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THE REACTION OF N-PYRIDINIUM PHENACYLIDS WITH NITRILE IMINES

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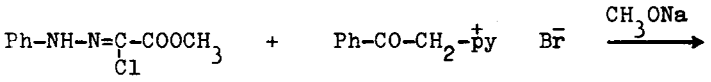
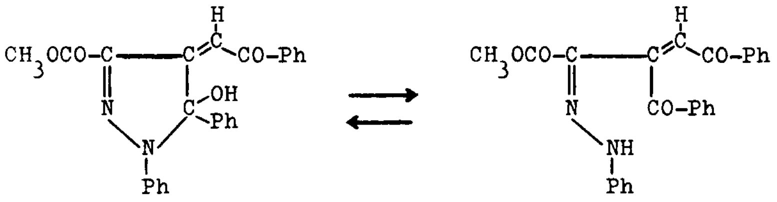
The recent publication by Y. Hayashi and coworkers(1) about the reaction of carbonyl-stabilized sulphur ylids with some 1,3-dipoles, prompts us to publish our results about nitrogen ylids.

The reaction of methyl phenylhydrazonochloroacetate (I) (1 mole) with N-phenacylpyridinium bromide (II) (2 moles) in presence of sodium methoxide (2 moles) in methanol-dioxane 70:30 (v./v.) at 0° for 12 hrs. furnished a red product (m.p. 184°) in 60% yield(*).



$$\underset{\text{(I)}}{\text{Ph-NH-N=}\underset{\text{Cl}}{\text{C}}\text{-COOCH}_3} \quad + \quad \underset{\text{(II)}}{\text{Ph-CO-CH}_2\text{-}\overset{+}{\text{py}} \quad \overset{-}{\text{Br}}} \quad \xrightarrow{CH_3ONa}$$

(I) (II)



(III) (IIIa)

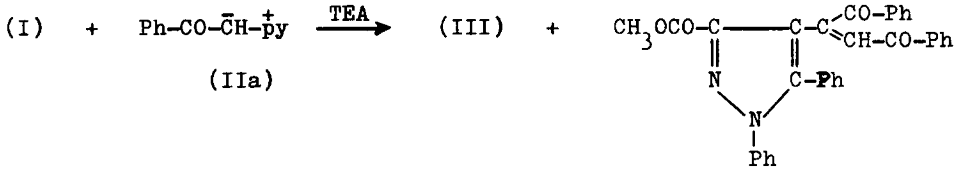
Structure (III) or (IIIa) could be assigned to this compound on the basis of chemical and spectroscopical data:

(*) Analogous results have been obtained starting from (I) and (II) bearing substituents in the phenyl ring.

UV spectrum (ethanol solution): absorption maxima at 248,296 and 465 mμ (log ε : 4.25, 4.19, 4.25 respectively).
IR spectrum (nujol mull): 3330 cm^{-1} (OH); 1690 and 1640 cm^{-1} (C=O).
NMR spectrum (deuterochloroform solution): 4.0 τ (s) 3H (CH$_3$OCO); 2.5 τ (m) 15H (aromatic protons); 2.0 τ (s) 1H (OH); 1.8 τ (s) 1H (CH=C). The peak at 2.0 τ disappears by adding deuterium-water.

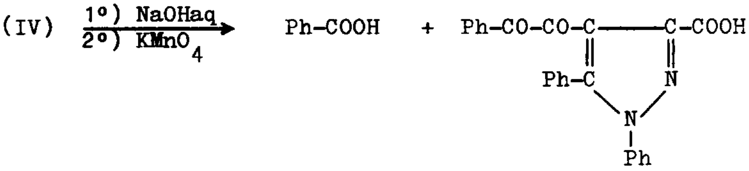
The X-ray crystal structure analysis(2) of the red compound strongly suggests the cyclic structure (III). However it seems likely that in solution structure (IIIa) may exist in equilibrium with structure (III).

The reaction of (I) (1 mole) with N-pyridinium phenacylid (IIa) (2 moles) and triethylamine (2 moles) in chloroform at 0° yielded after several hours a mixture of (III) and (IV) (m.p. 176°).



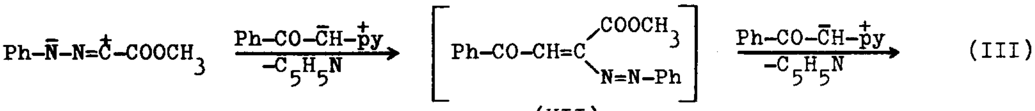
(IV)

Compound (IV) could also be obtained from (IIIa) by reaction with N-pyridinium phenacylid (IIa) in chloroform at 0°. Spectroscopic, analytical and chemical data are in agreement with the assigned structure (IV). In fact basic hydrolysis of (IV) followed by permanganic oxidation gave benzoic acid and the diketoacid (VI) (m.p. 223°).



(VI)

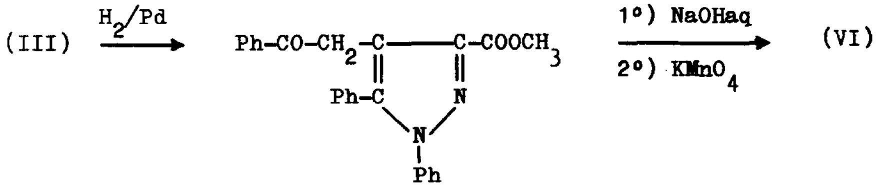
The mechanism of formation of compound (III) should involve addition of ylid (IIa) to the nitrile imine and subsequent elimination of pyridine. Addition of a second mole of (IIa) to the unstable intermediate (VII) yields compound (III).



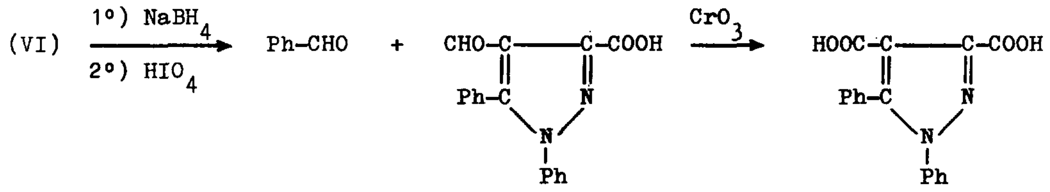
(VII)

The formation of (IV) can be easily understood as a Michael-type addition of N-pyridinium phenacylid to the activated double bond of (III), followed by elimination of pyridine and cyclisation.

Hydrogenation of (III) furnished 1,5-diphenyl-3-carbomethoxy-4-phenacylpyrazole (VIII) (m.p. 136°), which after hydrolysis and permanganic oxidation was converted to the diketoacid (VI). (VI) was reduced with sodium borohydride and the intermediate dihydroxy compound oxidized with periodic acid to benzaldehyde and acid (IX). The latter was then converted to the known dicarboxylic acid (X) (m.p. 218°)(3)

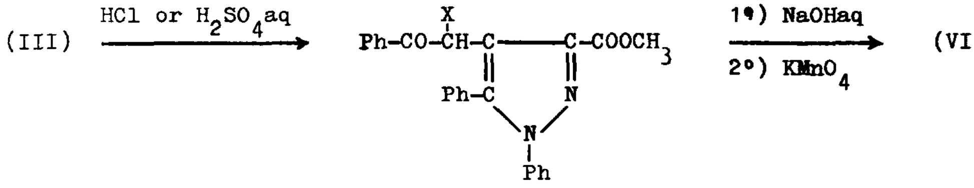


(VIII)



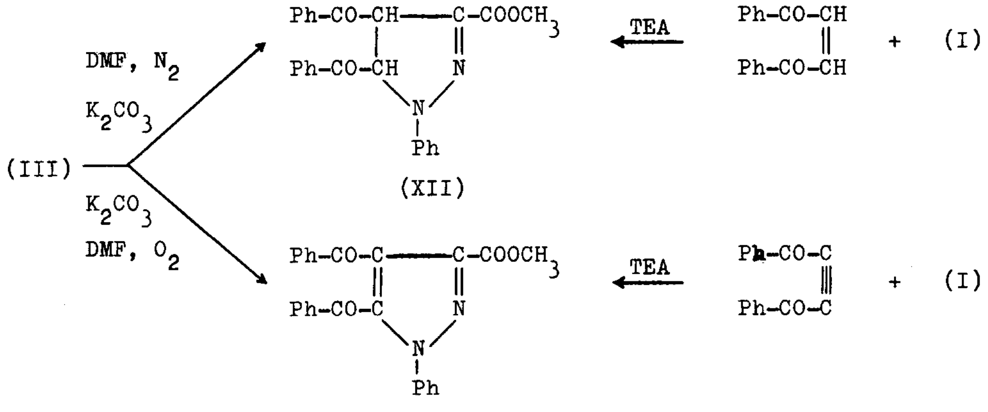
(IX) (X)

The action of hydrogen chloride and of 20% aqueous sulphuric acid on substrate (III) afforded compounds (XIa) and (XIb)respectively. (XIa) and (XIb) after hydrolysis were converted by the action of potassium permanganate to the diketoacid (VI).



XIa, X=Cl ; XIb, X=OH

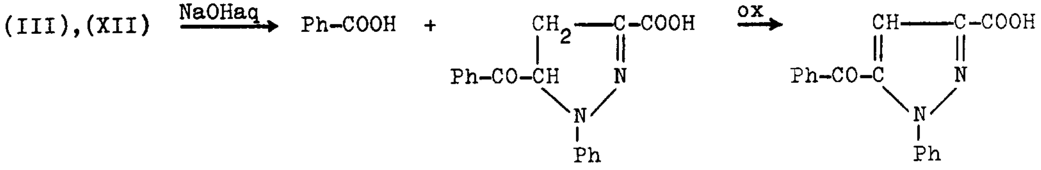
Compound (III) in D.M.F. solution in the presence of potassium carbonate under nitrogen was converted after 2-3 hrs. at room temperature into the trans 1-phenyl-3-carbomethoxy-4,5-dibenzoylpyrazoline (XII) (m.p. 140°). The same compound could be obtained *via* cycloaddition of (I) with *trans*-1,2-dibenzoylethylene in the presence of triethylamine. If the conversion (III) ⟶ (XII) was not carried in an inert atmosphere but in the presence of oxygen the reaction yielded 1-phenyl-3-carbomethoxy-4,5-dibenzoylpyrazole (XIII) (m.p. 138°), which was also obtained from (I) and 1,2-dibenzoylacetylene.



(XII)

(XIII)

The action of an excess of sodium hydroxide in methanol water 1:1 (v./v.) converted compounds (III) and (XII) into 1-phenyl-3-carboxy-5-benzoylpyrazoline (XIV) (m.p. 211°) which, after treatment with potassium ferricyanide, gave the known compound (XV)$^{(4)}$.



(XIV) (XV)

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