of 4 in 6 mL of acetonitrile was heated at 60 °C for 24 h. After the ampule was unsealed, 163 mg (1.5 mmol) of benzyl alcohol was added to the resulting solution and reacted for additional 24 h. The reaction mixture was analyzed by GLC with both a 30% SE-30 and a $DEGS_{12}$ column at 105 and 110 °C. The yield of 14 was 74% based on TCNQ.

Registry No. 1, 1072-59-9; 2, 931-57-7; 3, 19980-43-9; 4, 6651-36-1; 5, 80975-78-6; 6, 80975-79-7; 7, 80975-80-0; 8, 80975-81-1; 9, 80965-28-2; 10, 80965-29-3; 12, 80975-82-2; 13, 17888-62-9; 14, 14642-79-6; TCNQ, 1518-16-7.

Preparation of 2,6-Diphenyl-4*H*-chalcogenapyran-4-ones

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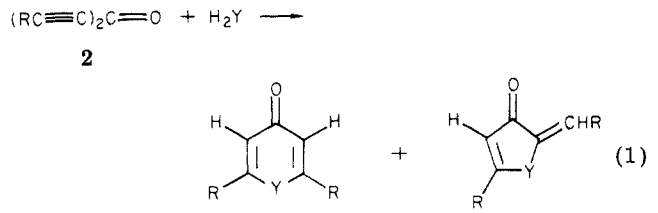
4*H*-Chalcogenapyran-4-ones (1; R = hydrogen, alkyl, or aryl) are compounds of considerable theoretical interest and practical use.[1] Although sulfur analogues have been studied since early in this century,[2] the corresponding selenium compounds have been prepared only recently.[3] The 4*H*-tellurapyran-4-ones have not been reported. Herein we report a facile, high-yield preparation of the 2,6-diphenyl-4*H*-chalcogenapyran-4-ones 1 from 1,5-diphenyl-1,4-pentadiyn-3-one (2, R = Ph).

An obvious approach to compounds 1 is illustrated in eq 1, in which a hydrogen chalcogenide is added across the



(1)

1a, Y = S; R = Ph
b, Y = Se; R = Ph
c, Y = Te; R = Ph

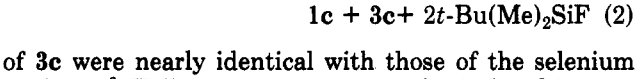
3a, Y = S; R = Ph
b, Y = Se; R = Ph
c, Y = Te; R = Ph

triple bonds of a diacetylenic ketone. Such an approach has been used with various degrees of success for 2,6-dimethyl- and 2,6-diphenylthiapyranones (1a[4,5] and 1, R = Me[4]) and for 2,6-dimethyl- and 2,6-diphenylselenapyranones (1b and 3, R = Me).[3] The instability of hydrogen telluride has precluded its use in similar reactions.

The major problems of this approach have been low yields and the unpredictable generation of chalcogenacyclopentenone derivatives 3.[3,6] In view of earlier work on "anti-Michael" additions of thiols and selenols to aryl propiolates,[7] we felt that formation of products of type 3 could be eliminated by adding the elements of hydrogen chalcogenides across diacetylenic ketones under strongly basic conditions. Such conditions would minimize the concentration of species containing chalcogen-hydrogen bonds, which are believed to be necessary for the "anti-Michael" addition.[7]

When dilithium chalogenides were added to 2 (R = Ph) under basic conditions, 1a-c were obtained in good yields (70%, 70%, and 51%, respectively). The dilithium chalcogenides were prepared from elemental sulfur, selenium shot, or tellurium shot with lithium triethylborohydride in tetrahydrofuran (THF).[8] Ethanolic THF solutions of the chalcogenides which were 0.3 M in sodium ethoxide were added to cold (0 °C) ethanolic THF solutions of 3 which were 0.5 M in sodium ethoxide. The inverse addition and added base were important to the success of the reaction. Commercially available dilithium sulfide was used to give 1a in similar yields.

None of the isomeric materials 3 were detected. The presence of 3c was rigorously excluded only after its preparation by an alternative procedure. The unknown tellurium analogue 3c was isolated in 28% yield from the reaction of bis(*tert*-butyldimethylsilyl) telluride[9] with tetra-*n*-butylammonium fluoride in the presence of 2 and *tert*-butyl alcohol in THF (eq 2). The spectral properties



(2)

of 3c were nearly identical with those of the selenium analogue.[3] Telluropyranone 1c was also isolated in 19% yield. This method represents a poorer but alternative preparation of 1c.

The preparation of the 4*H*-chalcogenapyran-4-ones by this procedure offers much better yields than the literature precedent for 1b[3] and allows the facile preparation of the tellurium analogue 1c. The preparation of 1a by this method is quite competitive with more elegant procedures starting with dibenzalacetone and hydrogen sulfide.[10]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. ^1H NMR spectra were run on a Varian EM390 instrument. IR spectra were run on a Perkin-Elmer 137 spectrophotometer. Microanalyses were performed on a Perkin-Elmer C, H, and N analyzer.

Preparation of 1,5-Diphenyl-1,4-pentadiyn-3-one (2). The diacetylenic ketone 2 was prepared from a slight modification of a method described earlier by Chauvelier.[11] Under a nitrogen atmosphere, magnesium turnings (19.2 g, 0.800 mol) were placed in 250 mL of anhydrous ether. The resulting mixture was cooled to 0 °C, and ethyl bromide (65.5 g, 0.601 mol) in 60 mL of anhydrous ether was added dropwise at a rate sufficient to maintain gentle reflux. (A crystal of iodine was added to initiate reaction.) After the addition of ethyl bromide was complete, phenylacetylene (64.5 g, 0.630 mol) was added dropwise with cooling. When the addition was complete, the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was cooled to 0 °C, and ethyl formate (23.3 g, 0.315 mol) was added dropwise. After the addition was complete, 200 mL of ether was immediately added, followed by the dropwise addition at 0 °C of 200 mL of 6 N hydrochloric acid (exothermic, foaming). The organic layer was separated, washed with dilute hydrochloric acid, dried over magnesium sulfate, and concentrated. The residue was crystallized from ligroine to give 54.5 g (78.3%) of a tan solid, mp 69-72 °C (lit.[11] mp 69 °C). A second run on the same scale gave 56.0 g (80%) of 1,5-diphenyl-1,4-pentadiyn-3-ol, mp 69-72 °C.

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1,5-Diphenyl-1,4-pentadiyn-3-ol (56.0 g, 0.241 mol) was dissolved in 240 mL of acetone and cooled to ice-bath temperature. Kiliani reagent[12] was prepared by adding sodium dichromate (45 g, 0.15 mol) to a cooled solution of sulfuric acid (60 g) in 200 mL of water. This solution was added dropwise over 30 min to the diynol. The reaction mixture was poured over 1500 g of ice. The product was extracted with methylene chloride (1 × 800 mL, 2 × 200 mL). The combined methylene chloride extracts were dried over $MgSO_4$ and filtered through a short Florisil column. Concentration and recrystallization of the residue from ligroine gave 40.0 g (72%) of **2** as a yellow solid, mp 65–65 °C (lit.[11] mp 60 °C).

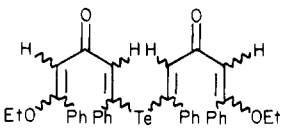
Preparation of 2,6-Diphenyl-4*H*-thiapyran-4-one (1a). Undr a nitrogen atmosphere was added 40 mL of a 1 M solution of lithium triethylborohydride in THF (0.040 mol) to sulfur (0.64 g, 0.020 mol). The reaction mixture was stirred at room temperature for 1 h, and 80 mL of a 1 M solution of sodium ethoxide in ethanol was added. The resulting solution was added dropwise over 5 min to a solution of **2** (4.60 g, 0.0200 mol) in 50 mL of THF and 50 mL of 1 M sodium ethoxide in ethanol cooled in an ice bath. After 1 h at 0 °C, the reaction mixture was stirred at room (temperature for 17 h and then concentrated in vacuo. The residue was partitioned between methylene chloride and water. The methylene chloride solution was dried over sodium sulfate and concentrated to give 5.0 g (95%) of a pale yellow solid. Recrystallization from acetonitrile gave 3.71 g (70%) of **1a** as pale yellow needles: mp 132 °C (lit.[3] mp 132–133 °C); ^1H NMR ($CDCl_3$) δ 7.0 (s, 2 H), 7.35 (m, 10 H); IR (KBr) 3050, 1600, 1580, 1560, 1450, 1348, 768, 734, 695, 686 cm^{-1}.

Preparation of 2,6-Diphenyl-4*H*-selenapyran-4-one (1b). Selenium shot (3.20 g, 0.0400 mol) was treated with 80 mL (0.080 mol) of 1 M lithium triethylborohydride for 2 h as described. The dilithium selenide in 160 mL of 1 M sodium ethoxide in ethanol was added to a solution of **2** (9.20 g, 0.0400 mol) in 100 mL of THF and 100 mL of 1 M sodium ethoxide in ethanol as described. Workup as before and recrystallization from acetonitrile gave 8.63 g (70.2%) of **1b** as a tan solid: mp 147–148 °C (lit.[3] mp 145–146 °C); ^1H NMR ($CDCl_3$) δ 7.50 (m, 10 H, 7.27 (s, 2 H); IR (KBr) 3050, 1580, 1560, 1360, 910, 875, 765, 755, 696 cm^{-1}.

Preparation of 2,6-Diphenyl-4*H*-tellurapyran-4-one (1c). A procedure similar to the ones described above was followed except that the solvents were degassed with a stream of nitrogen for 15 min before use. Tellurium shot (7.65 g, 0.0600 mol) was treated with 120 mL of 1 M lithium triethylborohydride for 4 h as described. The dilithium telluride mixture in 240 mL of 1 M sodium ethoxide in ethanol was added dropwise to a solution of **2** (13.8 g, 0.0600 mol) in 200 mL of THF and 200 mL of 1 M sodium ethoxide in ethanol as described. After 1 h at 0 °C, the reaction mixture was stirred in a 35 °C bath for 17 h. A workup as described followed by careful chromatography on silica gel (50:1 w/w, eluted with 10% ethyl acetate/methylene chloride) gave crude **1c** (R_f 0.4). Recrystallization from acetonitrile gave 10.9 g (50.5%) of a yellow crystalline solid: mp 127.5–129 °C; ^1H NMR ($CDCl_3$) δ 7.47 (m, 10 H), 7.31 (s, 2 H); IR (KBr) 1570, 1550, 1430, 1310, 902, 870, 768, 755, 698 cm^{-1}; UV (CH_2Cl_2) λ_{max} 365 nm (log ϵ 4.08); mass spectrum, m/e 362 ($C_{17}H_{12}O^{130}Te$).

Anal. Calcd for $C_{17}H_{12}OTe$: C, 56.7; H, 3.4. Found: C, 56.8; H, 3.5.

A second product (R_f 0.7) was isolated as an orange-red crystalline compound: 2.1 g (10%); mp 187–190 °C. Spectral and analytical data indicated the structure I: ^1H NMR ($CDCl_3$) δ 7.45



I

(m, 10 H), 6.80 (m, 6 H), 6.45 (s, 2 H), 6.37 (m, 4 H), 5.70 (s, 2 H), 4.03 (q, 4 H, J = 7 Hz), 1.42 (t, 6 H, J = 7 Hz); IR (KBr) 1580, 1550, 1210, 1120, 1085 cm^{-1}; mass spectrum, m/e 684 ($C_{38}H_{34}O_4{}^{130}Te$).

Anal. Calcd for $C_{38}H_{34}O_4Te$: C, 66.9; H, 5.0; Te, 18.7. Found: C, 66.7; H, 5.1; Te, 18.9.

A noncrystalline mixture of other isomers of the above structure was also isolated in a 1.1-g (6%) yield.

Preparation of 2-Benzylidene-3-oxo-5-phenyl-2,3-dihydrotellurophene (3c). To a 25-mL flask, flame dried and cooled under a stream of argon, were added **2** (0.23 g, 1.0 mmol), *tert*-butyl alcohol (0.20 g, 2.7 mmol), and 5 mL of dry THF. The resulting solution was degassed with a stream of argon for 15 min. The reaction mixture was cooled to 0 °C in an ice bath, and bis(*tert*-butyldimethylsilyl) telluride (0.41 g, 1.1 mmol) was added. A degassed 1 M solution of tetra-*n*-butylammonium fluoride in THF (2.5 mL, 2.5 mmol) was added dropwise over 5 min. The resulting mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was diluted with methylene chloride, washed with brine, filtered through a Celite pad, dried over sodium sulfate, and concentrated. The residue was purified by chromatography on silica gel (50:1 w/w, eluted with methylene chloride) to give 0.10 g (28%) of **3c** (R_f 0.7; brick-orange solid; mp 123–126 °C) and 0.07 g (19%) of **1c** (R_f 0.3). For **3c**: ^1H NMR ($CDCl_3$) δ 8.40 (s, 1 H), 7.43 (m, 10 H), 7.25 (s, 1 H); IR (KBr) 1630, 1540, 1440, 1240, 1175, 762 cm^{-1}; UV (CH_2Cl_2) λ_{max} 340 nm (log ϵ 4.28), 470 (3.58); mass spectrum, m/e 362 ($C_{17}H_{12}O^{130}Te$).

Anal. Calcd for $C_{17}H_{12}OTe$: C, 56.7; H, 3.4. Found: C, 56.8; H, 3.5.

Registry No. 1a, 1029-96-5; **1b**, 52774-25-1; **1c**, 80697-46-7; **2**, 15814-30-9; **3c**, 81028-19-5; I, 81064-44-0; ethyl bromide, 74-96-4; phenylacetylene, 100-42-5; sulfur, 7704-34-9; selenium, 7782-49-2; bis(*tert*-butyldimethylsilyl)telluride, 80594-86-1.

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Novel Rearrangement of 1,2,4-Oxadiazoles to 1,2,4-Triazolinones

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It is well-known that 1,2,4-oxadiazoles undergo ring rearrangements to various other heterocyclic compounds, such as 1,2,3-triazoles,[1-3] 1,2,5-oxadiazoles,[3-8] imidazoles,[9] 1,2,4-triazoles,[10,11] benzisoxazoles,[12] 1,2,4-thiadiazoles,[13] and indazoles.[14] We now report a novel rearrangement of 3-(arylamino)-1,2,4-oxadiazoles **1** leading to 2-aryl-1,2,4-triazolin-3-ones **2**.

In the presence of sodium methoxide in methanol, oxadiazole[15] **1a** rearranged smoothly to triazolinone **2a** (Scheme I). The structure of **2a** was inferred by the consistency of its spectral features with those reported in the literature[16,17] and was subsequently confirmed by X-ray crystallographic methods. Substitutions on the phenyl ring

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