

Synthesis of Some Heterocyclic and Condensed Aromatic Substituted γ -Pyrones

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In the course of our study on the behaviour of acetylenic esters toward compounds having active methylene groups (1,2), the condensation between the acetyl compounds (II) and ethyl phenylpropiolate (I) was carried out in the presence of sodium ethoxide. The reaction pathway seems to proceed by simple Claisen addition as indicated by the isolation of the intermediate acetylenic β -diketones (III) (Scheme 1). Although variable amounts of similar diketones were isolated from analogous reactions involving a limited number of substituted acetophenones, acetophenone itself failed to give such diketones (3,4).

The diketones (III) form an interesting class of compounds as they easily form bluish-green copper complexes and therefore they could be considered as organic ligands similar to those of simple β -diketones.

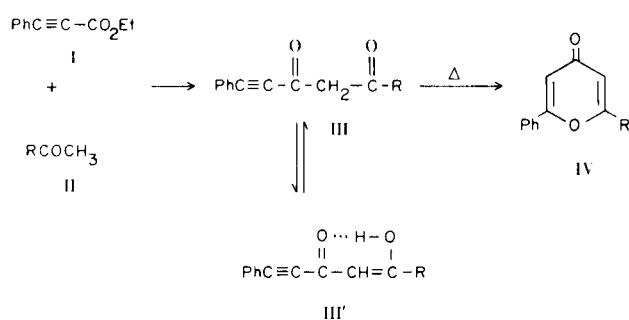
In general these diketones (III) were sensitive toward heat as noticed during recrystallization and melting point determination (see Experimental).

In support of the structural assignments we have determined the ir and nmr spectra of the diketones under study. Both ir and nmr spectra (Table I) indicate that these compounds exist in their enolic chelated form (III'). The ir spectra showed two bands in the range of 2400-

3500 and 1570-1587 cm^{-1} characteristic of chelated β -diketones beside the acetylenic stretching band near 2200 cm^{-1} (5). In the nmr spectra the enolic form of these compounds is identified by the absorption of the ethylenic proton and/or the enolic proton. In some cases either the enolic proton is broadened or the ethylenic

Table I

| Compound | Ir and Nmr Spectral Data of Various γ -pyrones and Acetylenic β -Diketones | |
|----------|--|-----------------------------------|
| | Ir (chloroform) (a) | Nmr (deuteriochloroform) (b) |
| IVa | 1650, 1619, 1385 | 3.12(d), 2.80(d), 2.46-0.86(m) |
| b | 1648, 1618, 1395 | 3.15(d), 3.02(d), 2.68-0.88(m) |
| c | 1649, 1621, 1382 | 3.25(d), 2.92(d) 2.5-1.16(m) |
| d | 1650, 1644, 1605, 1380 | 3.25(d), 2.6-1.36(m) |
| e | 1651, 1645, 1603, 1397 | 3.14(d), 3.04(d) 2.5-1.7(m) |
| f | 1653, 1647, 1620, 1400 | 3.28(d), 3.2(d), 2.54- 1.7(m) |
| g | 1655, 1650, 1635, 1627, 1347 | 3.44-2.1(m) |
| IIIa | 3400-2700(br), 2199, 1570(br) | 3.25(s), 2.68-1.14(m) |
| b | 3300-2650(br), 2200, 1580(br) | 3.17(s), 2.64-0.67(m) |
| c | 3250-2800(br), 2205, 1587(br) | 3.7(s), 3.0-1.48(m) |
| e | 3220-2750(br), 2212, 1585(br) | 2.9-1.59(m), -0.92(s) |
| f | 3200-2400(br), 2220, 1575(br) | 3.1-2.0(m), -1.03(s) |
| g | 3500-2700(br), 2215, 1590(br) | 3.2(s), 3.0-2.0(m) |



- a. R 2-Phenanthryl
 b. R 3-Phenanthryl
 c. R 9-Anthracyl
 d. R α -Naphthyl
 e. R β -Naphthyl
 f. R α -Thienyl
 g. R α -Furyl

d = doublet, m = multiplet, s = singlet, br = broad band
 (a) Strong stretching frequency band in cm^{-1} . (d) Chemical shifts reported in τ -values. Enolizable proton in β -diketone was exchanged with deuterium oxide.

proton is resonated together with the aromatic protons present in these compounds (6). In the latter case the spectrum was rescanned after shaking the sample with deuterium oxide. A signal due to HOD appeared near 5.2

τ which is a good indication of the presence of an enolisable proton.

Similarly, the γ -pyrones were identified from their ir and nmr spectra (Table I). Generally the ir spectra of these compounds showed bands in the range of 1645-1655, 1600-1620 and 1380-1400 cm^{-1} characteristic of γ -pyrones (7). The nmr spectra showed two doublets between 2.8-3.3 τ with an average value of $J \cong 2.1$ cps due to the 3 and 5 protons (8). Similar cross ring coupling with $J = 2.7$ was given for certain γ -pyrones (9,10). Furthermore, complex patterns due to aromatic protons were observed between 2.6-3.1 τ in both the diketones and γ -pyrones.

Table II

| Ketone (b) | Experimental Conditions (a) | |
|------------|--|---|
| | Time and temperature required after addition of ketone | Time and temperature required after addition of ester |
| IIa | 24 hours (30-40°) | 2 hours (room) and then 72 hours (0°) |
| IIb | 24 hours (room) | 4 hours (room) and then 48 hours (0°) |
| IIc | 3.5 hours (30-40°) | 24 hours (0°) |
| II-d-g | 15 minutes (0°) | 24 hours (0°) |

(a) The time periods indicated represent the best time required to get maximum yield of the diketones. (b) Benzene was used as a solvent in case of IIa,b and ether in case of IIc-g.

EXPERIMENTAL

Ir spectra were recorded with a Beckmann IR-10 spectrometer and nmr spectra with a Varian A-60 spectrometer in deuterochloroform containing TMS as the internal standard. Tlc was carried out using silica absorbant eluted with 3:1 chloroform-benzene. Microanalytical samples were analysed in West Germany by Max Plank Institute, Ruhr.

Table III

Melting Points and Percentage Yields of Acetylenic Diketones and γ -Pyrones

| R | Acetylenic β -diketones | | M.p. | 2,6-substituted γ -Pyrones | |
|---|-------------------------------|-----------|------------|-----------------------------------|---------------------|
| | M.p. (a) | Yield (%) | | Yield (%) (f) | Total Yield (%) (g) |
| a | 122-124 | 51 | 206-207(c) | 20.2 | 70.4 |
| b | 124-125 | 53 | 210-212(c) | 11.3 | 63.6 |
| c | 144-146 | 50 | 248-250(c) | 16.3 | 65.8 |
| d | (b) | 28.6 | 102-104(d) | 32.2 | 48.2 |
| e | 97-99 | 13.6 | 137-139(d) | 51.5 | 55.1 |
| f | 98-100 | 22.0 | 155-157(e) | 55.3 | 76.3 |
| g | 133-135 | 16.1 | 139-141(a) | 26.7 | 40.2 |

(a) All diketones were recrystallized from diethyl ether. (b) Isolated as its sodium salt. (c) Recrystallized from acetone. (d) Recrystallized from benzene-(petroleum ether). (e) Recrystallized from methanol. (f) The yield based on the amount pyrone obtained directly from the reaction mixture. (g) The yield based on the amount pyrone obtained directly and from the corresponding diketone.

Table IV

Analysis Results of the Diketones and Pyrones

| R | Diketone or Pyrone Formula | Diketone or Pyrone % Calcd. | | Diketone % Found | | Pyrone % Found | |
|---|--|-----------------------------|------|------------------|------|----------------|------|
| | | C | H | C | H | C | H |
| a | $\text{C}_{25}\text{H}_{16}\text{O}_2$ | 86.19 | 4.58 | 85.99 | 4.58 | 85.87 | 4.31 |
| b | $\text{C}_{25}\text{H}_{16}\text{O}_2$ | 86.19 | 4.58 | 85.40 (a) | 4.39 | 85.83 | 4.63 |
| c | $\text{C}_{25}\text{H}_{16}\text{O}_2$ | 86.19 | 4.58 | 85.50 (a) | 4.52 | 86.60 | 4.69 |
| d | $\text{C}_{21}\text{H}_{14}\text{O}_2$ | 84.55 | 4.72 | --- | --- | 84.60 | 4.60 |
| e | $\text{C}_{21}\text{H}_{14}\text{O}_2$ | 84.55 | 4.72 | 84.99 | 4.74 | 84.96 | 4.71 |
| f | $\text{C}_{15}\text{H}_{10}\text{O}_2\text{S}$ | 70.85 | 3.95 | 71.02 | 4.04 | 71.01 | 4.01 |
| g | $\text{C}_{15}\text{H}_{10}\text{O}_3$ | 75.62 | 4.20 | 75.49 | 4.10 | 75.56 | 4.19 |

(a) No better carbon analysis was obtained on repeated analysis.

Reaction Between Ethyl Phenylpropiolate (I) and Acetyl Compounds (IIa-g).

General procedure.

To a stirred suspension of sodium ethoxide (1 mmole) in dry ether (50 ml.), the acetyl compound (1 mmole) was dissolved in the appropriate solvent and added dropwise. The reaction mixture allowed to stand under specified experimental conditions (Table II) followed by addition of the propiolic ester (1 mmole), cooled and acidified with dilute sulphuric acid. Extraction with chloroform, drying (magnesium sulfate) and evaporation of the solvent afforded a mixture of acetylenic diketone and the corresponding γ -pyrone (as shown from tlc) in the proportions indicated by yield (Table III). When the above diketone was taken into chloroform and shaken with aqueous copper acetate solution, a bluish-green coloration of the chloroform layer was observed. In the case of the diketone derived from 3-acetylphenanthrene, the chloroform layer was dried (magnesium sulfate) and evaporated to give a pale greenish precipitate of the copper complex, m.p. 168-170° dec.; ir (chloroform): 2200, 1520, 1407 and 1385 cm^{-1} .

Conversion of Acetylenic Diketones to the Corresponding γ -Pyrone.

The diketone III was heated in an oil bath for 5-10 minutes just above its melting point followed by trituration with ether or acetone. Filtration followed by recrystallization from the appropriate solvents (Table III) gave the pure γ -pyrone (IV). The same conversion was initially observed during melting point

determination of the diketone.

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