Journal of Organometallic Chemistry, 108 (1976) 183—195

THE PHOTOCHEMISTRY OF 2-PHENYLSELENOPHENE AND 2-PHENYLTELLUROPHENE

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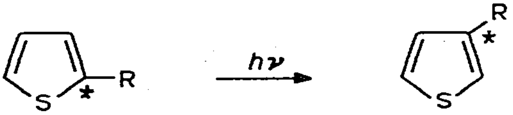
(Received October 14th, 1975)

Summary

2-Phenylselenophene is found to yield a mixture of 3-phenylselenophene, phenylvinylacetylene (PVA) and selenium upon irradiation. Photolysis of 2-phenyltellurophene produces only PVA and tellurium. Deuterium labeling studies revealed that PVA did not arise from a unimolecular reaction but involved hydrogen abstraction from solvent. These results are interpreted within an extension of van Tamelen's general mechanism for the photochemistry of aromatic heterocyclopentadienes.

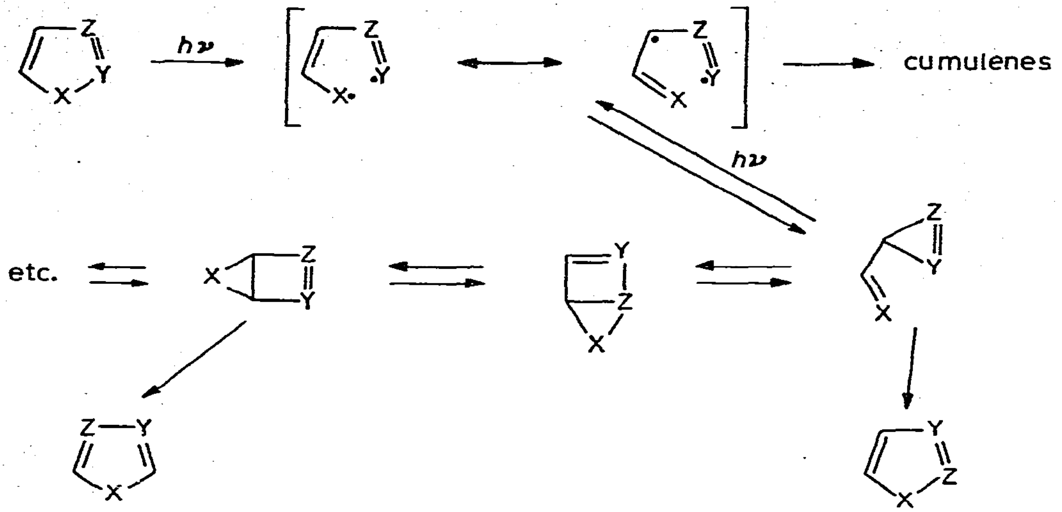
Introduction

Probably the most studied photorearrangement in the heterocyclopentadiene series is the photorearrangement of various 2-substituted thiophenes to the corresponding 3-substituted derivatives. First reported in 1965 [1] by Wynberg, this rearrangement has been extensively investigated by that group [2—5] in a search for mechanistic details. A variety of subtly different mechanisms have been proposed [6—9] most of which involve intermediates which are bridged valence tautomers analogous to Dewar benzene, benzvalene or prismane. In 1971 van Tamelen [10] proposed the following general mechanism (Scheme 1) for the photorearrangement of five-membered aromatic heterocycles to accommodate all reported results.



In this mechanism absorption of light leads to cleavage of the weakest of the single bonds in the ring. The intermediate diradical then closes to a cyclopropene or a heterocyclic analog thereof, which is apparently in equilibrium with Dewar-

SCHEME 1



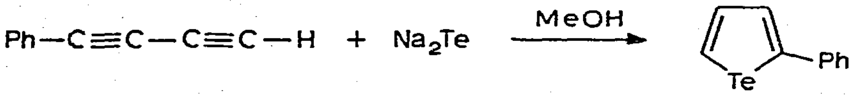
type isomers. Alternatively, a substituent can migrate with the formation of a cumulene or triple bond.

Most recently Kellogg [9] has proposed a more simplistic model to explain all the thiophene rearrangements in which any two adjacent atoms in the ring may exchange positions. This model, wherein a two atom fragment is wrenched 90° out of the plane formed by the remaining three atoms, is suggested to provide an energetic minimum to a greatly distorted excited singlet state.

The differences in photoproducts from furans and thiophenes, the change in bond strengths and a presumed change in ability to accommodate strained bicyclic intermediates as one proceeds down Group VI, combined to suggest that a study of the photochemistry of substituted selenophenes and tellurophenes would prove interesting and hopefully instructive.

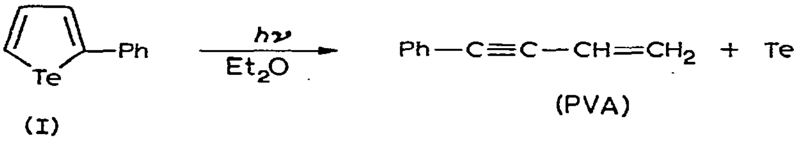
Results and discussion

The photochemistry of the selenophenes and tellurophenes was examined through their phenyl derivatives, first because of the high yield of the phenylthio phene photolysis, second because of their low volatility, and third because of their ease of preparation. The 2-phenyltellurophene was obtained by an extension of the procedure of Mack [11] who treated disubstituted butadiynes with sodium telluride in methanol. Monophenylbutadiyne also gave the corresponding tellurophene (I) in a yield of 58% based on the diacetylene.

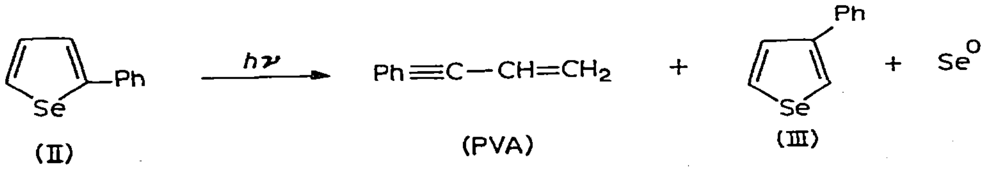


(I) 58%

The ultraviolet spectrum of 2-phenyltellurophene (I) consisted of a single broad maximum at 292 nm ($\epsilon = 12600$). Irradiation was accomplished through Pyrex using ethereal solutions thoroughly degassed with argon. Although the photochemistry showed no evidence of concentration dependence, reasonably high dilution (ca. 1 mg ml^{-1}) was necessary as a heavy black precipitate appeared immediately and soon a black tellurium mirror coated the vessel walls. Examination of the reaction mixture after 10 h revealed a new volatile component which was shown by comparison of its mass spectrum and NMR spectrum with those of an authentic sample to be phenylvinylacetylene (PVA). PVA was formed in 46% yield and no other volatile components were observed.

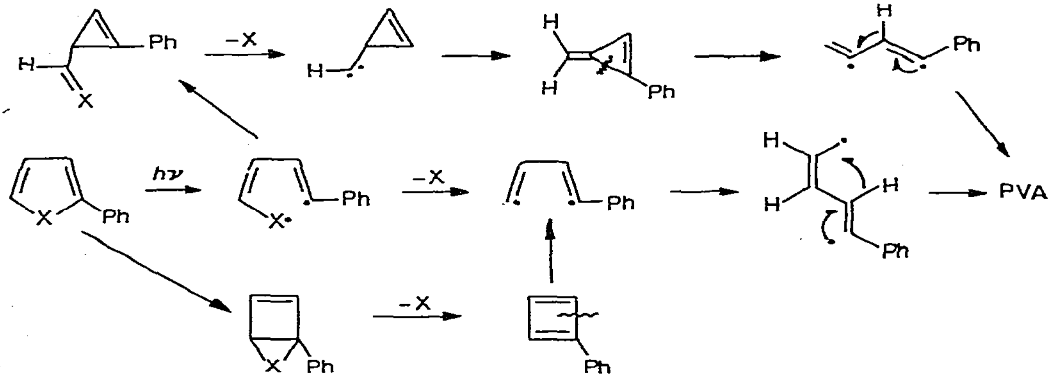


A sample of 2-phenylselenophene (II) was synthesized in a manner analogous to the 2-phenyltellurophene synthesis and it was photolyzed in a like manner. The NMR spectrum of the product mixture showed the absorption of phenylvinylacetylene in the olefinic region and a new absorption in the region of the selenophene protons (δ 7.5) suspected of being due to 3-phenylselenophene (III). Identification of III was accomplished by NMR, mass spectra and GC retention time comparison with an authentic sample prepared by the procedure of Yur'ev et al. [12]. After 48 h of irradiation the yields of PVA and 3-phenylselenophene were 15% and 10% respectively with ca. 10% of II still remaining. Kinetic studies of the reactions were not undertaken because of the unavoidable variance in the light intensity entering the solution due to the precipitated selenium and tellurium. It was determined that both the 3-phenylselenophene and PVA were stable under the reaction conditions. The stability of the 3-phenylselenophene is to be expected when one considers the hypsochromic shift in the ultraviolet absorption in going from the 2-phenylselenophene to the 3-substituted isomer. The absorption maximum for the 2-substituted isomer is at 289 nm with broad tailing well beyond 300 nm while the 3-phenylselenophene has a maximum at 227 nm with the tailing ending at 300 nm [12]; however, even when the 3-phenylselenophene was irradiated with the 254 nm lamps through quartz for an extended period only slight selenium discoloration of the solution was observed and the GC trace indicated only the starting material with no observable products.

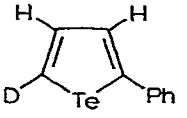


It was assumed that the rearrangement of the 2-phenylselenophene occurred in a manner analogous to the thiophene rearrangement and little additional meaningful information could be added to the understanding of its mechanism. We therefore undertook to investigate the mechanism of the formation of PVA from the 2-phenyl-selenophene and -tellurophene. Several pathways by which the PVA might be formed are shown in Scheme 2. In support of these mechanistic suggestions it should be noted that vinylacetylene has been isolated from a reaction for which cyclobutadiene was postulated as an intermediate [15] and there is evidence indicating that the decomposition of methylenecyclopropene can lead to vinylacetylene [13,14].

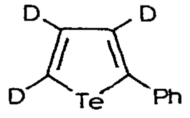
SCHEME 2



The phenyltellurophene was the best candidate for a mechanistic investigation because of its higher yield of PVA. Two deuterium labeled phenyltellurophenes (IV and V) whose photolyses could reveal some mechanistic information were synthesized.

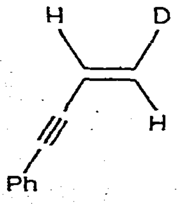


(IV)

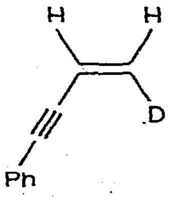


(V)

2-Phenyl-5-deuterotellurophene (IV) was synthesized from the 5-protio compound by utilization of that proton's relatively high acidity [16]. A sample of 2-phenyltellurophene (I) was dissolved in excess methyllithium in ether and allowed to stand at room temperature overnight. The solution was then quenched with D_2O. Our normal method of purification of I included elution through a column of activated alumina; however, the deutero compound was found to undergo deuterium—hydrogen exchange with residual water in the alumina, resulting in poor overall deuterium incorporation. The reaction was repeated and the ether/D_2O mixture was simply extracted with hexane to yield the 5-deutero (IV) compound (95% D by mass spec.). Photolysis of IV in ether afforded VI and VII in approximately a 1 : 1 ratio.

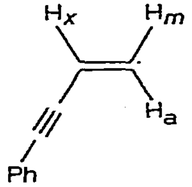


(VI)



(VII)

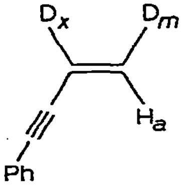
The 100 MHz NMR spectrum of authentic phenylvinylacetylene shows an aromatic multiplet from δ 7.15 to 7.5 and the three olefinic protons appear as a multiplet centered at approximately δ 5.7 which lends itself to first-order analysis as an *AMX* system. Each proton consists of a doublet of doublets. The absorptions centered at δ 5.44, 5.64, and 5.97 are assigned to protons *m*, *a*, and *x*, respectively. Their coupling constants are J_{ma} 3.1, J_{mx} 10.5, and J_{ax} 17.5 Hz.



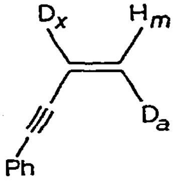
The spectrum of the reaction mixture after 5-deutero-2-phenyltellurophene (IV) was photolyzed to approximately 50% completion revealed that the deuterium labeling of the reactant was intact. Examination of the olefinic region of the NMR spectrum shows a multiplet centered at approximately δ 5.95, a doublet at δ 5.62 split by 18.0 Hz and the doublet at δ 5.43 split by 11.6 Hz. By analogy to the unlabeled PVA these splittings were assigned to *ax* and *mx* couplings respectively. The absence of *am* coupling while both H_a and H_m are present is attributed to a 50 : 50 mixture of the isomeric 1-deutero-4-phenyl-but-1-ene-3-ynes (VI and VII).

The 3,4,5-trideuterotellurophene (V) was synthesized in the same manner as the trihydrocompound (I), the difference being the use of methanol-d_1 as the solvent. The product was purified by elution through a column of activated alumina and then position 5 was made isotopically pure with methyllithium and D_2O quenching in the manner of the 5-deutero-2-phenyltellurophene. A sample of the trideuterophenyltellurophene (96% D_3 by mass spec.) was photolyzed in ether and mass spectral analysis indicated that the PVA produced contained only two deuterium atoms.

The NMR spectrum of the product mixture revealed two triplets of equal intensity at δ 5.63 and 5.43 with splittings of 2.9 and 1.8 Hz respectively. This spectrum is entirely consistent with the formation of a 50 : 50 mixture of VIII and IX. Note that the couplings observed are J_{ax} 2.9 and J_{mx} 1.8 Hz approximately 1/6 of the analogous proton—proton couplings for the same system as expected. Resolution of the expected *am* coupling (3.1 Hz/6 = 0.5 Hz) was apparently beyond the capabilities of the instrument.



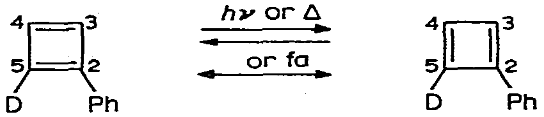
(VIII)



(IX)

The latter experiment proved that the decomposition is not a unimolecular reaction, thus casting doubt on all of the mechanisms embodied in Scheme 2.

The photolysis of the monodeuterophenyltellurophene provided additional evidence against a cyclobutadiene intermediate. Regardless of the actual symmetry of cyclobutadiene [17] one would expect carbon atoms 5 and 3 in the proposed phenylcyclobutadiene intermediate to become equivalent (eq. 1).



(1)

The trideuterophenyltellurophene photolysis showed that one carbon atom had to lose a deuterium and another carbon had to abstract a proton from the solvent, thus one would expect the proposed monodeuterophenylcyclobutadiene to lose ~50% of its deuterium in going to PVA, contrary to the full retention of deuterium observed.

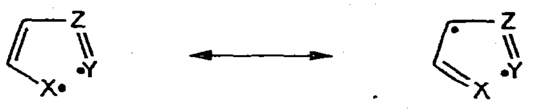
Now that the proposed mechanisms (Scheme 2) have been discredited, it remains to propose a new mechanism consistent with the facts. Although there is not enough information to demand a particular mechanism, certain clear implications can be drawn from the experiments. The fact that a proton is abstracted from ether in the trideuterophenyltellurophene photolysis could hardly be rationalized as anything but a free radical hydrogen abstraction. When this is taken in conjunction with the fact that a 50 : 50 mixture of VI and VII was obtained from the monodeuterophenyltellurophene photolysis, the radical Ph—C≡C—CH=CH · (X) seems the most reasonable final intermediate of the reaction.

One can envision that the radical X could result from a diradical such as XI after an intermolecular hydrogen atom abstraction from the carbon β to the

(XI)

phenyl ring; however, an intramolecular abstraction would be expected to occur more readily. Since we find that an intramolecular abstraction does not occur, XI is presumably not an intermediate in the reaction.

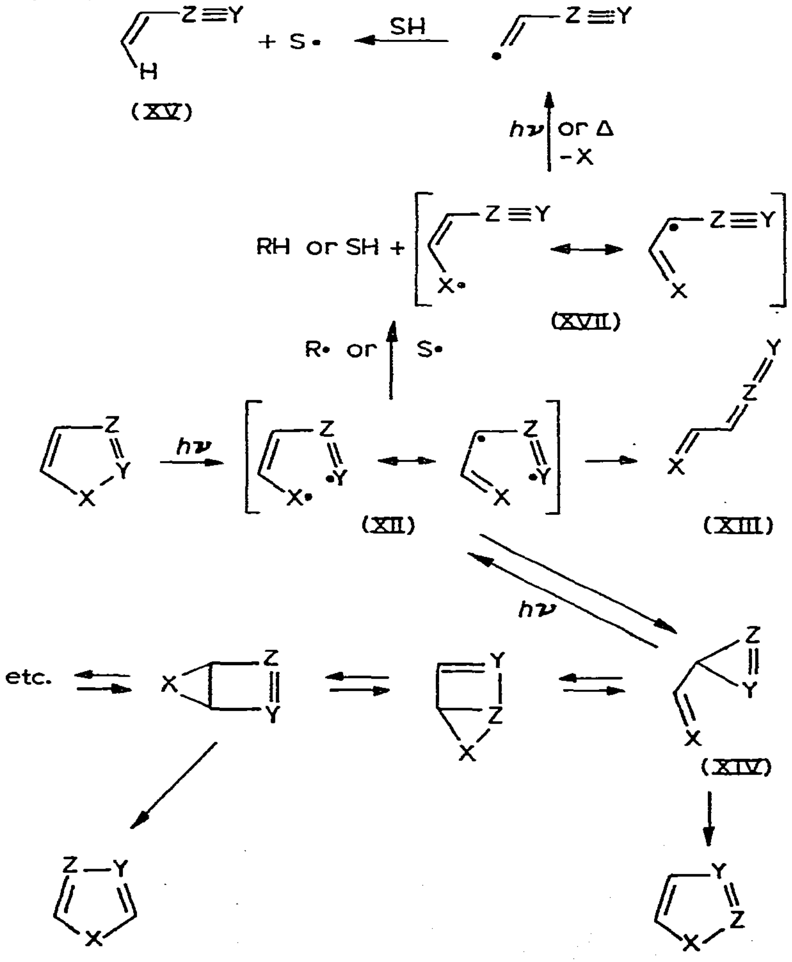
All of these experimental results can be explained within van Tamelen and Whitesides' framework (Scheme 1) for the photochemical rearrangements of five-membered heterocycles with one extension (Scheme 3). The first step in the reaction is homolytic cleavage of the weakest bond in the ring. Diradical XII then has three product-forming pathways open to it: (1) intramolecular hydrogen abstraction to give a cumulene (XIII); (2) closure to a cyclopropene (XIV); (3) intermolecular hydrogen abstraction followed by hetero atom extrusion to give vinylacetylene (XV). Factors influencing the path of the reaction are probably the strength of the carbon—hetero atom double bond and the stability and reactivity of the hetero radical. The trend in going down Group VI from oxygen to tellurium is toward a weaker carbon—hetero atom double bond and a more stable hetero radical. One would expect a substantial decrease in the relative contribution of the resonance form XVI.



(XVI)

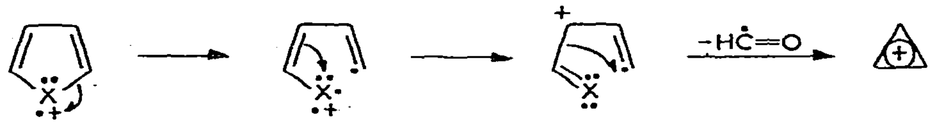
The 2,5-di-t-butylfuran goes to cyclopropene and its subsequent reaction products and to cumulene [10] via an intramolecular hydrogen abstraction from carbon Z to carbon Y. The thiophenes give products explainable via cyclopropene [7] although no such intermediate has ever been isolated as in the furan case. A Dewar-type isomer has, however, been isolated from the gas phase photolysis of tetra(trifluoromethyl)thiophene [18]. 2-phenylselenophene gives one product explainable via a cyclopropene and another, PVA, from a new pathway which can be visualized as beginning with an intermolecular hydrogen abstraction from carbon Z by either more excited starting material or a solvent radical. The vinylselenyl (XVII) radical produced then extrudes elemental selenium either thermally or photochemically giving a vinyl radical. This vinyl radical then abstracts a proton from solvent to give PVA and produce the solvent

SCHEME 3



radicals aforementioned. The 2-phenyltellurophene gives exclusively the product of the last described process, namely PVA.

It is interesting to note a similar gradual change in the pattern of mass spectral fragmentation of the Group VI heterocyclopentadienes. Principal peaks in the fragmentation of furans and thiophenes [19] include cyclopropenium cations for which the following mechanism has been suggested.



(X = O,S)

For the selenophenes the loss of selenium is a more important fragmentation than the formation of cyclopropenium cations. For the tellurophenes the formation of cyclopropenium cations is barely observable in comparison to the loss of tellurium.

Thus there is a great variety in the modes of decomposition of excited Group VI heterocyclopentadienes, but at the same time there is a high degree of continuity in going from furans to tellurophenes with selenophenes providing a key link in that continuity at the interface of the non-metallic elements of the group with the metallic members of the group.

Experimental

Routine NMR spectra were obtained on a Hitachi R20-B spectrometer or a Varian model A-60, and chemical shifts were reported as ppm (δ scale) from tetramethylsilane as an internal standard. The Varian HA-100 spectrometer was used to record all 100 MHz spectra. Routine mass spectra were obtained on an Atlas CH-4 spectrometer. The Perkin—Elmer PE-270 was used to obtain GC-mass spectra. An asterisk (m/e^*) is used to indicate that the ion reported is the most abundant in a cluster of ions containing different isotopes of either selenium or tellurium. High resolution mass spectra were recorded on a MS-902 mass spectrometer manufactured by AEI. Ultraviolet spectra (UV) were recorded using a Cary model 14 spectrophotometer. All melting points were obtained on a Thomas—Hoover capillary melting point apparatus and are uncorrected.

Phenylbutadiyne

The procedure of Bohlman et al. [20] was used to prepare this compound as a yellow oil which was stored cold: 60 MHz NMR (CCl_4) δ 7.35 (m, 5H), 2.63 (s, 1H).

2-Phenyltellurophene (I)

Sodium telluride (10 mmol) was prepared in liquid ammonia by the method of Brandsma and Wijers [21]. Care should be taken in addition of the tellurium to the solutions of sodium in liquid ammonia because the reaction appears to have an incubation period after which it can become violent! The liquid ammonia was allowed to evaporate under nitrogen. After the reaction flask reached room temperature, heat was applied (hot water bath) to drive off residual ammonia. Deoxygenated absolute methanol (30 ml) was added to the reaction flask resulting in a deep purple solution of methanolic sodium telluride. To this solution was added dropwise (10 min) a deoxygenated solution of 0.80 g (6.3 mmol) phenylbutadiyne in 20 ml of absolute methanol. The mixture was stirred for two hours at room temperature, then opened to the air to oxidize the excess telluride. After the mixture became dark grey (tellurium suspension) it was filtered. The filtrate was extracted with two 50 ml portions of hexane after the addition of 50 ml of water. Evaporation of the combined hexane washings gave 1.1 g crude product. The solid was dissolved in hexane and chromatographed on a column of alumina packed in pentane (5.5 X 10 cm) to yield 0.94 g (58%) of a cream-colored solid: m.p. 47.5—48°C; 100 MHz NMR (CCl_4) δ 8.69 (m, 1H), 7.71 (m, 2H), 7.29 (m, 5H); mass spectrum (70 eV) *m/e* (% rel. intensity) 258* (80), 128 (100), 127 (22), 115 (01), 102 (37), 77 (12), 51 (13), 39 (4); mass spectrum, found: *m/e* 257.9684 ± 0.0013. $C_{10}H_8Te$ calcd.: *m/e* 257.9693.

General photolyses

All photolyses were carried out in a Rayonet Photochemical Reactor. The general details for analytical and preparative scale reactions are given below.

Analytical scale reaction. A precisely weighed sample of reactant (10—12 mg) was placed in a quartz tube equipped with a watercooled jacket (7 mm I.D. X 21 in.) which had a mark indicating a level of 10 ml of solution. A precisely weighed amount of diphenyl ether (3—4 mg) was then added to the tube for a GC standard. The tube was then filled with solvent (anhydrous ether unless otherwise indicated) to approximately 1—2 inches above the mark. A rubber septum was placed on the top of the tube and a hypodermic needle attached to an argon tank was inserted through the septum and into the solution. After another much shorter needle had been inserted through the septum for exhaust, argon was bubbled through the solution until the level of liquid reached the 10 ml mark through evaporation. The reaction mixtures were analyzed using an Aerograph Hy-Fi Model 600-C gas chromatograph equipped with a 6′ X 1/8″ column packed with 10% Ucon LB 550X on Chromosorb P and a flame-ionization detector. Calibration factors for relative amounts of the various products to the amount of the internal standard, diphenylether, were obtained by measuring the relative areas of their peaks in the chromatograms of samples containing known mixtures of each of the various compounds with the internal standard. Using these calibration factors and knowing the amount of internal standard added to the reaction mixture, the absolute amount of each component in

TABLE 1

GC CALIBRATION FACTORS (Z) FOR COMPOUNDS (Y) RELATIVE TO INTERNAL STANDARD (DIPHENYL ETHER)

Y	Z
2-Phenylselenophene	1.4
Phenylvinylacetylene	1.1

$$Z \cdot \frac{\text{area of Y}}{\text{area of } Ph_2O} = \frac{\text{mass of Y}}{\text{mass of } Ph_2O}$$

the reaction mixture could be readily determined simply be measuring the area of its peak relative to the internal standard.

Preparative scale reaction. These reactions were carried out in essentially the same manner as the analytical scale reactions. The amounts of reactant and solvent were increased tenfold and the diphenyl ether was excluded. In general this scale reaction was carried out only when NMR or mass spectral analysis of the reaction mixture was required.

Photolysis of 2-phenyltellurophene (I)

A preparative scale photolysis of I in ether was carried out in a quartz vessel irradiated by 300 nm lamps for ten hours. The reaction mixture was decanted from the tellurium residue as cleanly as possible and then evaporated to a volume of approximately 10 ml. The cloudy black suspension was centrifuged, then decanted and evaporated. NMR (100 MHz, CCl_4) of the residue included in addition to a minute amount of I, a broad phenyl absorption centered at δ 7.35, a complex multiplet in the olefinic region, δ 5.4—6.2, and additional absorption between δ 1 and 1.5. GC-mass spectral analysis of the NMR solution revealed a volatile product with an apparent molecular ion at *m/e* 128. An authentic sample (see below) of phenylvinylacetylene (PVA) gave a mass spectrum identical to that observed for the volatile photolysis product. The olefinic region of the NMR of the authentic PVA duplicated the olefinic multiplet observed in the photolysis mixture, and GC retention times also matched.

Several analytical scale reactions were carried out to optimize the yields of PVA. Photolyses at 254 nm in ether, isopropanol, or acetone resulted in little, if any, volatile products. Starting material had usually disappeared after four to five hours of irradiation. Irradiation at 300 nm using either quartz or Pyrex resulted in appreciable quantities of PVA though the best yields were obtained with pyrex filters. Irradiation for 30—40 h was required for complete disappearance of starting material. The yield of PVA was 46% in ether solution, 20% in isopropanol, and less than 20% in acetone.

Phenylvinylacetylene (PVA)

A slight modification of the procedure of Quelet and Golse [22] was used to prepare PVA. The dehydrobromination of 4-bromo-1-phenyl-1-butyne was effected using a twofold excess of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) in dimethylsulfoxide with overnight stirring at room temperature. Pentane and 10% H_2SO_4 were then added to the mixture followed by several extractions with water. Evaporation of the pentane yielded essentially pure phenylvinylacetylene as a yellow oil: 100 MHz NMR (CCl_4) δ 7.30 (m, 5H), *AMX* pattern, centers at δ 5.64, 5.44, and 5.97 respectively, J_{am} 3.1, J_{ax} 17.5, J_{mx} 10.5 Hz; mass spectrum (70 eV) *m/e* (% rel. intensity) 128 (100), 127 (15), 102 (23), 77 (6), 51 (10).

2-Phenylselenophene (II)

Excess hydrogen selenide was bubbled over a period of 30 min into a refluxing, magnetically stirred, deoxygenated solution of 100 ml acetone, 12 ml 1 *N* aqueous sodium hydroxide, and 1.1 g phenylbutadiyne under nitrogen. After refluxing the mixture an additional 30 min, nitrogen was bubbled (one hour) through the refluxing mixture to remove excess hydrogen selenide. The mixture was cooled and then concentrated in vacuo to a volume of approximately 20 ml. Water (100 ml) was added to the residue which was then extracted with pentane. Evaporation of the pentane left a very dark, foul liquid. Purification by chromatography as described above furnished 0.82 g (46%) of a cream colored solid: m.p. 41—43°C [lit. [12] m.p. 38°C]; 100 MHz NMR (CCl_4) δ 7.81 (dd, 1H, J 1.3 and 5.5 Hz), 7.05—7.60 (m, 7H); mass spectrum (70 eV) *m/e* (% rel. intensity) 208* (100), 128 (77), 127 (13), 115 (24), 103 (19), 77 (11), 51 (12), 39 (8).

Another sample of the title compound was prepared by the method of Yur'ev et al. [12] which was identical to that previously described.

Photolysis of II

A preparative scale photolysis was carried out on a sample of 2-phenylselenophene in ether solution using 300 nm lamps through pyrex for 24 h. NMR analysis of the residue after evaporation found the olefinic multiplet characteristic of PVA and a new multiplet at δ 7.95 which was duplicated by an authentic sample (see below) or 3-phenylselenophene. The GC trace of the product mixture showed a peak corresponding to PVA and a new peak whose retention time was slightly longer than 2-phenylselenophene which corresponded exactly with authentic 3-phenylselenophene and produced an identical mass spectrum. The yields of PVA and 3-phenylselenophene from an analytical scale reaction (48 h) were found to be 15% and 10% respectively. An analytical sample containing both authentic PVA and authentic 3-phenylselenophene was photolyzed under the reaction conditions for three days with no observable change by GC.

3-Phenylselenophene (III)

The compound was prepared by the method of Yur'ev et al. [12] as a cream colored solid: m.p. 91—92°C [lit. [12] m.p. 97°C]; 100 MHz NMR (CCl_4) δ 7.95 (m, 2H), 7.05—7.55 (m, 6H); mass spectrum (70 eV) *m/e* (% rel. intensity) 208* (100), 128 (75), 127 (10), 115 (24), 102 (22), 77 (12), 51 (17), 39 (12).

Photolysis of II

An analytical sample of 3-phenylselenophene in ether was irradiated through quartz with 254 nm lamps for four days with no change observable by GC and only slight selenium discoloration of the solution.

2-Phenyl-5-deuterotellurophene (IV)

To 0.25 g I under nitrogen was added 10 ml 1 *M* methyllithium in ether all at once. After standing overnight at room temperature the solution was added via syringe to a mixture of 10 ml D_2O and 20 ml hexane with cooling (ice bath). The water layer was removed after agitation and the organic layer then washed with 10 ml D_2O. The aqueous layer was removed and the organic layer carefully decanted from a tiny amount of white precipitate into a dry flask. Evaporation of the solvent afforded 0.23 g of a yellow solid: 100 MHz NMR (CCl_4) δ 8.62 (m, <0.05H), 7.66 (s, 2H), 7.05—7.45 (m, 5H), also some nondescript aliphatic absorption δ 0.8—1.8 (non-volatile impurity by GC); mass spectrum (16 eV) *m/e* (% rel. intensity) 259* (100), 130 (3), 129 (18), 128 (1).

Photolysis of IV

A preparative scale photolysis of IV in ether through pyrex using 300 nm lamps was carried out for 24 h. The work-up was identical to that for the photolysis of I. The MHz NMR of the residue is discussed in the Results and discussion section. GC-mass spectrum (16 eV) of PVA showed ions at: *m/e* (% rel. intensity) 131 (2), 130 (18), 129 (100), 128 (7), 103 (9), 102 (7).

2-Phenyl-3,4,5-trideuterotellurophene (V)

This compound was prepared in the same manner as I with the following exceptions. The sodium telluride was dissolved in methanol-d_1 (from D_2O—acid hydrolysis of dimethylcarbonate). The phenylbutadiyne was allowed to exchange (one hour) in methanol-d_1 to which a small piece of sodium had been added before the solution was added to the sodium telluride.

After work-up identical to that of I, the NMR spectrum of the product showed substantial proton absorption at the 5-position of the tellurophene nucleus (δ 8.55 at 60 MHz, presumably exchange at this labile position occurred on the alumina). The substitution at the 5-position was then made isotopically pure in the same manner as in the preparation of IV to furnish a yellow solid: 100 MHz NMR (CCl_4) slight absorption at δ 8.62 (less than 0.01H) and 7.68 (less than 0.02H), 7.0—7.5 (m, 5H), also some nondescript aliphatic absorption δ 0.8—1.8 (non-volatile impurity by GC); mass spectrum (16 eV) *m/e* (% rel. intensity) 261* (100), 132 (7), 131 (65), 130 (3).

Photolysis of V

A preparative scale photolysis of V in ether was carried out under the same conditions as the photolysis of IV except that the time was extended to 48 h. The 100 MHz NMR of the residue after work-up is discussed in the Results and discussion section. Mass spectrum (16 eV) *m/e* (% rel. intensity) 131 (13), 130 (100), 129 (6).

Acknowledgment

The authors thank the National Institutes of Health (GM16689) for generous funding of this work.

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