success of the present procedure depends upon the reluctance with which the electron-deficient double bond is protonated. Thus, the procedure described here may not be generally applicable to the preparation of other β,γ-unsaturated amino acids, although this remains to be tested by experiment. The chloramine procedure is, however, an effective method for the preparation of the β-methyleneaspartic acid hydrochloride (II·HCl) described here, an instance in which a variety of other methods were not successful.

Experimental Section

1-Amino-1,1,2-tricarbethoxyprop-2-ene (VII). 1,1,2-Tricarbethoxyprop-2-ene (V)[13] (15 g, 0.058 mol) was dissolved in 200 mL of benzene in a 500-mL three-necked, round-bottomed flask equipped with an addition tube charged with sodium hydride (3.6 g, 50% dispersion in mineral oil, 0.075 mol). The reaction flask was evacuated three times and flushed with nitrogen and then cooled to 0 °C. The sodium hydride was added slowly at a rate such that the evolution of hydrogen and attendant foaming were controlled. When the addition was complete, the ice bath was removed and the solution was stirred at room temperature for 1 h. The benzene was removed under vacuum, yielding the white solid sodium salt VI. The solid VI was suspended in 140 mL of ether, placed in a dropping funnel, and added to 185 mL of an ice-cold, stirred solution of chloramine (0.63 M) in ether. When the addition was complete, the reaction mixture was stirred for 1 h at 0 °C. The ice bath was removed and the reaction was allowed to warm to room temperature and stirred for an additional 2-h period. The reaction mixture was then filtered and extracted with four 20-mL portions of a 10% HCl solution. The combined aqueous acid layers were made basic with Na_2CO_3 and extracted with four 20-mL portions of ether. The combined ether layers were dried with $MgSO_4$ and concentrated under vacuum, yielding 9.205 g of a light green oil.

The crude product from three such amination reactions was placed on a column of 65 g of silica gel and eluted with 60:40 hexane–ethyl acetate; 200-mL fractions were collected. The course of chromatographic purification can be followed by using thin-layer chromatography. The desired amino triester VII is characterized by R_f 0.57 in 50:50 benzene–hexane. Fractions 2 and 3 contain pure product and were combined, yielding 31 g (65%) of colorless oil.

The amino triester VII showed in its proton NMR spectrum (CCl_4) a nine-proton methyl triplet (J = 7 Hz) at δ 1.27, a two-proton amine singlet at δ 2.18, a six-proton methylene quartet at δ 4.13, and a pair of one-proton vinyl singlets at δ 5.87 and 6.17. The carbon-13 NMR spectrum ($CDCl_3$) showed peaks at 13.24 (quartet, $\mathbf{C}H_3CH_2O$), 60.51 (triplet, $CH_3\mathbf{C}H_2O$), 61.56 (triplet, $CH_3\mathbf{C}H_2O$), 67.33 (singlet, CNH_2), 125.32 (triplet, $\mathbf{C}H_2{=}C$), 130.37 (singlet, $CH_2{=}\mathbf{C}$), 164.87 (singlet, COOEt), and 169.17 (singlet, COOEt) ppm relative to tetramethylsilane as an internal standard. The infrared spectrum (neat) showed a carbonyl band at 1730 cm^{-1} and NH_2 bands at 3320 and 3400 cm^{-1}. The mass spectrum (70 eV) showed m/e (percent relative intensity) 274 (7.1, M^+ + H), 227 (4.6, M^+ - EtOH), 200 (100, M^+ - COOEt), 172 (12.7, M^+ - COOEt - C_2H_4), 154 (1.06, M^+ - COOEt - EtOH), 153 (11.5, M^+ - COOEt - EtOH - H), 127 (90.1, M^+ - 2 COOEt - H), and 98 (76.1 $HC{=}CCOOEt^+$). Exact mass calcd for $C_9H_{14}NO_4$, 200.0923; found, 200.0916.

β-Methyleneaspartic Acid Hydrochloride (II·HCl). The amino triester VII (2 g, 0.007 mol) was dissolved in 21 mL of a 20% hydrochloric acid solution in a 50-mL round-bottomed flask. The reaction was heated 82 h at 65 °C. The solvent was removed, yielding 1.46 g of white foam. The continued presence of an ethyl ester absorption in the NMR spectrum showed that the reaction was not complete. The residue was taken up in 20 mL of fresh acid solution, and the mixture was heated for 23 h at 65 °C. Evaporation of the aqueous solution yielded 1.462 g of a very hygroscopic noncrystalline product. The NMR spectrum (CD_3OD) showed a one-proton methine singlet at δ 4.97, a pair of one-proton vinyl singlets at δ 6.33 and 6.67, and a three-proton broad singlet (OH and NH) at δ 5.77. When the decarboxylation was carried out in DCl–D_2O the singlet at δ 4.97 was absent from the NMR spectrum. The infrared spectrum (KBr) showed a very broad, strong peak at 3500–2750 cm^{-1} together with expected bands at 1710 and 1630 cm^{-1}.

(±)-β-Methyleneaspartic Acid. A solution of 4.2 g of amino triester VII in 50 mL of 20% hydrochloric acid was heated for 68 h at 74 °C. The solution was then taken to dryness, leaving a yellow hygroscopic solid. An NMR spectrum of the solid showed that the hydrolysis was not complete. The solid was redissolved in 50 mL of fresh 20% hydrochloric acid, and the mixture was heated for an additional 48 h at 74 °C. The reaction mixture was concentrated under vacuum, leaving a solid residue. The solid was treated with small portions of a solution of 2 N sodium hydroxide until the solid dissolved and the pH of the solution became approximately 5 (approaching the isoelectric point). At this point 1.08 g of a white solid precipitated from the solution. The mother liquor was made acidic with 10% hydrochloric acid, concentrated under vacuum, and re-treated with 4 N NaOH, yielding a white solid. Two further repetitions of the latter process gave a total of 0.78 g of white solid of sufficient purity that it was combined with the first crop above. The total crude weight of the desired amino acid II was 1.87 g (84% yield). The product thus obtained was slightly off-color, but the NMR spectrum taken as the hydrochloride (D_2O/DCl, TSP reference) showed only the expected three singlets at δ 5.02, 6.37, and 6.73 together with a solvent singlet at δ 5.16. The carbon-13 NMR spectrum (D_2O/DCl, $CHCl_3$ external reference taken as 77.20 ppm) showed a pair of carboxyl singlets at 167.12 and 169.73 ppm, a vinyl triplet at 136.59 ppm, a vinyl singlet at 131.65 ppm, and a methine doublet at 53.93 ppm.

Crystallization from 15 mL of hot water yielded 1.59 g (72%) of white crystalline product II. The amino acid II does not have a sharp melting point; it begins to decompose at 170 °C, becoming progressively darker in color as the temperature is raised above this point.

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Registry No. (±)-II, 71195-09-0; (±)-II·HCl, 71195-10-3; V, 71195-11-4; VI, 71195-12-5; VII, 71195-13-6.

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Organotellurium Chemistry. 3. (*o*-Nitrophenyl)tellurenyl Bromide: A Highly Stabilized Tellurenyl Halide

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Among the arylchalcogen monohalides, the synthetically valuable arylselenenyl halides[1] have been the object of much more intensive study by organic chemists than their less stable sulfur[2] and tellurium[3] counterparts. The least-studied class of this group has been the aryltellurenyl

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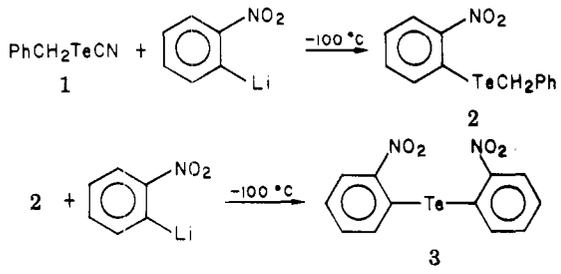
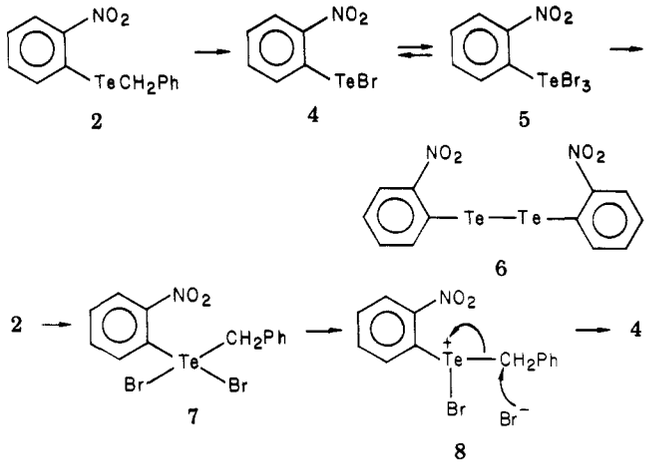
0022-3263/79/1944-3957$01.00/0

Scheme I



Scheme II



halides (ArTeX), the simpler members of which seem to be thermally unstable and polymeric in nature.[4] Recent work by Renson[5] has shown, however, that tellurenyl halides bearing an *o*-carbonyl-containing function are isolable crystalline compounds. This intramolecular coordination effect is apparently related to the well-known stabilization of arylsulfenyl chlorides by an *o*-nitro substituent.[6]

The object of the work reported here was the synthesis of the hitherto unknown (*o*-nitrophenyl)tellurenyl bromide (**4**). We felt that **4** should be a sufficiently stable substance to enable us to investigate its possible utility as a synthetic reagent.

Results and Discussion

We have shown earlier that the readily prepared benzyl tellurocyanate (**1**) undergoes Te–CN bond cleavage on treatment with a variety of reagents, including bromine, α-toluenethiol, hypophosphorus acid, and sodium hydroxide.[7] Although no reaction of **1** with a carbanion has yet been reported, it seemed reasonable to expect that an aryllithium should displace a cyanide ion from **1** with the formation of an aryl benzyl telluride. Indeed, *o*-nitrophenyllithium,[8] generated from *o*-nitroiodobenzene and phenyllithium at −100 °C, reacted smoothly with benzyl tellurocyanate to give, in 72% yield, the orange-red *o*-nitrophenyl benzyl telluride (**2**), mp 85–86 °C. A minor (2%) tellurium-containing product of the reaction proved to be bis(*o*-nitrophenyl) telluride[9] (**3**). The latter compound arose by attack of the *o*-nitrophenyl anion on the benzyl telluride **2**; it could indeed be obtained in fair yield (20%) by treating *o*-nitrophenyl benzyl telluride with *o*-nitrophenyllithium under the original reaction conditions.

Simple aryl benzyl tellurides have been cleaved previously by bromine to give benzyl bromide and an aryltellurium tribromide, no intermediate being detectible.[10] Indeed, telluride **2** reacted smoothly with excess bromine (3.5 equiv) in carbon tetrachloride solution to give, in 95% yield, the yellow crystalline (*o*-nitrophenyl)tellurium tribromide (**5**), mp 164–165 °C. When tribromide **5** was stirred at 0 °C for 3 h with excess aqueous sodium bisulfite,[11] it was converted in 91% yield to the red-orange bis(*o*-nitrophenyl telluride) (**6**), mp 204–206 °C. Treatment of ditelluride **6** with 1 equiv of bromine in carbon tetrachloride solution resulted in immediate cleavage of the Te–Te bond with the formation of the desired (*o*-nitrophenyl)tellurenyl bromide (**4**) in 90% isolated yield.

Bromide **4** forms red-black crystals, mp 75–76 °C. It appears to be stable indefinitely in the solid state. It dissolves readily in dichloromethane, acetone, and ethyl acetate to give deep red solutions from which it is recovered on solvent evaporation. More surprisingly, it remains unchanged on recrystallization from ethanol. Its mass spectrum shows both a molecular ion and an M–Br ion. Its structure was confirmed by elemental analysis and its reaction with excess bromine to give tribromide **5**.

The remarkable stability of (*o*-nitrophenyl)tellurenyl bromide encouraged us to seek shorter alternative methods of synthesis. It was found that the reaction of tribromide **5** with 2 equiv of cold aqueous sodium bisulfite afforded bromide **4** in over 90% yield. To our knowledge, this reaction represents the first example of the controlled reduction of an aryltellurium trihalide to the corresponding tellurenyl halide.

Finally, it was found that direct treatment of *o*-nitrophenyl benzyl telluride (**2**) with 1 equiv of bromine in carbon tetrachloride solution at 25 °C, followed by brief warming of the reaction mixture, yielded the tellurenyl bromide **4** in 90% yield; benzyl bromide was also obtained in 71% yield. This reaction proceeds in two stages, since the deep red color of the final product develops only after warming the initially yellow solution. We propose that the initial product is an (arylbenzyl)tellurium dibromide (**7**), which collapses to benzyl bromide and the tellurenyl bromide by way of the transient ion pair **8**.

The ready accessibility of (*o*-nitrophenyl)tellurenyl bromide, as well as its stability, make it an ideal substance for study as a potential analogue of the arylselenyl halide reagents; a study of its behavior with various organic substrates is underway in our laboratory.

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Mass, infrared (KBr), and ultraviolet spectra were determined, using Perkin-Elmer 270B, 137, and 202 spectrometers, respectively. All tellurium-containing mass peaks are reported for ^{130}Te. NMR spectra were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ units. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

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o-Nitrophenyl Benzyl Telluride (2). To a dry, three-necked flask was added a solution of o-nitroiodobenzene (8.98 g, 36 mmol) in THF (freshly distilled from $LiAlH_4$). The mixture was stirred at −100 °C (liquid N_2/Et_2O) under argon while a solution of phenyllithium (19.2 mL of a 1.89 M solution in ether–benzene) was introduced slowly via syringe. The mixture was stirred at −100 °C for 50 min. Further manipulation was conducted in the dark. Benzyl tellurocyanate (8.78 g, 36 mmol) was added quickly, and the mixture was stirred at −100 °C for 4 h and left to warm to 25 °C overnight. The solvent was removed in vacuo, and the residue was partitioned between water and benzene. The aqueous layer was separated and extracted with benzene. The combined organic layers were dried (Na_2SO_4) and removed in vacuo to yield a deep red gum. Column chromatography over neutral alumina (hexane elution) followed by recrystallization from hexane afforded o-nitrophenyl benzyl telluride (2) as orange needles (8.81 g, 72%): mp 85–86 °C; UV (EtOH) max 210 (16 800), 222 (17 000), 266 nm (9400); IR (KBr) 1580, 1575, 1490, 1250, 1050, 850; NMR ($CDCl_3$) δ 8.35–8.55 (m, 1 H), 7.15–7.92 (m, 9 H), 4.26 (s, 2 H); MS m/e 343 (M^+), 252, 106 (base). Anal. Calcd for $C_{13}H_{11}NO_2Te$: C, 45.81; H, 3.25; N, 4.11. Found: C, 45.77; H, 3.33; N, 4.01.

Further elution with hexane yielded red crystals of bis(o-nitrophenyl) telluride (3) (0.28 g, 2.1%), after recrystallization from hexane, mp 138–142 °C. Recrystallization from hexane afforded an analytical sample: mp 141–142 °C; IR (KBr) 1500, 1310, 1295, 788, 715; MS 374 (M^+), 106 (base). Anal. Calcd for $C_{12}H_8N_2O_4Te$: C, 38.74; H, 2.17; N, 7.54; Te, 34.52. Found: C, 38.65; H, 2.05; N, 7.55; Te, 34.07.

When o-nitrophenyllithium was generated as above and treated with 1 equiv of o-nitrophenyl benzyl telluride (2), bis(o-nitrophenyl) telluride (3) was produced in 20% yield, and 2 was recovered in 68% yield.

(o-Nitrophenyl)tellurium Tribromide (5). A solution of 2 (3.43 g, 10 mmol) in carbon tetrachloride was treated dropwise with a solution of bromine (5 g, 31.25 mmol) in carbon tetrachloride. The color of the mixture turned from orange to pale yellow and eventually red. After the solution was warmed for 5 min on a steam bath, hexane was added, and the solution was left to cool. Filtration afforded yellow needles of (o-nitrophenyl)tellurium tribromide (4.45 g, 95%): mp 164–165 °C; UV (EtOH) λ_{max} 306 (16 600), 285 (5100); IR (KBr) ν 1580, 1550, 1490, 1470, 1270, 1030, 1100, 850; MS m/e (M − Br) 252, 106 (base). Anal. Calcd for $C_6H_4NO_2TeBr_3$: C, 14.72; H, 0.82; N, 2.86; Br, 48.98. Found: C, 14.81; H, 0.85; N, 2.78; Br, 48.85.

Bis(o-nitrophenyl telluride) (6). To a stirred solution of sodium bisulfite (1.624 g, 6 mmol) in water at 0 °C was added 5 (0.492 g, 1 mmol). After 3 h at 25 °C, the orange solid which had formed was filtered, dried with suction, washed with hexane, then recrystallized from benzene–hexane to yield reddish-orange needles of bis(o-nitrophenyl telluride) (6) (0.225 g, 91%): mp 204–206 °C dec; UV (EtOH) λ_{max} 210 (35 000), 245 (16 200); IR (KBr) 1580, 1550, 1470, 1400, 1280, 1160, 850; MS m/e 504 (M^+), 252, 234, 106 (base). Anal. Calcd for $C_{12}H_8N_2O_4Te_2$: C, 28.86; H, 1.61; N, 5.61; Te, 51.10. Found: C, 28.98; H, 1.62; N, 5.54; Te, 51.35.

(o-Nitrophenyl)tellurenyl Bromide (4). A stirred solution of 6 (0.5 g, 1.0 mmol) in carbon tetrachloride was treated dropwise with a solution of bromine (0.054 mL, 1.0 mmol) in carbon tetrachloride. After the solution was stirred for 30 min, the solvent was removed in vacuo, and the deep red residue was crystallized from petroleum–ether to yield (o-nitrophenyl)tellurenyl bromide (4) (0.395 g, 90%) as a deep red solid, mp 72–74 °C. Two recrystallizations from ethanol afforded an analytical sample: mp 75–76 °C; IR (KBr) 1590, 1490, 1325; MS m/e 330 (M^+), 255 (M − Br, base); exact mass 330.8483 (calcd for $C_6H_4NO_2TeBr$ 330.8492). Anal. Calcd for $C_6H_4NO_2TeBr$: C, 21.86; H, 1.22. Found: C, 22.15; H, 1.14.

Controlled Bromination of o-Nitrophenyl Benzyl Telluride. A solution of 2 (0.342 g, 1.0 mmol) in carbon tetrachloride was treated dropwise with a solution of bromine (0.055 mL, 1.0 mmol) in carbon tetrachloride. After the addition was complete, the yellow solution was heated on a steam bath for 20 min. The resultant deep red solution was cooled, and the solvent was removed in vacuo. Column chromatography over silica gel (hexane elution) afforded benzyl bromide (0.12 g; 71%) which was identical (IR) with an authentic sample. Further elution with ether afforded (o-nitrophenyl)tellurenyl bromide (4) (0.3 g; 90%) indistinguishable from a sample prepared as before from 6.

Conversion of (o-Nitrophenyl)tellurenyl Bromide to o-Nitrophenyl Tellurium Tribromide. A solution of 4 (0.059 g, 0.179 mmol) in carbon tetrachloride was treated dropwise with bromine (0.022 mL, 0.4 mmol) in carbon tetrachloride. A yellow solid precipitated immediately, and the slurry was stirred at 25 °C for 3 h. The mixture was diluted with petroleum–ether and suction filtered to yield (o-nitrophenyl)tellurium tribromide (5) (0.065 g, 75%) as a yellow solid which was identical with a sample prepared as before.

Controlled Reduction of (o-Nitrophenyl)tellurium Tribromide. To a stirred suspension of 5 (1.0 g, 3.0 mmol) in water at 0 °C was added solid sodium bisulfite (0.42 g, 6.0 mmol) in small portions over a period of 20 min. The resultant deep red slurry was stirred for 20 min at 0 °C and suction filtered. The red paste was dissolved in CH_2Cl_2, filtered through glass wool, diluted with hexane, and crystallized to yield (o-nitrophenyl)tellurenyl bromide (4) (0.59 g, 89%) as a deep red solid which was indistinguishable from a sample prepared as before.

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Registry No. 1, 62404-99-3; 2, 71129-53-8; 3, 71129-54-9; 4, 71129-55-0; 5, 71129-56-1; 6, 71129-57-2; o-nitroiodobenzene, 609-73-4; o-nitrophenyllithium, 27329-57-3; benzyl bromide, 100-39-0.

Structure and Stereochemistry of Condensation Products from 1-Morpholino-1-cycloheptene and Methyl Vinyl Ketone

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In order to examine the effect of substituents and ring size on the course of photochemically induced rearrangements of β,γ-unsaturated ketones,[1] we wanted to prepare compound 1. Our projected synthesis paralleled the reported synthesis of 2 and utilized the reaction between 1-morpholino-1-cycloheptene and methyl vinyl ketone.[2] While, however, the reported procedure yields

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