REACTION OF PYRYLIUM SALTS WITH NUCLEOPHILES—IX¹

FORMATION OF 1,2-DIAZEPINE OR 2-PYRAZOLINE DERIVATIVES FROM 2,4,6-TRIPHENYLPYRYLIUM SALTS AND HYDRAZINE

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Abstract—2,4,6-Triphenylpyrylium salts (I) afford with hydrazine an unstable pseudobase-monohydrazone (IV, X = NH) possibly by a 1,5 hydrogen transfer; it readily dehydrates to the 7-membered 3,5,7triphenyl-4H-1,2-diazepine (III). The reaction of 2,4,6-triphenylpyrylium pseudobase (VI) with hydrazine proceeds similarly to reactions with hydroxylamine or phenylhydrazine, affording the 5-membered 3,5diphenyl-5-phenacyl-2-pyrazoline (II, X = NH) which can be cleaved into acetophenone and 3,5-diphenylpyrazole.

ALKYL and aryl substituted pyrylium salts are easily converted^{2a, b} into 6-membered heterocycles (pyridines and pyridinium salts) by ammonia^{3a} and primary amines,^{3b} respectively. It was reported⁴ that 2,4,6-trimethylpyrylium is converted by hydrazine in equimolar amounts into a similar pyridinium compound, but that excess hydrazine leads to a pyrazoline derivative. On the other hand, as shown recently, hydroxylamine and phenylhydrazine convert 2,4,6-triarylpyrylium salts (e.g. I) into 5-membered 2-isoxazoline (II, X = O) and 2-pyrazoline derivatives (II, X = NPh)^{5,6} whereas hydrazine converts them into 7-membered 1,2-diazepine derivatives (III).^{5,7} The present paper concerns the mechanism of the latter reaction.

If 2,4,6-triphenylpyrylium perchlorate (I) is briefly shaken at 20° with dilute aqueous hydrazine and ether, and the ethereal layer is evaporated under reduced pressure,^{3a} a colourless cyrstalline compound m.p. 108–110° is obtained. It presents a CO stretching band at 1688 cm⁻¹ with a shoulder at 1696 cm⁻¹ in CCl₄ solution, and two NH stretching bands at 3280 and 3400 cm⁻¹ in nujol.

In deuterochloroform it has singlet sharp peaks at τ 3.40 (1H) and τ 5.90 (2H) and a broad peak at τ 4.12 (2H of NH₂).⁸ Though it is stable in the solid state, in solution it dehydrates (half-life ca. 1 h at 40° in CDCl₃) affording 3,5,7-triphenyl-4H-1,2-diazepine (III) and the solution becomes red-brown (as do the crystals of IV with traces of solvents). Accordingly, this compound is the monohydrazone of the pseudobase (VI) and could have either formula IV (X = NH) or V(X = NH), i.e. the double bond can be conjugated either with the hydrazo or with the CO group. By analogy with the structure of the pseudobase formed from 2,4,6-triphenylpyrylium and H₂¹⁸O,⁹ we assume that it has the former structure (IV, X = NH) which can be formed via a 1,5-hydrogen transfer in a 6-membered cyclic transition state.¹⁰ This in agreement with the IR vCO frequency similar to that of acetophenone (for structure V, X = NH) a lower frequency, ca. 1660 cm⁻¹, as in chalcone, would be expected¹¹⁻¹⁴). Also, formula V (X = NH) would be expected to present the vinyl proton in the NMR

spectrum below $\tau 2.8$, as in chalcone, whereas chalcone thiosemicarbazone possessing a structure related to IV presents a vinylic proton 3.49 τ .⁸

1,3,5-Triphenyl-2-penten-1-one (VI, pseudobase of I) reacts in a different fashion with hydrazine in ethanol: with a transient red-brown coloration, a crystalline colourless compound m.p. 133° is formed. It presents a CO stretching band at 1690 cm⁻¹ and a single NH stretching band at 3400 cm⁻¹ (in KBr pellet) or 3370 cm⁻¹ (in CCl₄) consistent with vNH in 2-pyrazolines.^{15, 16} Its UV absorption bands appear at 245, 285, 349 sh, and 369 sh nm (in ethanol), and at 246 (\$ 15,000), 290 (11,400), 346 sh (2000) and 370 sh (1100) nm in 1,2-dichloroethane. According to its NMR spectrum⁸ and elementary analysis, this compound is 3,5-diphenyl-5-phenacyl-2pyrazoline (II, X = NH). Similarly to other compounds with formula II,⁵ (but unlike other 2-pyrazolines which afford nitrogen and cyclopropane)¹⁷⁻²⁰ this compound II (X = NH) cleaves on treatment with acids, on recrystallization from acetic acid, or on heating above the m.p. affording acetophenone (VII) and an aromatic azole (VIII): 3,5-diphenylpyrazole (X = NH), m.p. 199°, identified by mixed m.p. and IR spectrum with an authentic product.²¹ Acetophenone is therefore a convenient leaving group in aromatization reactions of phenacyl-dihydronaphthalenes²² or phenacyl-azolines (cf. diethyl malonate as leaving group in reactions with hydrazine²³).

Thus, the pseudobase (VI) reacts with hydrazine like other α,β -unsaturated ketones affording a 2-pyrazoline derivative (II, X = NH).¹⁷⁻²⁰ Though no intermediate in this reaction could be detected, the above data make it clear that IV is not an intermediate in the conversion of VI into II (X = NH).

Therefore the initial attack of nucleophiles like N_2H_4 on the unsaturated 1,5diketone (VI) can either involve a condensation of the more reactive non-conjugated CO group leading to V (X = NH) which cannot be isolated because it cyclizes, or the addition of N_2H_4 to the activated C=C double bond followed by intramolecular condensation (cf. Ref. 24), affording II (X = NH). Treatment of the pseudobase (VI) with hydroxylamine or phenylhydrazine* affords 3,5-diphenyl-5-phenacyl-2-isoxa-



* These reactions were mentioned by Dilthey,²⁵ but the structure of the products was not elucidated.

zoline (II, X = O) or 1,3,5-triphenyl-5-phenacyl-2-pyrazoline (II, X = NPh), respectively, identical with the products obtained from triphenylpyrylium (I) and the same reagents by cyclization of the intermediately formed IV (X = O or NPh). Only with hydrazine as the nucleophile is there a difference between the reactions of 2,4,6-triphenylpyrylium (I) and its pseudobase (VI) because in this case the intermediate (IV, X = NH) reacts more rapidly by intramolecular condensation of CO and NH₂ groups leading to III than by intramolecular addition of the NH₂ group to the activated C=C group (a pathway leading to II).

EXPERIMENTAL

Formation of 1,3,5-triphenyl-2-penten-5-on-1-hydrazone (β -phenacylchalconhydrazone) IV, X = NH. A suspension of I (1.5 g) in 20 ml water and 20 ml ether was shaken in a separating funnel with a cold soln of 1 g hydrazine hydrate in 10 ml water for 5 min when most of the perchlorate dissolved. The yellow ethereal layer was separated, concentrated at normal temp in vacuum until it became cloudy, and scratched until it crystallized. The crystals were transferred on a porous plate to absorb the red-brown mother liquor and washed with ether until they became white, m.p. 108-110°. (Found: N, 8·26. C₂₃H₂₀N₂O requires; N, 8·23%), The NMR spectrum shows in CDCl₃ a gradual conversion into water and III.

Formation of 3,5-diphenyl-5-phenacyl-2-pyrazoline (II, X = NH). A soln of VI (1 g) m.p. 119° in 10 ml warm EtOH was treated with excess hydrazine hydrate. A transient red colour appeared, then the soln became pale yellow and on cooling and dilution with water a white compound, m.p. 133° (from EtOH), crystallized in ca. 90% yield. (Found: C, 81·22; H, 5·80; N, 8·00. C₂₃H₂₀N₂O requires: C, 81·15;, H, 5·92; N, 8·23%).

Decomposition of 3,5-diphenyl-5-phenacyl-2-pyrazoline. Dry II (X = NH) was heated above the m.p. on a small flame at atm press. The distillate consisted of VII, whereas the residue crystallized in white needles which melted, after recrystallization from dilute EtOH, at 199°: IR spectra and mixed m.p. with authentic product²¹ indicated that the latter compound was VIII.

If the same decomposition is carried out with $HClO_4$ under reflux in AcOH, the product which crystallizes on cooling is 3,5-diphenylpyrazolium perchlorate m.p. 245° (from AcOH) identical (IR spectrum) with an authentic product. (Found : C, 63·64; H, 4·29; N, 7·16. C₂₁H₁₇ClN₂O₄ requires : C, 63·56; H, 4·32; N, 7·06%).

Reaction of 1,3,5-triphenyl-1,5-pentenedione VI with hydroxylamine. After heating a soln of VI with excess hydroxylamine hydrochloride and sodium acetate (1:1.5 moles) in aqueous EtOH for 5 min, the pale yellow soln was diluted with water. An oil separated. It was taken up in ether, the ether was evaporated and the oil was scratched and seeded. After several days most of its crystallized affording II (X = O), identified by IR and NMR spectra. A minor amount of another product was present in the oily product, whose constitution was not investigated further.

Reaction of 1,3,5-triphenyl-1,5-pentenedione VI with phenylhydrazine. The reaction between VI and phenylhydrazine (1:2.5 moles) was carried out in EtOH and heated under reflux for 10 min. The soln was cooled and scratched, affording the pale yellow II (X = NPh, " β -triphenyl-pyranol hydrazide")^{26, 27} m.p. 124°, identified by IR and NMR spectra.

IR spectra were recorded with a Perkin-Elmer grating spectrophotometer 125; thanks are expressed to Dr. E. Proksch and Dr. W. Szinowatz for making this instrument available.

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