH	none	23 days
9.2×10^{-4}	abs C_2H_5OH	1 drop of $(C_2H_5)_3N$	43 h
5.3×10^{-2}	abs C_2H_5OH	2.2×10^{-1} M Na_2CO_3	3 h

Table II

run no.	pH	concn of 1, M	time to completion	% yield of 4
1	4.5	4×10^{-3}	no change	
2	6.6	9.2×10^{-4}	253 days	86
3	9.2	4×10^{-3}	65 days	95

and time were required for reaction in dry acetonitrile and 95:5 Me_2SO/H_2O. Amidine 2 was also obtained by refluxing 1 in dry dioxane with excess of cyclohexylamine.

(2) An NMR tube was charged with 72 mg (0.3 mmol) of 1, 33 mg (0.3 mmol) of cyclohexylamine, and 1.25 mL of a mixture of 60:40 acetonitrile and water. On the basis of the NMR peak at 8.77 ppm, the isoxazolone had fully reacted within 75 min. The tube contents were extracted with 100 mL of ether. After drying over anhydrous magnesium sulfate, the ether was removed by distillation. The product was shown to be a 60:40 mixture of $(C_6H_{11}NHCO)_2CHCOOC_2H_5$ (3) and $C_6H_{11}NHCOCH_2COOC_2H_5$ (4) by NMR. The NMR spectrum was compared with those of samples of 3[9] and 4[10] synthesized via other routes. The enol H signal of 3 at 19.5 ppm is particularly distinctive.

Reaction of 1 with Ethanol. Dilute solutions of 1 as shown in Table I were allowed to stand at room temperature. Disappearance of isoxazolone was followed by changes in UV absorption. In runs 2 and 3, the product was shown by NMR to be $C_6H_{11}NHCOCH(COOC_2H_5)_2$ (5). In run 4, the product was isolated and recrystallized from ethanol/water to give a 78% yield of 5, mp 74–75 °C (lit.[9] mp 75–76 °C). The structure was confirmed by NMR and IR.

Reaction of 1 with Water. Solutions of 1 in 50:50 THF/H_2O were allowed to stand at room temperature. Disappearance of isoxazolone was followed by changes in UV spectra. In run 1 the pH was adjusted to 4.5 by addition of acetic acid and in run 3 the pH was ajusted to 9.2 by addition of NaOH solution. The pH of run 2 (solution of 1 in solvent mixture) was 6.6. Results are shown in Table II. The hydrolysis product, $C_6H_{11}NHCOCH_2COOC_2H_5$ (4) was recrystallized from *n*-hexane, mp 73–74 °C (lit.[10] mp 73–73.5 °C). The structure was confirmed by NMR.

Reaction of 1 with Acetic Acid. A solution of 1×10^{-3} mol of 1 and glacial acetic acid in 0.5 mL of CCl_4 showed no change in the NMR peak at δ 8.77 after standing 90 h at room temperature. However, the δ 8.77 NMR peak disappeared completely when a solution of 1×10^{-3} mol of each of 1, glacial acetic acid, and triethylamine stood at room temperature for 195 h. Ethyl acetyl-*N*-cyclohexylmalonamate (6) was recovered by distilling off the CCl_4 and recrystallizing from *n*-hexane. The melting point was 44–46 °C (lit.[10] mp 47.2–48 °C). The structure was confirmed by NMR.

Acknowledgment. The financial support of Inmont Corporation by providing funds for the Ralph L. Pitman Memorial Fellowship for P. P. Patel is gratefully acknowledged. The advice and suggestions of Dr. S. P. Pappas are also gratefully acknowledged.

Registry No. 1, 78514-48-4; 2, 78514-49-5; 3, 65179-95-5; 4, 71433-06-2; 5, 65179-99-9; 6, 73453-43-7; *N*-cyclohexylhydroxyamine·HCl, 25100-12-3; diethyl ethoxymethylenemalonate, 3377-21-7; cyclohexylamine, 108-91-8.

---

[9] Wicks, Z. W., Jr.; Kostyk, B. W. *J. Coat. Technol.* **1977**, *49*(634), 77.

[10] Wicks, Z. W., Jr.; Wu, K. J. *J. Org. Chem.* **1980**, *45*, 2446.

2,3,4,5-Tetraphenyliodolium Ion and an Isomer

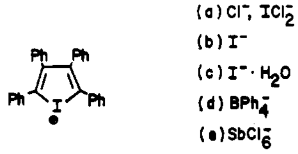
Vernon R. Sandel,* Gary R. Buske, Stephen G. Maroldo,
Dallas K. Bates, David Whitman, and George Sypniewski

*Department of Chemistry and Chemical Engineering,
Michigan Technological University,
Houghton, Michigan 49931*

Received April 22, 1981

In 1972 Beringer and co-workers[1] reported a low-yield (2.5%) synthesis of the novel Hückel aromatic 2,3,4,5-tetraphenyliodolium ion (1), isolated as the chloride and iodide salts. These authors did not report conclusive evidence for the ionic nature of their compounds, nor did they investigate the chemical properties of the ion beyond the thermal decomposition of their salts in a mass spectrometer.

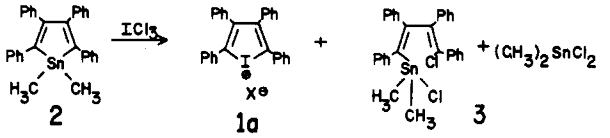
1



As early as 1969 we prepared a compound which we believed to be the monohydrate **1c**,[2] but after several successful preparations the method no longer yielded product. The melting behavior of our product differed markedly from that of the compound reported by the Beringer group, raising doubts that the basic structures were the same. Moreover, the ionic nature of both products was presumed mainly because one of the halogens exchanged very readily. The work of Doorakian et al.,[3] who reported facile vinylic halide exchange in the related mono and dihalides of 1,2,3,4-tetraphenyl-1,3-butadiene, casts doubt on the validity of this presumption. In this paper we present a modification of our original method which reliably produces either 1 or its hydrate **1b** in 12–18% yield, the ionic structure of 1 is confirmed, and some of its reactions are briefly investigated. In addition, an interesting isomer of 1 believed to be 5-ioda-1,2,3,4-tetraphenylbicyclo[2.1.0]pentenium hexachloroantimonate is reported.

Results and Discussion

Originally 1 was prepared by treatment of an ether slurry of 1,1-dimethyl-2,3,4,5-tetraphenylstannole[4] (2) with a solution of freshly prepared iodine trichloride[5] in ether at −68 °C. This yielded a yellow crystalline product with a melting point which varied from 79 to 104 °C in different preparations. The material was unstable, decomposing to a dark colored tar with the release of iodine vapor upon



---

[1] F. M. Beringer, P. Ganis, G. Avitabile, and H. Jaffe, *J. Org. Chem.*, **37**, 879 (1972).

[2] G. Buske and V. R. Sandel, Abstract, 6th Great Lakes Regional Meeting of the American Chemical Society, Houghton, MI, June 22–23, 1972.

[3] G. A. Doorakian, H. H. Freedman, R. F. Bryan, and H. P. Weber, *J. Am. Chem. Soc.*, **92**, 399 (1970).

[4] F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternhas, and D. S. Lehman, *J. Am. Chem. Soc.*, **82**, 5099 (1960).

[5] H. Booth and W. Morris, *Inorg. Synth. 1*, 167 (1939).

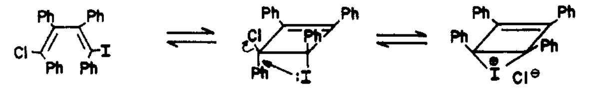
standing at room temperature for several hours to several days. This instability was attributed to a product mixture in which 1 was precipitated with a mixture of anions including Cl^-, ICl_2^-, and/or ICl_4^- (**1a**). The presence of oxidizing complex anions was inferred from the isolation of iodine and 1,4-dichloro-1,2,3,4-tetraphenylbutadiene from the tarry decomposition product of **1a**, and from the fact that iodine was produced when **1a** was treated with sodium iodide. The byproducts in the synthesis of **1a** were (4-chloro-1,2,3,4-tetraphenyl-(*Z,Z*)-1,3-butadienyl)dimethyltin choride[6] (**3**) and dimethyltin dichloride, which were isolated from the ether filtrate. By treatment of **1a** in methanol with a methanolic solution of sodium iodide, an iodide monohydrate **1c** was obtained which was stable indefinitely in the solid state. The mole of water picked up from the solvent was tenaciously held and was not removed under vacuum at 56 °C. The compound melted at 192–197 °C, with an obvious color change from orange to light yellow occurring suddenly at about 140 °C. By contrast, Beringer[1] reports the melting point of **1b** as 133–133.5 °C.

The yields in the above synthesis were erratic at 1–35% in six preparations and then became vanishingly small. By the simple expedient of changing the solvent to acetone or chloroform and running the reaction at 0 °C, consistent yields of 12–18% of 1 were obtained. In these solvents the initial product **1a** did not precipitate. After the addition of ICl_3, the solution was concentrated under vacuum at room temperature, and an acetone solution of sodium iodide was added to precipitate the yellow-orange tetraphenyliodolium iodide.

Unless special precautions were taken to dry all solvents before use, the hydrate **1c** was obtained. The compound was insoluble in hydrocarbon solvents, slightly soluble in chloroform and methylene chloride, and moderately soluble in dimethyl sulfoxide. Attempts to purify **1c** by recrystallization were unsuccessful. The reprecipitated product had bands in its infrared spectrum not present in the original spectrum of **1c**. Purification of **1c** for analysis was affected by simply washing the sample with acetone and then water until the washings no longer gave a precipitate with silver nitrate. Analysis of **1c** showed that exactly half of the iodine is precipitated by $AgNo_3$.

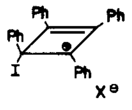
The use of rigorously dried acetone as a solvent in the synthesis yielded **1b** melting at 139 °C, whose infrared spectrum was identical with that of **1c** except for the absence of a band at 3460 cm^{-1}, attributed to the water of hydration. This material picked up water from air as well as from solvents. Our sample of **1b** picked up moisture to become **1c** upon being stored for 7 months in a screw-capped vial. Although our **1b** melted as a somewhat higher temperature than that of Beringer[1] (133–133.5 °C), the infrared spectra of the two compounds corresponded well. The difference in melting points may be due to polymorphism or to varying amounts of water present in the crystal. In any event, it is clear that the much higher melting point of our hydrate **1c** (192–197 °C) resulted from the presence of the associated water rather than from any gross structural differences from the **1b** of Beringer.

Further structure proof was necessary to show that **1a**, **1b**, and **1c** are not 1,4-dihalo-1,2,3,4-tetraphenylbutadienes. Doorakian et al.[3] have reported that the halogens of the 1,4-dihalo-1,2,3,4-tetraphenylbutadienes are labile toward nucleophilic displacement because the dienes reversibly cyclize to cyclobutenes in which the halogens are both allylic and benzylic. An analogous cyclization of a 1-chloro-4-iodo-1,2,3,4-tetraphenylbutadiene followed by anchimerically assisted displacement of a chloride ion could easily account for the halogen exchange attributed to 1 by both Beringer and ourselves. Therfore, we sought to exchange the anion of **1c** with a nonnucleophilic anion to demonstrate the ionic nature of the one halogen bond.

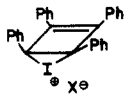


The iodolium tetraphenylborate (**1d**) was prepared by treating a methanolic solution of **1a** with an excess of sodium tetraphenylborate in methanol, yielding yellow crystals melting at 125–135 °C dec. The iodolium hexachloroantimonate (**1e**) was prepared by adding a chloroform solution of $SbCl_5$ to a suspension of **1c** in chloroform. A deep red solution resulted from which orange crystals precipitated (mp 110–114 °C). An analytically pure sample was not obtained by this method, presumably because the anion also contained some iodine. Alternatively, **1e** was prepared by adding stannole **2** to an equimolar mixture of ICl_3 and $SbCl_5$. An analytically pure sample (mp 121–122 °C) was obtained by recrystallization from methylene chloride–hexane solution.

Having substantiated the ionic nature of the iodolium salts, one still must consider alternative ionic structures such as **4** and **5**. Cations similar to **4**[7] and **5**[8] have been reported to react avidly with water and other nucleophiles, in contrast to the iodolium salts, which are stable to water and methanol. Thus, there can be little doubt that our compounds are iodolium salts of structure 1.



4



5

A brief study of the reactivity of 1 was undertaken. The color change in **1c** at 140 °C and melting point close to that of 1,4-diiodo-1,2,3,4-tetraphenyl-(*Z,Z*)-butadiene (**6**) (203–204 °C) made us suspicious that rearrangement was occurring. Upon heating a sample of **1c** to 140 °C the color change took place without any melting or observable change in crystalline form. The resulting light yellow product was identified as **6** by comparison of the infrared spectrum with that of an authentic sample prepared by the method of Braye et al.,[9] and by mixed melting point. In solution the isomerization takes place at room temperature. A slurry of **1c** in CH_2Cl_2 dissolved slowly and yielded only **6** upon evaporation of the solvent. Thus, the rearrangement occurs with a high degree of stereoselectivity both in the solid state and in solution. Beringer et al.[1] also reported the isomerization of **1b** at the melting point but not the stereoselective nature of the isomerization. The sharpness of the solid-state transition, less than 2°, is typical of a physical transition rather than a chemical one. Therefore, it is likely that the ions gain some freedom in the crystal lattice which allows the reaction to occur. The facile isomerization in solution gives support for this assumption. The enthalpy of isomerization of **1c** to **6** was determined by differential scanning calorimetry to be −7.5 ± 0.5 kcal/mol. It is likely that the water of hydration is

---

(6) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962).

(7) R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964); H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

(8) G. A. Olah, G. Liang, and J. Staral, *J. Am. Chem. Soc.*, **96**, 8112 (1974).

(9) E. H. Braye, W. Hübel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).

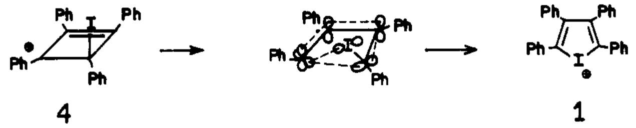
lost simultaneously, since there were no other transitions observable except for the melting point. Since the water loss is endothermic, the exothermicity of the isomerization alone is probably greater than the measured value. It is tempting to conclude from the exothermicity of the isomerization that 1 is not aromatic. Without proper models for a comparison, however, we can only state that if aromatic stabilization is present, it must be small. Beringer et al.[1] have reported the X-ray crystallographic structure of the benzo and dibenzo derivative of 1. They found that the C–I bond lengths of the benzo derivatives were almost identical with those of the diaryliodonium salts, again indicating little, if any, aromatic stabilization. The lack of appreciable aromatic stabilization may result from inefficient overlap of the large 5p orbital containing the unshared electron pair from iodine with the 2p π system.

In contrast to **1c**, the hexachloroantimonate **1e** was stable in solution. This made it possible to study the reaction of nucleophiles other than a halide counterion with 1. The reaction of **1e** with sodium hydroxide in aqueous acetone at reflux yielded a complex mixture of products. The major component was isolated by thin-layer chromatography and analyzed by mass spectrometry. Major peaks occurred at 178 (36%, $C_{14}H_{10}$), 356 (100%, $C_{28}H_{20}$), 483 (22%, $C_{28}H_{20}I$), and 518 (0.8%, $C_{28}H_{20}ClI$), suggesting 1-chloro-4-iodo-1,2,3,4-tetraphenylbutadiene as the structure of the product. The treatment of **1e** with an acetone solution of sodium cyanide at reflux followed by basic hydrolysis yielded no acidic product. Instead tetraphenylfuran[10] was obtained in 22% yield. Thus, it appears from this limited study that the reaction of 1 with nucleophiles is simple only when the attacking nucleophile is the halogen counterion. Beringer et al.[1] have reported similarly complex reactions of the benziodolium system.

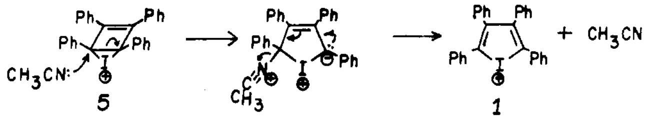
An attempt to prepare **1e** by treating 1,4-diiodo-1,2,3,4-tetraphenyl-(*Z*,*Z*)-butadiene with antimony pentachloride in carbon disulfide led to an interesting isomer of **1e**. Iodine was generated, and a dark brown precipitate formed. The solid, collected and washed with copious amounts of CS_2, melted sharply but with decomposition between 100 and 117 °C in different preparations. Carbon and hydrogen analysis indicated the same empirical formula ($C_{28}H_{20}ISbCl_6$) as **1e**. The infrared spectrum of the solid product was very similar to, but not identical with, that of **1e**, whereas the ^1H NMR spectrum (Me_2SO-d_6) was identical.

The solid reacted with moisture in the air and in solvents not rigorously dried, and also abstracted hydride ion from cycloheptatriene to yield tropylium hexachloroantimonate. This typical carbonium ion reactivity leads us to believe that the structure is the hexachloroantimonate of 5. Structure 5 is favored over structure 4 because iodine is not exchanged for chlorine in the presence of $SbCl_5$. Freedman and Frantz[7] report that 3,4-dibromo-1,2,3,4-tetraphenylbutene readily undergoes exchange of both halogens when treated with tin tetrachloride to yield 4-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate.

The compound 5 is indefinitely stable in the solid state but isomerizes to the more stable **1e** when dissolved in either Me_2SO-d_6 or acetonitrile, accounting for the identity of the ^1H NMR spectra obtained from 5 and **1e**. The solid-state stability of 5 can be attributed to the orbital symmetry-forbidden nature of the electrocyclic rearrangement, which must be distrotatory as long as the bicyclic structure remains intact. In polar solvents, however, the three-membered ring may open to the cyclobutenium ion 4 in which electrocyclic four-membered ring opening can proceed by an allowed conrotatory process. One problem with this explanation, however, is that the chloro analogue of 4 reported by Freedman and Frantz[7] apparently does not undergo similar ring opening in solution at ambient temperature. The greater lability of 4 may be due to concerted opening of the four-membered ring and closing of the five-membered iodolium ring. Since iodine is more likely to share a pair of electrons in the transition state than chlorine, the concerted rearrangement in 5 would probably occur more readily than in the chloro analogue.



An alternative mechanism in which the isomerization of 5 to 1 is catalyzed by nucleophilic solvent was suggested by a referee. Halonium ions have been shown to undergo nucleophilic attack by acetonitrile at the carbon adjacent to the positive halogen.[11]



Experimental Section

Infrared spectra were run on Perkin-Elmer 621 or 700 spectrometers, ^1H NMR spectra on a Varian T-60 spectrometer, and mass spectra on a Varian M-66 mass spectrometer.

Preparation of the 2,3,4,5-Tetraphenyliodolium Ion (1) in Ether. To a slurry of 5.05 g (0.0100 mol) of 1,1-dimethyl-2,3,4,5-tetraphenylstannole[4] in 150 mL of anhydrous ether at −68 °C was added a cold (−68 °C) solution of 2.8 g (0.012 mol) of freshly prepared ICl_3[5] in 50 mL of ether. During the addition all solids dissolved. The solution was allowed to warm to room temperature, whereupon 0.302 g of a yellow crystalline product (**1a**) precipitated. The melting point of **1a** varied from 78.5–79 to 104 °C in different preparations, and variable analyses indicated it was not a single compound.

Concentration of the filtrate from **1a** yielded 2.31 g (40%) of (4-chloro-1,2,3,4-tetraphenyl-(*Z*,*Z*)-1,3-butadienyl)dimethylytin chloride, identified by its infrared spectrum and mixed melting point (152–3 °C) with an authentic sample prepared by the method of Freedman.[6] Dimethyltin dichloride was isolated from the filtrate by evaporation to dryness and sublimation of the residue.

The above procedure was used successfully 6 times, and then succeeding attempts gave vanishingly small yields. The following procedure is more reliable.

2,3,4,5-Tetraphenyliodolium Iodide Hydrate (1c). A solution of 0.200 g (0.40 mmol) of 1,1-dimethyl-2,3,4,5-tetraphenylstannole in 3 mL of acetone was added dropwise to a rapidly stirred solution of 0.096 g (0.40 mmol) of freshly prepared ICl_3 in 3 mL of the same solvent of 0 °C under a nitrogen atmosphere. The resulting dark amber solution was concentrated at room temperature under vacuum, and a saturated solution of NaI in acetone was added. Yellow-orange crystals of **1c** were filtered and washed first with cold acetone and then with water until the washings no longer gave precipitate when treated with $AgNO_3$. Yields of **1c** ranged from 0.029–0.043 g (12–18%) of mp 193–197 °C with a sharp (<2° range) transition marked by a bleaching of the color to a pale yellow occurring between 137–142 °C: IR (KBr) 3460 (br), 3080 (w), 3060 (w), 3025 (w), 1600 (w), 1483 (m), 1442 (s), 1073 (w), 1028 (w), 1000 (w), 955 (w), 918 (w), 792 (m), 780 (w), 756 (w), 701 (s), 690 (s), 670 (w), 624 (w), 615 (w), 560

---

(10) R. E. Lutz, C. R. Bauer, R. G. Lutz, and J. S. Gillespie, *J. Org. Chem.*, **20**, 218 (1955).

(11) P. E. Peterson, P. R. Clifford, and F. J. Slama, *J. Am. Chem. Soc.*, **92**, 2840 (1970).

(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