(0.2 or 1.1 mmol), and the alcohol (2.5 mmol, except with benzyl alcohol where 2.10 mmol was used) in 8 mL of methylene chloride was cooled with stirring in an ice bath. 1-Ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDCI, 2.4 mmol) was added, and the reaction mixture was stirred at 0 °C for 2 h and at room temperature overnight. The solution was concentrated to dryness in vacuo, and the residue was taken up in ethyl acetate (25 mL) and water (5 mL). The organic layer was separated, washed with saturated sodium bicarbonate (2 × 15 mL) and water (2 × 15 mL), and dried (Na_2SO_4). The solvent was removed in vacuo, and the product was purified by MPLC on a column of silica gel 60 (230–400 mesh) with hexane–acetone (9:1) as the eluant.

General Procedure of Esterification by Diazomethane. The esters listed in Table I (entries 10–13) were also prepared by esterification with diazomethane. A solution of N-protected amino acid (1.2 mmol) in absolute methanol (5 mL) was cooled to 0 °C in an ice bath, and a ice cooled solution of diazomethane (2 equiv, generated from diazald) was added. The reaction mixture was kept at 0 °C for 15 min and then overnight at room temperature. The solvent was removed, and the residue was taken up in ethyl acetate (25 mL), washed with saturated sodium bicarbonate solution (2 × 10 mL) and water (2 × 10 mL), and dried (Na_2SO_4). The solvent was removed in vacuo, and the product was purified by MPLC as above. The ester products obtained were shown to be identical (NMR, TLC) with those prepared by esterification by the carbodiimide–(dimethylamino)pyridine method.

Acknowledgment. Appreciation is expressed to the National Institutes of Health (National Institute of Allergy and Infectious Diseases, Grant AI 15759) for support of this research.

Registry No. 1, 7536-58-5; 2, 13574-13-5; 3, 80975-50-4; 4, 80963-08-2; 5, 28812-54-6; 6, 80963-09-3; Z-Ala-OH, 1142-20-7; Z-Val-OH, 1149-26-4; Z-Gly-OH, 1138-80-3; Z-Pro-OH, 1148-11-4; Boc-Gly-OH, 4530-20-5; Boc-Phe-OH, 13734-34-4; Boc-Val-OH, 13734-41-3; Boc-Ser(Bzl)-OH, 23680-31-1; Boc-Cys(Bzl)-OH, 5068-28-0; Boc-Met-OH, 2488-15-5; Boc-Orn(Cbz)-OH, 2480-93-5; Z-MeAla-OH, 21691-41-8; Z-Ala-OBu-*t*, 50300-96-4; Z-Val-OBu-*t*, 16874-02-5; Z-Gly-O-Bu-*t*, 16881-32-6; Z-Pro-O-Bu-*t*, 16881-39-3; Boc-Gly-OBzl, 54244-69-8; Boc-Phe-OBzl, 66617-58-1; Boc-Val-OBzl, 66447-55-0; Z-Ala-OMe, 28819-05-8; Boc-Val-OMe, 58561-04-9; Boc-Ser(Bzl)-OMe, 80963-10-6; Boc-Cys(Bzl)-OMe, 55478-08-5; Boc-Met-OMe, 33900-24-2; Boc-Orn(Cbz)-OMe, 2480-95-7; Z-Ala-OTce, 67850-37-7; Z-MeAla-OTce, 80963-11-7; Z-Glu(OBzl)-OH, 5680-86-4; Boc-Asp(OBzl)-OMe, 80963-12-8; Z-Glu(OBzl)-OEt, 80963-13-9; Boc-Glu(OBzl)OBzl, 80963-14-0; Z-D-Ser-Ala-OTce, 63478-49-9; Boc-MeVal-OH, 45170-31-8; Boc-Cys(Acm)-Val-OH, 80963-15-1; Z-D-Ser(Boc-Val)-Ala-OTce, 63478-50-2; Z-D-Ser(Boc-MeVal)-Ala-OTce, 68098-67-9; Z-D-Ser[Boc-Cys(Acm)-Val]-Ala-OTce, 63478-51-3.

Reaction of 7,7,8,8-Tetracyanoquinodimethane with Cyclic Enol Ethers

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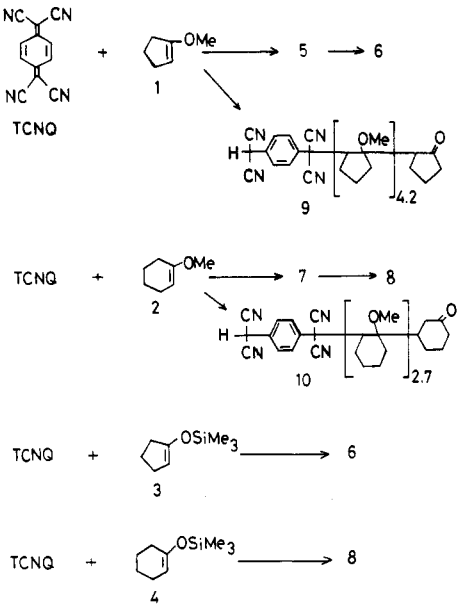
7,7,8,8-Tetracyanoquinodimethane (TCNQ)[1] is a well-known powerful π-electron acceptor. TCNQ undergoes the alternating copolymerization with styrene,[2] 2-chloroethyl vinyl ether, phenyl vinyl ether, and vinyl acetate,[3] while it causes the cationic polymerization of more powerful electron-donor monomers such as *N*-vinylcarbazole[4] and alkyl vinyl ethers.[5] For the latter reaction, Stille et al.[6] proposed that a zwitterion-type adduct is formed between TCNQ and alkyl vinyl ether and that its cationic end initiates the cationic polymerization of the alkyl vinyl ether.

Scheme I



In this paper were described the reactions of TCNQ with cyclic enol ethers such as 1-methoxy-1-cyclopentene (**1**),[7] 1-methoxy-1-cyclohexene (**2**),[7] 1-[(trimethylsilyl)oxy]-1-cyclopentene (**3**),[8] and 1-[(trimethylsilyl)oxy]-1-cyclohexene (**4**),[8] and their reaction schemes were also discussed.

Equimolar amounts of TCNQ and **1** were reacted in acetonitrile at 60 °C for 12 h. Then, the mixture was placed under reduced pressure to remove the solvent, and the solid residue obtained was found by its IR and ^1H NMR spectra to be compound **5**. The residue was chromatographed on silica gel to give a mixture of compounds **5** and **6**. Pure **5** was dissolved in aqueous ethanol with a catalytic amount of *p*-toluenesulfonic acid and was converted into **6** in quantitative yield. Comparable reaction between TCNQ and **2** gave compound **7**. On silica gel chromatography, **7** also was converted into **8**. The structures of **5**, **6**, and **8** were established by elemental analyses and IR and ^1H NMR measurements, as shown in Table I.

TCNQ and an excess amount of **1** or **2** (about 12 times the molar quantity of TCNQ) were heated at 60 °C for 48 h, and the resulting mixtures were chromatographed on silica gel to give pale yellow **9** or **10**, respectively. It was pointed out on the basis of their spectral, elemental, analysis, and molecular weight data that **9** and **10** are oligomers of **1** and **2**, respectively, with a terminal TCNQ unit and another cycloalkanone unit, conceivably derived from hydrolysis of cycloalkenyl methyl ether unit.

When equimolar amounts of TCNQ and **3** or **4** were heated in acetonitrile at 60 °C for 15 h, only one compound, **6** or **8**, was obtained, respectively, in contrast with the above-mentioned cases of **1** and **2**. Any compound

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0022-3263/82/1947-1965$01.25/0

Table I. Properties and Analysis of the Products from the Reaction of 1-4 with TCNQ

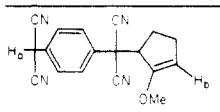
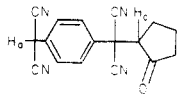
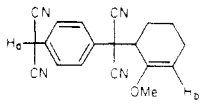
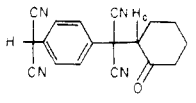
compd	mp, °C	IR, cm^{-1}	anal. calcd (found)	^{1}H NMR, δ
 5	151-152	2250 (C≡N), 1655 (C=C)	C, 71.51 (71.77) H, 4.67 (4.37) N, 18.53 (18.30)	7.62 (s, 4 H, Ar H), 5.10 (s, 1 H, H_a), 4.77 (m, 1 H, H_b), 3.58 (s, 3 H, OMe), 2.5-1.5 (m, 5 H)
 6	111-112	2250 (C≡N), 1750 (C=O)	C, 70.82 (70.82) H, 4.20 (4.21) N, 19.44 (19.15)	7.72 (s, 4 H, Ar H), 5.23 (s, 1 H, H_a), 3.03 (m, 1 H, H_c), 2.5-1.3 (m, 6 H)
 7		2250 (C≡N), 1660 (C=C)		7.55 (s, 4 H, Ar H), 5.12 (s, 1 H, H_a), 4.90 (m, 1 H, H_b), 3.53 (s, 3 H, OMe), 2.5-1.5 (m, 7 H)
 8	154-154.5	2250 (C≡N), 1710 (C=O)	C, 71.51 (71.80) H, 4.67 (4.69) N, 18.53 (18.23)	7.70 (s, 4 H, Ar H), 5.15 (s, 1 H, H_a), 3.03 (m, 1 H, H_c), 2.8-1.2 (m, 7 H)

Table II. Reaction of Enol Ethers with TCNQ

TCNQ	enol ether (amt)	product (yield)
1 mmol	1 (1 mmol)	5 (43%), 6 (38%)
103 mg	1 (614 mg)	9 (360 mg)
1 mmol	2 (1 mmol)	8 (62%)
102 mg	2 (659 mg)	10 (420 mg)
1 mmol	3 (1 mmol)	6 (94%)
1 mmol	3 (10 mmol)	6 (98%)[a]
1 mmol	4 (1 mmol)	8 (73%)
1 mmol	4 (10 mmol)	8 (98%)[a]

[a] Yield based on the amount of TCNQ.

other than 6 or 8 could not be detected when the reaction mixtures were examined by IR and ^{1}H NMR spectroscopy prior to silica gel chromatography. The reaction of an excess amount of 3 or 4 with TCNQ gave only 6 or 8, while the reaction of an excess amount of 1 or 2 with TCNQ gave the oligomers. These results are summarized in Table II and the outline of the reactions involved is shown in Scheme I.

An interaction between TCNQ and 1, 2, 3, or 4 was examined by the UV-vis spectrometric method. The spectrum of a mixture of the TCNQ solution in acetonitrile (2.13×10^{-3} M) and the donor monomer solution in acetonitrile (1.58×10^{-1} M) exhibited broad signals with four maxima in the wavelength range of 660–790 nm, attributable to the TCNQ anion radical.[9] In addition, the spectra of the 1–TCNQ and 3–TCNQ systems exhibited maximum at 480 nm, conceivably due to a charge-transfer transition between the component compounds. The spectra of the 2–TCNQ and 4–TCNQ systems exhibited an increase in intensity at the longer wavelength side (470–510 nm) of the absorption band of TCNQ probably due to the charge-transfer transition.

The reactions of TCNQ with 2 or 4 were attempted in a less polar solvent such as chloroform or benzene instead of acetonitrile. The reaction of TCNQ with 2 did not take place in these solvents. The reaction with 4 took place in chloroform to give 8 in 86% yield, while it did not in benzene. The solvent effect, which represents the important role of the polarity of the reaction medium on the reaction, implies that a charge-separation reaction should be involved in the rate-determining step.

The reactions of TCNQ with 2 or 4 were carried out in acetonitrile-d_3 in a sealed NMR tube, and their ^{1}H NMR spectra were observed with passage of time. At the beginning of the reaction the spectrum of the TCNQ–2 system exhibited two olefinic proton signals at 4.88 and 4.49 ppm, attributable to 7 and 2, respectively. As the reaction proceeded, the signal at 4.88 ppm increased in intensity whereas the signal at 4.49 ppm decreased, indicating direct conversion of 2 to 7 without the intervention of an intermediate stable enough to be detected spectroscopically by ^{1}H NMR. The spectra of the TCNQ–4 system, after the system was heated for 5 h, exhibited two kinds of aromatic proton signals at 7.70 (s) and 7.30 ppm (AB q), multiplet signals at 3.5–1.0 ppm, and a singlet at 0.50 ppm. The area ratios of the signals at 7.70 and 7.30 ppm and at 7.30 and 0.50 ppm were 1/5 and 4/9, respectively. The singlet at 7.70 ppm conceivably arises from the aromatic proton signals of 8, but no signal due to the dicyanobenzyl proton of 8 could be observed. Probably the reaction product should be different from 8 in a strict sense. When 1 drop of water was added to the reaction mixture, both signals at 7.30 and 0.50 ppm disappeared immediately and completely, while new signals at 5.70[10] and 0.05 ppm appeared, and the signal at 7.70 ppm increased in its intensity. The resulting spectrum of the hydrolyzed reaction product was similar to that of 8. However, the peak area of the signal at 5.70 ppm due to dicyanobenzyl proton is only 5.6 times as small as that of the signal 7.70 ppm, while the peak area ratio of the signal is 0.25 for 8. The IR spectrum of the reaction product was very similar to that of 8. Therefore, it is conceivable that 4 reacted with TCNQ to give the main product as an intermediate, which reacts readily with water to give compound 8 and a minor product, deuterated compound 8-*d* with a deuterium attached on the dicyanobenzyl carbon of 8.

The aromatic proton of the intermediate between TCNQ and 4 is obviously more subject to shielding than the corresponding one of 8. It was observed as an AB quartet, whereas the corresponding one was observed as a singlet, indicating equivalent protons on the benzene ring. Therefore, it is presumed that the benzene ring of the

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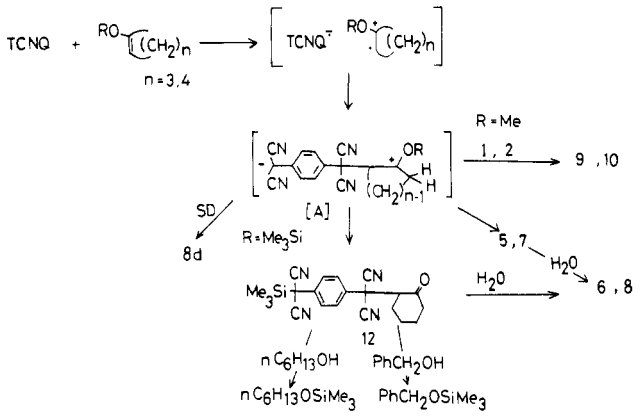
Scheme II



intermediate will be substituted with an electron-donating group and that its protons will be split into two nonequivalent kinds of protons. The trimethylsilyl proton signal of the intermediate appears at lower field than that of **4**, indicating that this trimethylsilyl group is attached to a lower electron-density part than that of **4**. Trimethylsilyl and dicyanobenzyl groups are known to be electron donating[11,12] and withdrawing, respectively. It was, therefore, supposed even though intuitively that the intermediate is an organosilane, **12**, in which both groups link directly to each other.

The supposition of **12** was supported by the following experiments. To the reaction mixture of TCNQ and **4** was added an equivalent amount of 1-hexanol or benzyl alcohol with respect to TCNQ, and the mixture was heated at 60 °C for additional 24 h. The reaction mixture was examined by GLC and found to be [(1-hexyl)oxy]trimethylsilane (**13**)[13] or (benzyloxy)trimethylsilane (**14**)[14] (68% and 74% yields, respectively). Thus, the trimethylsilyl group in the intermediate was found to be very susceptible even to a very weak base such as alcohol and water. (Trimethylsilyl)acetone, ethyl (trimethylsilyl)acetate, and (trimethylsilyl)acetonitrile were reported to react readily with ethanol to give acetone, ethyl acetate, and acetonitrile, respectively, together with ethoxytrimethylsilane,[15] indicating that a silyl group in a α position to the ketone, ester and nitrile group is susceptible to nucleophilic substitution. Therefore, organosilane **12** presumably manifests a reactivity similar to that of the intermediate.

In analogy with the Stille's mechanism[6] it can be postulated that the reactions of TCNQ with cyclic enol ethers take place as shown in Scheme II. First the zwitterionic intermediates [A] are formed probably through charge-transfer complex formation and a further electron-transfer reaction. In cases of **1** and **2**, their anionic end may attack intra- or intermolecularly protons β to their cationic end to give **5** and **7**, respectively. When **1** and **2** undergo successive addition to the cationic end of [A], the oligomers **9** and **10** are formed, respectively. In the oligomerization, the β-proton abstraction corresponds to termination reaction. In case of **4**, the anionic end of [A] may attack intra- or intermolecularly the silicon atom in [A] to give **12**, which is converted into **8** during the postreaction treatment. In addition, the anionic end abstracts a deuterium from the deuterated solvent to yield **8-d**. The reaction of TCNQ with **4** yielded only **8** regardless of the feed ratio of **4** to TCNQ. Very high reactivity of the silicon–oxygen bond of [A] to the dicyano benzyl anion end is probably responsible for the exclusive formation of **12** without oligomerization.

Experimental Section

All melting points were uncorrected. IR spectra were determined with a JASCO-IR-G spectrophotometer. ^{1}H NMR spectra were obtained on a Varian A-60 D NMR spectrometer. Elemental analyses were performed with a Yanaco MT-2-CHN corder. The molecular weights were determined with a Knaur vapor pressure osmometer. All GLC analyses were carried out on a Yanaco G 180 instrument (30% SE-30 or $DEGS_{12}$; 0.6-m column; He carrier gas).

General Procedure for Reaction of TCNQ with Enol Ethers. Given amounts of TCNQ, enol ether, and solvent were placed in an ampule, which was degassed by the freeze–thaw method (repeated three times) and then sealed. It was placed in a bath thermostated at 60 ± 0.1 °C for the time of reaction. After evaporation of the solvent, the residue was purified by chromatography on a silica gel column with chloroform–methanol as the eluent.

(A) With 1-Methoxy-1-cyclopentene (1). (a) A mixture of 203 mg (1 mmol) of TCNQ and 102 mg (1.04 mmol) of **1** in 4 mL of acetonitrile was heated for 12 h to give 130 mg of **5** and 110 mg of **6**. (b) A mixture of 103 mg (0.5 mmol) of TCNQ and 614 mg (6.27 mmol) of **1** in 2 mL of acetonitrile was heated for 80 h to give 360 mg of **9**: IR (KBr) 2250 (C≡N), 1730 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 7.8–7.3 (4 H), 5.1–4.8 (1 H), 3.8–1.0 (45 H); mol wt (VPO) 790.

Anal. Calcd for $C_{12}H_4N_4 \cdot C_5H_7O \cdot (C_6H_{10}O)_{4.2}$: C, 72.46; H, 7.64; N, 8.01. Found: C, 72.30; H, 7.37; N, 7.89.

(B) With 1-Methoxy-1-cyclohexene (2). (a) A mixture of 206 mg (1.01 mmol) of TCNQ and 114 mg (1.02 mmol) of **2** in 4 mL of acetonitrile was heated for 48 h to give 190 mg of **8**. (b) A mixture of 102 mg (0.5 mmol) of TCNQ and 659 mg (5.9 mmol) of **2** in 2 mL of acetonitrile was heated for 80 h to give 420 mg of **10**: IR (KBr) 2250 (C≡N), 1715 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 7.8–7.3 (4 H), 5.1–4.9 (1 H), 3.0–1.0 (45 H); mol wt (VPO) 510.

Anal. Calcd for $C_{12}H_4N_4 \cdot C_6H_9O \cdot (C_7H_{12}O)_{2.7}$: C, 73.35; H, 7.57; N, 9.27. Found: C, 73.85; H, 7.40; N, 9.28.

(C) With 1-[(Trimethylsilyl)oxy]-1-cyclopentene (3). (a) A mixture of **3** in 6 mL of acetonitrile was heated for 15 h to give 270 mg of **6**. (b) A mixture of 204 mg (1 mmol) of TCNQ and 1.56 g (10 mmol) of **3** in 6 mL of acetonitrile was heated for 24 h to give 282 mg of **6**.

(D) With 1-[(Trimethylsilyl)oxy]-1-cyclohexene (4). (a) A mixture of 204 mg (1 mmol) of TCNQ and 170 mg (1 mmol) of **4** in 6 mL of acetonitrile was heated for 10 h to give 220 mg of **8**. (b) A mixture of 204 mg (1 mmol) of TCNQ and 1.7 g (10 mmol) of **4** in 6 mL of acetonitrile was heated for 24 h to give 300 mg of **8**.

Hydrolysis of 5. A solution of 50 mg of **5** and 2 mg of *p*-toluenesulfonic acid in 20 mL of 95% aqueous EtOH was stirred for 6 h at room temperature. After evaporation of the solvent, the reaction mixture was analyzed by IR and then purified by chromatography on a silica gel column to give 45 mg of **6**.

General Procedure for the Reaction in an NMR Tube. In an NMR tube were placed 30 mg of TCNQ, a stoichiometric amount of **2** or **4**, and 0.4 mL of solvent. After the atmosphere was replaced with nitrogen, the tube was sealed and set in an oil bath thermostated at 60 ± 0.1 °C for the time of reaction. The tube was removed and cooled to room temperature, and then the NMR spectrum was obtained.

Reaction of Intermediate 12 with Alcohols. (a) A mixture of 305 mg (1.5 mmol) of TCNQ and 255 mg (1.5 mmol) of **4** in 6 mL of acetonitrile was heated in an ampule at 60 °C for 24 h. After the ampule was unsealed, 182 mg (1.8 mmol) of 1-hexanol was added, and then the ampule was sealed again. The reaction mixture was heated for additional 24 h. The content of the ampule was analyzed by GLC with both a 30% SE-30 and a $DEGS_{12}$ column at 90 °C. The yield of **13** was 68% based on TCNQ. (b) A mixture of 305 mg (1.5 mmol) of TCNQ and 255 mg (1.5 mmol)

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(15) Chvalousky, V. *Organomet. React.* **1972**, *3*, 191.

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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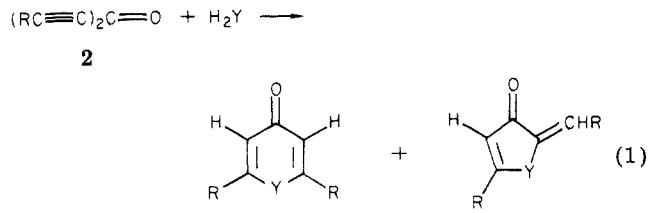
4*H*-Chalcogenapyran-4-ones (1; R = hydrogen, alkyl, or aryl) are compounds of considerable theoretical interest and practical use.[1] Although sulfur analogues have been studied since early in this century,[2] the corresponding selenium compounds have been prepared only recently.[3] The 4*H*-tellurapyran-4-ones 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

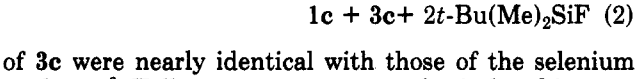
3a, Y = S; R = Ph
b, Y = Se; R = Ph
c, Y = Te; R = Ph

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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