912, 818, 757, 730, and 700 cm^{-1} (ir of **3**: 1716, 1600, 1318, 1296, 1200, 1172, 1160, 1070, 1030, 1015, 1000, 950, 912, 895, 862, 840, 820, 780, 760, 730, 720, 700 cm^{-1}). Elemental analyses (C, H) in agreement with calculated value were submitted for review.

1,2,3,4,9,10-Hexaphenylanthracene (**10**). A mixture of 0.5 gram of benzyne adduct (**8**) and 0.5 gram of activated zinc dust was refluxed 1$^1/_2$ hr in 25 ml of acetic acid. The hot solution was filtered, and 10 ml of water was added to precipitate the crude yellow product. Recrystallization (ether) gave a 40% yield of pale yellow crystals which exhibited blue fluorescence under an ultraviolet lamp; mp 285–90°C; ir 1600, 1160, 1072, 1030, 768, 760, 745, 700 cm^{-1}; uv λ_{max} of longest wavelength band (ethanol) 335 nm. Recrystallization and chromatography (alumina) failed to remove completely unreacted **8** as indicated by unsatisfactory analyses.

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Condensation of Acetylenic Esters with Biphenyl Compounds Having Active Methylene Groups

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Biphenyl derivatives of acetylenic B-diketone, B-keto-ester, and B-keto-cyanide were prepared by the interaction of ethyl phenylpropiolate and 4-acetylbiphenyl, ethyl 4-biphenylacetate, and 4-biphenylacetonitrile, respectively. The acetylenic B-diketone was converted to 4-pyrone, 4-thiopyrone, and 1-hydroxy-4-pyridone. In addition, ethyl phenylpropiolate reacted with 4-biphenylacetamide to give the substituted glutaconimide.

The acetylenic diketone, 1-(4-biphenyl)-5-phenylpent-4-yne-1:3-dione (III), was prepared by the interaction of ethyl phenylpropiolate (I) and 4-acetylbiphenyl in the presence of sodium ethoxide. The diketone (III) was converted to 4-pyrone (IV) upon heating over its melting point. In addition, partial conversion was affected even during recrystallization from benzene when boiled for a few minutes. Reactions of the diketone (III) or 4-pyrone (IV) with hydroxylamine hydrochloride or phosphorus pentasulfide gave the corresponding hydroxy pyridone (V) and thiopyrone (VI), respectively. Such diketone (III) is considered as a new sensitive complexing ligand. It forms intense yellow and greenish-blue complexes with uranium and copper metals, respectively. The acetylenic diketone could not be isolated in the case of 2,6-diphenylpyrone (*5*). Moreover, the acetylenic B-keto-cyanide (VII), B-keto-ester (VIII), and glutaconimide (IX) were obtained from the reaction between ethyl phenylpropiolate (I) and nitrile (IIb), ester (IIc) and amide (IId), respectively, as shown in Figure 1. The infrared spectra of compounds VII and VIII indicate their presence in the enol-forms. Compounds VII and IX were obtained by the modification of the reported procedure for the phenyl analog (*1*).

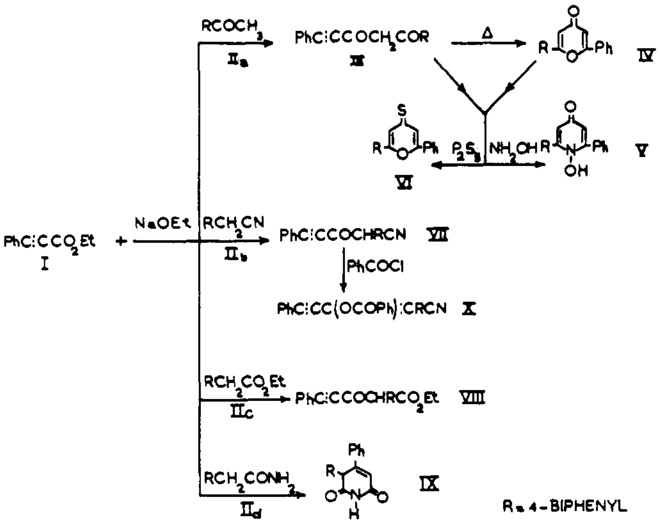

Figure 1. Reactions of ethyl phenylpropiolate with different 4-biphenyl compounds

EXPERIMENTAL

Infrared spectra were obtained with a Beckman IR-10 spectrophotometer and nmr spectra with a Varian A-60 instrument, with TMS as internal standard. Compounds were analyzed at the Max Planck Institute, Ruhr, West Germany. Light petroleum had a bp of 33–40°C.

1-(4-Biphenyl)-5-phenylpent-4-yne-1:3-dione (III). 4-Acetylbiphenyl (IIa, 8.0 grams) and ethyl phenylpropiolate (I, 7.0 grams) were added successively to an ice-cold suspension of sodium ethoxide (from 1.0 gram of sodium and 2 ml of absolute ethanol). The reaction mixture was left at 0°C for two days and then poured into water (200 ml). The solid which separated out was filtered and proved to be the sodium salt of III as shown by the infrared spectrum. This crude solid (12 grams) was suspended in chloroform to which 20% hydrochloric acid was added, and the slightly acidic solution was gently warmed in a water bath until a clear solution was obtained. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum. The diketone (III) was collected in 68%, mp 126–7°C (from benzene–petroleum ether). The infrared spectrum ($CHCl_3$) showed the absorption bands ν_{max} 2700–3400 (chelated OH), 2195 ($C\equiv C$), and 1590 (enolic $C{=}O$) cm^{-1} (*4*). The nmr spectrum ($CDCl_3$) showed δ 6.7 (s, $C{=}CH$) and 7.86 (m, aromatic). *Anal.* Calcd for $C_{23}H_{16}O_2$: C, 85.1; H, 4.9. Found: C, 85.1; H, 5.0.

2-(4-Biphenyl)-6-phenyl-4-pyrone (IV). When the diketone (III, 1.0 gram) was boiled with benzene (50 ml) for 15 min, 4-pyrone (IV, 0.5 gram) was obtained, mp 170–2°C (from benzene). The infrared spectrum ($CHCl_3$) showed the absorption bands ν_{max} 1656 ($C{=}O$) and 1611 ($C{=}C$) cm^{-1}. The nmr spectrum ($CDCl_3$) showed δ 6.94 (s, $C{=}CN$) and 7.86 (m, aromatic). *Anal.* Calcd for $C_{23}H_{16}O_2$: C, 85.1; H, 4.9. Found C, 85.1; H, 5.1. The picrate of IV had mp 184–6°C.

2-(4-Biphenyl)-6-phenyl-4-thiopyrone (VI). The procedure reported (*2*) was followed to give VI in 45% yield as reddish-brown needles, mp 166–8°C (from benzene–petroleum ether). The infrared spectrum ($CHCl_3$) showed the absorption bands ν_{max} 1650 and 1608 (due to ring vibrational modes) (*3*) and 1136 ($C{=}S$) cm^{-1}. The nmr spectrum ($CDCl_3$) showed δ 7.4 (s, $C{=}CH$) and 7.86 (m, aromatic). *Anal.* Calcd for $C_{23}H_{16}OS$: C, 81.2; H, 4.7. Found: C, 81.0; H, 4.7.

2-(4-Biphenyl)-1-hydroxy-6-phenyl-4-pyridone (V). The procedure reported (*2*) was followed to give V in 58% yield as pale-yellow needles, mp 190–1°C (from benzene–methanol). The infrared spectrum (Nujol) showed the absorption bands ν_{max} 2400–3400 (bonded OH), 1670 ($C{=}O$), and 1610 ($C{=}C$) cm^{-1}. The nmr spectrum (DMSO) showed δ 7.0 (s, $C{=}CH$), 7.8 (m, aromatic), and 11.6 (broad, NOH). *Anal.* Calcd for $C_{23}H_{17}O_2$: C, 81.2; H, 5.05; N, 4.1. Found: C, 80.9; H, 5.2; N, 4.3.

2-(4-Biphenyl)-3-hydroxy-5-phenylpent-2-en-4-ynenitrile (VII). The recently reported procedure for the phenyl derivative (*1*) was modified and used here: Equimolar amounts of ester (I), cyanide (IIb), and sodium ethoxide in ether were allowed to stand at room temperature for three days. The reaction mixture was worked out as for the diketone (III) to give VII as pale yellow plates, mp 205–7 (from ethanol). The infrared spectrum (Nujol) showed the absorption bands ν_{max} 2600–3100 (OH), 2208 ($C\equiv C$ and $C\equiv N$), and 1600 ($C{=}C$) cm^{-1}. The nmr spectrum (DMSO) showed only complex absorption at δ 7.8 (all protons). *Anal.* Calcd for $C_{22}H_{16}NO$: C, 86.0; H, 4.7; N, 4.4. Found: C, 86.5; H, 4.7; N, 4.2. The filtrate was worked out as usual to give more of compound VII (overall yield, 40%).

3-Benzoyloxy-2-(4-biphenyl)-5-phenylpent-2-en-4-ynenitrile (X). Compound VII was benzoylated using benzoyl chloride to give X in 86% yield as yellowish plates, mp 130–1°C (from methanol). The infrared spectrum (Nujol) showed the absorption bands ν_{max} 2180 ($C\equiv C$ and $C\equiv N$) and 1750 ($C{=}O$ of vinyl aromatic ester) cm^{-1}. *Anal.* Calcd for $C_{30}H_{19}NO_2$: C, 84.65; H, 4.5; N, 3.3. Found: C, 85.0; H, 4.4; N, 3.3.

Ethyl α-(4-Biphenyl)phenylpropioloylacetate (VIII). The condensation between I and IIc was carried out as for VII, except that the reaction temperature was maintained between 0–10°C and the reaction mixture was left at this temperature for two days before it was worked out. Compound VIII was obtained in 25% yield and melted at 85–6°C (from methanol). The infrared spectrum ($CHCl_3$) showed the absorption bands ν_{max} 2600–3400 (chelated OH), 2218 ($C\equiv C$), 1640 and 1600 (chelated $C{=}O$) cm^{-1}. The nmr spectrum ($CDCl_3$) showed δ 1.28 (t, Me), 4.4 (q, CH_2), 7.38–7.72 (m, aromatic), and 13.12 (s, exchangeable). This compound VIII gave greenish-blue copper and yellow uranium complexes. The sodium salt of VIII melted at 290–2°C (dec.). *Anal.* Calcd for $C_{25}H_{20}O_3$: C, 81.55; H, 5.4. Found: C, 81.9; H, 5.4.

5-(4-Biphenyl)-4-phenylpyridine-2,6(1H,5H)-dione (IX). Compounds I and IId were reacted using the reported procedure (*1*) which is modified as: Sodium ethoxide was used instead of sodium and the reaction mixture was refluxed for two days after addition of the ester (I). Compound IX was isolated in 32% yield as colorless cubes, mp 225–6°C (from ethanol). The infrared spectrum (Nujol) showed the absorption bands ν_{max} 3400 (NH), 1778 and 1690 ($C{=}O$), and 1639 ($C{=}C$) cm^{-1}. *Anal.* Calcd for $C_{23}H_{17}NO_2$: C, 81.2; H, 5.05; N, 4.1. Found: C, 80.8; H, 5.2; N, 4.4.

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Correction

In the article by Terezia Betancourt and A. F. McMillan [*J. Chem. Eng. Data*, **11** (3), 311 (1972)], the title on the Contents and on page 311 should read "Vapor-Liquid Equilibrium of Isobutyl Alcohol–Dimethyl Sulfoxide System," not "Vapor–Liquid Equilibrium of Isobutyl Alcohol–Dimethyl Sulfide System."