Table I. Yields[a] of Ar–S–S–Ar (2) from Reaction of $ArN_2^+BF_4^-$ (1) with NaI in a 1:1 Acetone/Carbon Disulfide Mixture

Ar	Registry no.	Yield, %	Ar	Registry no.	Yield,[a] %
Phenyl[6]	882-33-7	47	*m*-Anisyl[11]	59014-89-0	46
o-Tolyl[7]	4032-80-8	60	*p*-Tolyl[12]	103-19-5	45
o-Anisyl[8]	13920-94-0	10	*p*-Anisyl[13]	5335-87-5	45
2-Biphenylyl[4]	19813-97-9	33	*p*-Nitrophenyl[14]	100-32-3	34
o-Phenylthiophenyl[9]	58074-47-8	45	*p*-Chlorophenyl[15]	1142-19-4	40
o-Methylthiophenyl[10]	59014-88-9	0	2,6-Xylyl[16]	2905-17-1	30

[a] Based on the starting aryldiazonium fluoroborate (1).

well-dried samples of diaryldiazonium fluoroborates were used. Carbon disulfide was dried with calcium chloride and then distilled twice. Acetone was refluxed over $KMnO_4$ and distilled over P_2O_5 twice.

Decomposition of Aryldiazonium Fluoroborate (1). General Procedure. The salt (0.01 mol) was dissolved in acetone (30 ml). To the solution was first added CS_2 (30 ml) and then NaI (1.5 g) in small quantities under stirring. After nitrogen evolution the mixture was refluxed for 30 min and the solvent evaporated. The crude was dissolved in chloroform, washed with water and dried and the solvent removed under vacuum. The mixture was analyzed on GLC or chromatographed on a silica gel column.

A. From 1 (R = Ph) diphenyl disulfide (**2**, 47%) and diphenyl trithiocarbonate (**3**, 35%) were separated by column chromatography on silica gel, using light petroleum as an eluent.

B. From 1 (R = *o*-PhPh) were obtained 2-iodobiphenyl, 2-biphenylyl disulfide (**2**, 33%), and a yellow product identified as di-2-biphenylyl trithiocarbonate (**3**, 30%): mp 119 °C; mass spectrum *m/e* 414 ($M^{\cdot+}$, 11), 370 (6), 338 (35), 229 (100), 197 (40), 185 (39), 184 (43), 152 (40). Anal. Calcd for $C_{25}H_{18}S_3$: C, 72.42; H, 4.38; S, 23.22. Found: C, 72.1; H, 4.4; S, 23.4.

C. From 1 (R = *o*-PhPh) at 0 °C. The salt (0.01 mol) was dissolved in acetone (30 ml) under nitrogen in the dark and CS_2 (30 ml) was added. The solution was cooled to −5 to 0 °C and NaI (1.5 g) was added slowly under stirring. After 10 min, the nitrogen flow was increased and the solvent evaporated at 0 °C. The crude was rapidly extracted with light petroleum, and the organic layer filtered on silica gel (h = 15 cm) under nitrogen. A dilute solution of 2-biphenylyl iododithioformate (**4**) was obtained, and was kept at −20 °C. This solution, gently heated at 30–40 °C, or exposed to uv light, rapidly affords iodine, 2-biphenylyl disulfide (**2**), and di-2-biphenylyl trithiocarbonate (**3**) identified by TLC. An alcoholic solution of **4** gives a positive test with alcoholic $AgNO_3$: mass spectrum *m/e* 356 ($M^{\cdot+}$) (0.5), 280 (100), 184 (35), 185 (45), 153 (100).

D. From 1 (R = Ph) in Furan. The salt (0.01 mol) was suspended in a furan (30 ml) and CS_2 (30 ml) mixture, and NaI (1.5 g) was added in small quantities under stirring at room temperature. The solution was stirred for 5 h, washed with water, and dried, and the solvent was evaporated. By column chromatography of the crude on silica gel were separated diphenyl disulfide (**2**, traces) and phenyl 2-dithiofuroate (**8**, 75% yield) as a red oil: bp 85 °C (1 mm); mass spectrum *m/e* 220 ($M^{\cdot+}$, 21), 111 ($M^{\cdot+}$ − PhS·, 100). Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.0; H, 3.65; S, 29.4.

Photolysis of 2-Iodobiphenyl. A solution of 2-iodobiphenyl (0.9 g, 0.005 mol) in Et_2O (8 ml) and CS_2 (2 ml) mixture was photolyzed using a low-pressure mercury lamp Hanau Type P.L. 368 for 12 h. By column chromatography of the reaction mixture on silica gel, unreacted starting product (0.7 g), 2-biphenylyl disulfide (**2**, 30%), and di-2-biphenylyl trithiocarbonate (**3**, 30%) were separated.

Reaction of 2-Biphenylyl Chlorodithioformate (6) with $AlCl_3$. A solution of **6** (2.4 g, 0.0092 mol) in CS_2 (35 ml) was added at room temperature to a suspension of $AlCl_3$ (1.37 g, 0.0103 mol) in CS_2 (23 ml) under stirring. The mixture was refluxed for 1 h, and then poured into a cold solution of $NaHCO_3$, then extracted with Et_2O. The organic layer was dried and the solvent removed under vacuum. Dibenzo[*c*,*e*]thiin-2-thione (**7**) was obtained in quantitative yield as a red solid, mp 106–107 °C, which crystallizes from light petroleum (bp 75–120 °C): mass spectrum *m/e* 228 ($M^{\cdot+}$, 100), 184 (65). Anal. Calcd for $C_{13}H_8S_2$: C, 68.38; H, 3.53; S, 28.08. Found: C, 68.4; H, 3.53; S, 28.2.

2-Biphenylyl chlorodithioformate (6) was prepared according to the general procedure described by Rivier:[21] bp 164–165 °C; mass spectrum *m/e* 264 ($M^{\cdot+}$, 15), 229 (14), 185 (100), 152 (29).

Acknowledgment. We acknowledge support from the Consiglio Nazionale delle Ricerche, Rome.

Registry No.—1 (R = Ph), 369-57-3; 1 (R = *o*-MePh), 2093-46-1; 1 (R = *o*-MeOPh), 17685-76-6; 1 (R = *o*-PhPh), 318-13-8; 1 (R = *o*-PhSPh), 59014-91-4; 1 (R = *o*-MeSPh), 52959-17-8; 1 (R = *m*-MeOPh), 17569-84-5; 1 (R = *p*-MePh), 459-44-9; 1 (R = *p*-MeOPh), 459-64-3; 1 (R = *p*-NO_2Ph), 456-27-9; 1 (R = *p*-ClPh), 673-41-6; 1 (R = 2,6-diMePh), 2192-33-8; **3** (R = Ph), 2314-54-7; **3** (R = *o*-PhPh), 59014-92-5; **4** (R = *o*-PhPh), 59014-93-6; **6**, 54199-77-8; **7**, 54199-60-9; **8** (R = Ph), 59014-94-7; NaI, 7681-82-5; carbon disulfide, 75-15-0; 2-iodobiphenyl, 2113-51-1.

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A New Route to Acetylenes

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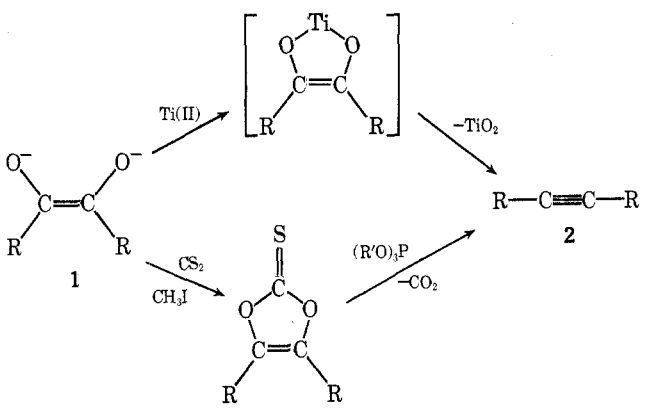
Most synthetic approaches to the formation of carbon–carbon triple bonds[1] involve eliminations which, unless the reactant is suitably constituted, can also lead to isomeric allenes, dienes, etc. A particularly useful acetylene synthesis, especially for strained cyclic acetylenes, is the conversion of an α-diketone to its bishydrazone, followed by oxidation (net *reduction* of carbon) with, e.g., mercuric oxide[2] or lead tetraacetate.[3]

In our quest for synthetic routes to a novel cyclic acetylene,

we attempted under many conditions but without success to make the bishydrazone of a tetra-α-substituted cyclic diketone. We attributed these failures to steric hindrance of attack at the carbonyl groups, as previously seen in attempts to make the 2,4-DNP derivative of hindered α-diketones such as dipivaloyl.[4] During this period there appeared in the literature two novel olefin syntheses which we hoped could be extended to acetylenes. McMurry[5] found that treatment of certain carbonyl compounds with titanium trichloride–lithium aluminum hydride complex led to olefins via reductive coupling. Similarly, Paquette[6] reported that vicinal diols react with carbon disulfide to form thiocarbonates, which give olefins upon treatment with phosphite esters.

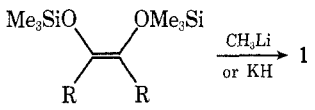
Scheme I



1a, R = C_6H_5
b, R = n-C_3H_7
c, 2R = -$(CH_2)_{10}$-

Scheme I shows how both of these might be used in acetylene syntheses. The key to this route is anion **1**, which is the intermediate in the acyloin condensation, and can also be prepared by reducing the corresponding α-diketones with ethylmagnesium bromide.[7] Note, however, that the success of Scheme I depends on **1** having cis stereochemistry, which is almost certainly less favorable than the trans isomer on both steric and electrostatic grounds. In fact **1** should resemble an α-diketone, but its barrier to rotation should be higher. Except when the R groups comprise a small ring, α-diketones prefer the s-trans geometry.[8] Thus we were not discouraged when initial attempts to make acetylenes via this route were unsuccessful. We also attempted without success to prepare **1** from α-diketones with "activated" magnesium,[9] in hopes that the incipient magnesium ions would coordinate best to cis oxygens.

The need for a covalent precursor to *cis*-**1** was, however, filled by the known[10] bis(trimethylsilyl) ethers (**3**), the stereoisomers of which are usually separable. Treatment of the cis diether with methyllithium[11] or potassium hydride[6] would then give only *cis*-**1**.[10d]



3

Starting with the known[10] ethers **3a–c**, attempts were first made to treat the corresponding anions **1a–c** with McMurry's reagent.[5] The reaction mixtures were complex, comprising only ca. 5% of the desired acetylenes, together with major amounts of the related olefins, diketones, ketones, and acyloins. A control experiment suggested that the acetylene products were themselves reduced to olefins by McMurry's reagent, although the reaction was not clean.[10e]

However, treatment of **1a–c** with carbon disulfide, followed by reaction with triethyl phosphite, afforded the corresponding acetylenes in moderate yield. These results are summarized in Table I.

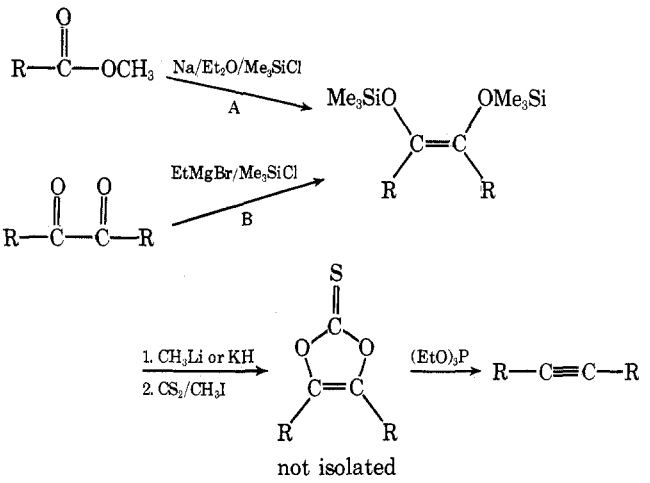


Table I. Yields of Acetylenes and Their Precursors

R	Yield of bis-Me_3Si ether, % A	Yield of bis-Me_3Si ether, % B	Yield of acetylene based on ether, %
C_6H_5	35 (100% cis)	33 (57% cis)	35
n-C_3H_7	90 (100% cis)		28
2R = -$(CH_2)_{10}$-	50 (100% cis)	35 (100% cis)	25

Significantly, when the bis-Me_3Si ether (**4**) of dipivaloyl [R = $C(CH_3)_3$], which is known to be trans,[12] is treated under these conditions, no di-*tert*-butylacetylene[13] is observed, further evidence for the cis requirement of the intermediate.

While this method constitutes a new route to acetylenes from diketones, combined yields are somewhat lower than via the bishydrazone. However, if one must first make the diketone from a diester, this method represents a considerable improvement.

Initial attempts to employ this procedure with the highly hindered diketone alluded to above have failed at the bis ether stage. Further work is being carried out to see if other low valent soluble transition metal ions might effect reduction of **1** to **2**.

Experimental Section

Materials and Methods. Methyl benzoate, methyl pivalate, ethyl butyrate, dodecanedioic acid, benzil, triethyl phosphite, and carbon disulfide were purchased from Aldrich Chemical Co. Cyclododecane-1,2-dione was prepared from known procedures.[16] Methyllithium was purchased from Alfa-Ventron Corp.

The following instruments were employed: Perkin-Elmer 337 infrared spectrophotometer (calibrated with polystyrene); Varian A-60 and T-60 [δ, parts per million downfield from internal $(CH_3)_4Si$]; Bruker HFX-90 (^{13}C data are given in parts per million upfield from CS_2); Hitachi RMU-7 (70 eV).

Melting and boiling points are not corrected.

Preparation of bis-Me_3Si ethers 3a–c and 4 was carried out by method A, as described previously.[10] Physical data for these compounds are summarized below.

3a: bp 83–85 °C (0.03 mm) [lit.[10a] 145–146 °C (2.2 mm)]; ir (neat) 3045, 3010, 2945, 1635, 1275, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 18 H), 6.9–7.3 (m, 10 H); MS *m/e* 356 (45), 147 (100).

3b: bp 106–108 °C (12 mm) [lit.[10b] 105–108 °C (12–13 mm)]; ir (neat) 1675, 1245, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 18 H), 0.90 (t, J = 6.5 Hz, 6 H), 1.50 (m, 4 H), 2.05 (m, 4 H).

3c:[10c] bp 96–98 °C (0.20 mm); ir (neat) 1676, 1238, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 18 H), 1.38 (s, $\Delta\nu_{1/2}$ = 8 Hz, 16 H), 1.85–2.25 (m, 4 H); MS *m/e* 342 (3), 148 (100).

4: bp 70–72 °C (0.1 mm); mp 48–49 °C (Et_2O) [lit.[12] bp 88–95 °C (1 mm); mp 47–49 °C]; ir ($CHCl_3$) 1255, 1245, 1145, 840 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.24 (s, 18 H), 1.16 (s, 18 H).

Preparation of 3c by Method B.[7] A THF solution of ethylmagnesium bromide was prepared from magnesium (4.86 g, 0.20 mol), ethyl bromide (25.06 g, 0.23 mol), and 125 ml of dry THF. The solution was cooled to 10–15 °C and 9.8 g (0.05 mol) of cyclododecane-1,2-dione in 30 ml of THF was added dropwise over a 30-min period. After the mixture was stirred at room temperature for 2 h, the reaction vessel was cooled in an ice bath and 21.6 g (0.20 mol) of chlorotrimethylsilane was added dropwise in approximately 30 min. After the mixture was stirred overnight at ambient temperature, pentane (500 ml) was added to the reaction solution to precipitate most of the inorganic salts. The mixture was filtered through alumina, concentrated in vacuo, and distilled to yield 5.98 g (35%) of clear colorless **3c**.

When benzil was subjected to the above conditions, a mixture of *cis*-**3a** (57%) and *trans*-**3a** (δ 0.05 ppm, 43%) was obtained in 33% yield.

Preparation of Acetylenes from Bis-Me_3Si Ethers. General Procedure A (Better of Two). Into a 65-ml round-bottom flask equipped with a magnetic stirring bar, a pressure-equalized dropping funnel, a nitrogen atmosphere, and cooled in a dry ice–acetone bath were placed the bis-Me_3Si ether (2 mmol) and 7.0 ml of dry THF. Methyllithium (4 mmol) in Et_2O was introduced dropwise to the reaction vessel over 10 min. The flask was allowed to warm slowly to room temperature then stirring was continued overnight at 30 °C. A solution of carbon disulfide (156 μl, 2.6 mmol) in 5.0 ml of THF was added at 0 °C, and the mixture was stirred at room temperature for 30 min, then at 70 °C for 30 min. The flask was cooled in an ice bath, and methyl iodide (156 μl) in THF (2 ml) was added, followed by stirring at room temperature for 30 min and then at 60 °C for 30 min. After cooling to room temperature, the mixture was diluted with 50 ml of ether. The ethereal solution was washed with water and brine, filtered through alumina, and concentrated in vacuo to yield an orange oily residue. Triethyl phosphite (2 ml) was added to the orange residue; the solution was gently refluxed under nitrogen for 3 days. The cooled reaction mixture was extracted with hexane (4 × 15 ml), and the combined organic layers were washed with water, dried, and evaporated under reduced pressure. The residue was chromatographed on silica gel (pentane elution) to yield the acetylenes, which were identical with authentic materials.

General Procedure B. To a 65-ml round-bottom flask containing pentane-washed potassium hydride (~700 mg) and dry THF (5 ml) was added a solution of bis-Me_3Si ether (2 mmol) in THF (10 ml) and this was stirred at 35 °C overnight under a nitrogen atmosphere. A solution of carbon disulfide (156 μl, 2.6 mmol) in 5 ml of THF was added to the reaction vessel, and the mixture was stirred at room temperature for 30 min, then at 70 °C for 30 min. The flask was cooled in an ice bath, and a solution of methyl iodide (156 μl) in THF (2 ml) was added, followed by stirring at room temperature for 30 min, then heating at 60 °C for 30 min. After cooling to room temperature the mixture was diluted with 50 ml of ether; then the entire solution was centrifuged. The organic solution was decanted from the residue which was subsequently washed with more ether (10 ml). The combined organic layers were treated with *tert*-butyl alcohol (5 ml) to destroy residue potassium hydride, filtered through a short column of alumina, and evaporated to leave an orange residue. After triethyl phosphite (2 ml) was added to the orange residue, the solution was gently refluxed under nitrogen for 3 days. The cooled reaction mixture was extracted with hexane (4 × 15 ml), and the combined organic layers were washed with water, dried, and evaporated. The residue was chromatographed on silica gel (pentane elution) to yield the acetylene.

Analytical Data for Acetylenes. 2a: mp 57–59 °C (lit.[14] 58–60 °C); ir ($CHCl_3$) 3070, 3050, 3000, 2210, 1600, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30–7.75 (m).

2b: bp 130–131 °C (lit.[15] 131.8 °C); ir (neat) 2970, 1460, 1380, 1340, 1280 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 6.5 Hz, 6 H), 1.51 (m, 4 H), 2.12 (t, J = 5.5 Hz, 4 H).

2c:[16] ir (neat) 2220, 1099, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (m, $\Delta\nu_{1/2}$ = 10 Hz, 16 H), 2.21 (m, 4 H); ^{13}C NMR (CS_2) 111.2, 166.4, 167.3, 173.8 ppm; MS *m/e* 164 (3), 66 (100).

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Registry No.—**1a,** 59034-61-6; **1b,** 59034-62-7; **1c,** 59034-63-8; **2a,** 501-65-5; **2b,** 1942-45-6; **2c,** 1129-90-4; **3a,** 37980-77-1; **3a** trans isomer, 26312-21-0; **3b,** 59034-64-9; **3c,** 59034-65-0; **4,** 59034-66-1; cyclododecane-1,2-dione, 3008-41-1; chlorotrimethylsilane, 75-77-4.

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New Reactions and Reagents. 5. Ketalization of 1,3-Dihydroxy-2-propanone with Alkanols. Formation of Acyclic and Cyclic Ethers Derived from Pyruvic Aldehyde[1]

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The transformations of 1,3-dihydroxy-2-propanone (dihydroxyacetone, DHA) and its derivatives have been of interest for over 20 years. DHA itself has been shown to undergo a variety of isomerization and dehydration reactions.[2,3] Among the more important homologues of DHA, the transformations of cortisone and related steroids containing a C-17 dihydroxypropanone moiety have been the subject of several reports. In this context it has been known for many years that the ketalization of these steroids resulted in low yields of the expected products. The generation of β-keto acetals as the by-products of these reactions was subsequently discovered in several laboratories. Their formation was eloquently postulated in terms of a Mattox rearrangement[4] involving a dehydration–ketalization sequence (Scheme I).[5–9] The rear-

Scheme I