

SYNTHESIS OF SOME NEW PYRONES

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6-[(2-Furyl)vinyl]-4-methoxy-6-[(2-thienyl)vinyl]-4-methoxy- α -pyrones and some related compounds were prepared to study their photochemistry. IR, UV and NMR data of these compounds is reported.

α,β -Ethylenic carbonyl compounds have long been known to undergo photochemical changes under the influence of light. Irradiation may lead to geometrical isomerization, to rearrangement and to intermolecular rearrangement, which include dimerization, polymerization and addition reactions. Although coumarins, quinones, α,β -unsaturated ketones, acids, esters and anhydrides were investigated and found to dimerize under the influence of light, the photochemistry of α -pyrones, which also contain ethylenic carbonyl moiety in the system, remained uninvestigated till de Mayo¹ carried out the irradiation of 4,6-dimethyl- α -pyrone in methanol and showed that it changed to methyl acetonycrotonate. Later, Corey and Streith⁴ carried out the irradiation of α -pyrone in ether and found that it changed into cyclobutene derivative. Padwa and Hartman³ investigated UV irradiation of 4,5-diphenyl- α -pyrone in dry ether and isolated from it tetraphenylcyclohexaene, *p*-terphenyl and diphenylacetylene. Recently, Edwards *et al.*⁴ carried out the photochemical study of 6-(2-,3-,4-methoxy-methoxystyryl)-methoxy- α -pyrones and found that these compounds dimerized in solid state but remained unchanged in solution when exposed to sunlight.

Results and Discussion

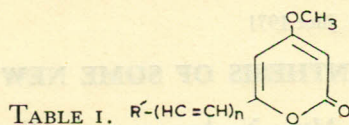
In the present work, it was decided to synthesize some novel pyrones and study their photochemical behaviours. Two types of compounds were synthesised; one in which heteroaromatic or aromatic moiety at C₆-position of α -pyrone was separated from the α -pyrone ring by one double bond, and another in which it was separated by two double bonds ($-\text{C}=\text{C}-\text{C}=\text{C}-$). The compounds were prepared by condensing appropriate aldehydes with 6-methyl-4-methoxy- α -pyrone in presence of magnesium methoxide in methanol. 6-Methyl-4-methoxy- α -pyrone was obtained from triacetic lactone by methylation with dimethyl sulphate, while the latter compound was obtained from dehydroacetic acid by treatment with sulphuric acid. Although all the appropriate aldehydes condensed to give the desired compounds, the condensation of isonicotinaldehyde with the pyrone resulted in a tarry

product. The IR spectrum of the 6-[(2-thienyl)vinyl]-4-methoxy- α -pyrone showed a peak at 1733 cm^{-1} , which was assigned to stretching frequency of pyrone carbonyl. The absorption bands at 1625 and 1548 cm^{-1} were interpreted as being due to the 3,4- and 5,6- double bonds of the pyrone ring.⁵ The IR spectrum of the compound further showed a peak at 961 cm^{-1} , which was taken to indicate the presence of *trans*-configuration. This was further substantiated by the NMR spectrum of the compound. The IR spectra of all other compounds showed similar absorptions (Table 2). The NMR spectrum of the 6-[(2-thienyl)vinyl]-4-methoxy- α -pyrone showed a singlet at $\tau 6.18$, (3H)_s. This was assigned to the methoxy signal of the pyrone ring. The spectrum further showed the presence of two doublets at $\tau 4.43$ and $\tau 3.99$, area ratio 1:1; they were coupled ($J 2.0$ c/s) forming AX system⁶ with chemical shift of 24 c/s. The doublet at $\tau 4.43$ was assigned to 5-H pyrone signal and doublet at $\tau 3.99$ to 3-H pyrone signal.⁷ The spectrum of the compound revealed two further doublets at $\tau 2.50$ and $\tau 3.40$. They were also coupled ($J 16.0$ c/s) forming AB system⁶. The doublet at $\tau 2.50$ was assigned to olefinic proton adjacent to pyrone ring, and the doublet at $\tau 3.40$ to olefinic proton adjacent to thiophene ring.⁷ The NMR spectra of all other compounds, except those of I and II, resembled the spectrum of 6-[(2-thienyl)vinyl]-4-methoxy- α -pyrone (Table 2). Although compounds I and II contained AA' BB' system in the molecule, they showed only one doublet near $\tau 3.6$. These signals were assigned to proton adjacent to pyrone ring. All other proton resonances of AA' BB' system ($-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$) were overlapped by the aromatic signals. The other parts of the NMR spectra of compounds I and II were similar to those of other compounds (Table 2). The photochemical behaviour of these compounds is at present under investigation.

Experimental

All m.ps are uncorrected.

Triacetic lactone.—Dehydroacetic acid (50 g) was dissolved in 90% sulphuric acid (150 g, 85 ml) and the mixture was heated quickly and maintain-



| No. | R' | n | M.P.°C | Recrystallization solvent | Yield | Formula | Found % | | Calc % | |
|-----|-----------|---|---------|---------------------------|-------|--|---------|-----|--------|-----|
| | | | | | | | C | H | C | H |
| I | Phenyl | 2 | 191-192 | M | 60.5 | C ₁₆ H ₁₄ O ₃ | 74.95 | 5.1 | 75.60 | 5.5 |
| II | 2-Furyl | 2 | 195-197 | E | 70.0 | C ₁₄ H ₁₂ O ₄ | 68.35 | 4.4 | 68.85 | 4.9 |
| III | 2-Thienyl | 1 | 177 | E | 65.0 | C ₁₂ H ₁₀ O ₃ S | 61.2 | 4.4 | 61.5 | 4.3 |
| IV | 2-Furyl | 1 | 172-174 | M | 62.0 | C ₁₂ H ₁₀ O ₄ | 65.65 | 4.8 | 66.15 | 4.6 |
| V | 2-Pyridyl | 1 | 182 | M | 40.0 | C ₁₃ H ₁₁ O ₃ N | 67.80 | 5.1 | 68.1 | 4.8 |
| VI | 3-Pyridyl | 1 | 166 | M | 15.0 | C ₁₃ H ₁₁ O ₃ N | 67.6 | 5.2 | 68.1 | 4.8 |

M—MeOH, E—EtOAc.

TABLE 2—IR, UR and NMR DATA OF PYRONES $R'-(HC=CH)_n$

| No. | R' | n | $\nu_{max} \text{ cm}^{-1}$ | | | $\lambda_{max} \text{ m}\mu$ | Chemical shifts (τ) and spin-spin coupling constants (c/s). | | | | | | |
|-----|-----------|---|-----------------------------|----------------|----------------|------------------------------|--|----------------|------|-----------|------------------|-------|-----------|
| | | | Pyrone C=O | Pyrone 3,4-C=C | Pyrone 5,6-C=C | | Pyrone -OCH ₃ | Pyrone protons | | | Olefinic protons | | |
| | | | | | | | | H-3 | H-5 | $J_{3,5}$ | 2-CH= | 1-CH= | $J_{1,2}$ |
| I | Phenyl | 2 | 1724 | 1637 | 1548 | 362 | 6.14 | 4.49 | 4.10 | 2.0 | — | 3.60 | — |
| II | 2-Furyl | 2 | 1712 | 1639 | 1550 | 360 | 6.14 | 4.45 | 4.00 | 2.0 | — | 3.65 | — |
| III | 2-Thienyl | 1 | 1733 | 1625 | 1548 | 355 | 6.18 | 4.43 | 3.99 | 2.0 | 2.50 | 3.40 | 16.0 |
| IV | 2-Furyl | 1 | 1712 | 1647 | 1550 | 356 | 6.19 | 4.21 | 4.05 | 2.0 | 2.60 | 3.35 | 16.0 |
| V | 2-Pyridyl | 1 | 1724 | 1640 | 1550 | 355 | 6.16 | 4.42 | 3.95 | 1.99 | 2.40 | 3.35 | 16.0 |
| VI | 3-Pyridyl | 1 | 1722 | 1639 | 1545 | 356 | 6.15 | 4.44 | 3.97 | 1.99 | 2.35 | 3.25 | 16.0 |

ed at 130°C until a drop of the mixture failed to produce crystals. The heating was then stopped, the mixture cooled rapidly in ice and then poured into water (200 ml). The deposited crystalline product was filtered, washed with water and dried in air. Recrystallisation of the solid from acetonitrile gave the product, m.p. 188-190°C (85%) (lit. 189°C).

4-Methoxy-6-methyl- α -pyrone.—Dimethyl sulphate (10 g) was added to a vigorously stirred and refluxing solution of triacetilactone (10 g) in dry acetone (300 ml) containing suspended anhydrous potassium carbonate (50 g). After 15 hr, the mixture was allowed to cool to room temperature, and the suspended solid removed by filtration and washed with dry acetone. Evaporation of the combined filtrate and washings gave a solid which was repeatedly extracted under reflux with petroleum-ether (60-80°C). The cooled extract deposited long needles of 4-methoxy-6-methyl- α -pyrone, (6 g), m.p. 88-90°C (lit. 88-89°C).

6-[(2-Thienyl)vinyl]-4-methoxy- α -pyrone.—A mixture of thiophene-2-aldehyde (2.24 g, 0.02 mole) and 6-methyl-4-methoxy- α -pyrone (2.8 g, 0.02 mole) was refluxed in the presence of magnesium methoxide (1.8 g) in methanol (30 ml) for 6 hr. The mixture was evaporated to dryness and the residue washed in chloroform with dilute acetic acid (15 ml). The chloroform layer was drawn off, washed with *N*-sodium hydrogen carbonate

solution and water, dried (Na₂SO₄) and passed through a column of neutral alumina. Development with chloroform and evaporation of the elute gave a yellow viscous oil which slowly solidified. Recrystallization (ethyl acetate) yielded 6-[(2-thienyl)vinyl]-4-methoxy- α -pyrone (2.5 g) as yellow needles, m.p. 177°C (Found: C, 61.2; H, 4.4%. C₁₂H₁₀O₄S requires: C, 61.5; H, 4.3%). All other compounds were prepared in a similar manner.

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