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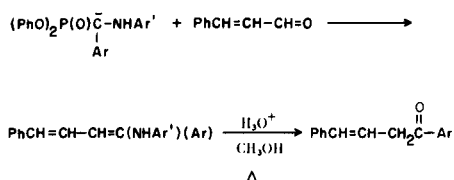
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The carbanions derived of certain diphenyl-1-(4-nitroanilino)-1-(substituted-aryl)methane-phosphonates reacted with phenylpropargyl aldehyde, giving not the expected yne-enamines, but rather 2-phenyl-4-benzylquinolines.

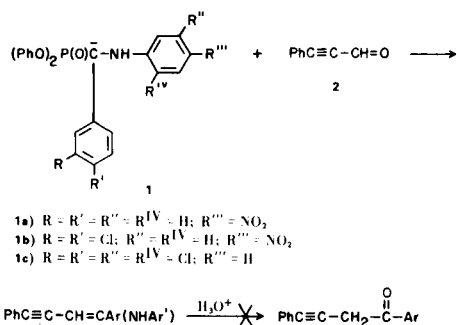
J. Heterocyclic Chem., 15, 1237 (1978)

Sir:

In a recent publication (7) we have shown that carbanions derived of diphenyl- α -1-anilino-1-arylmethane-phosphonates upon reaction with cinnamaldehyde give enamines, which after hydrolysis, lead to the formation of the practically unknown class of vinylogs of deoxybenzoines (2,3). The analogous reaction involving phenyl-

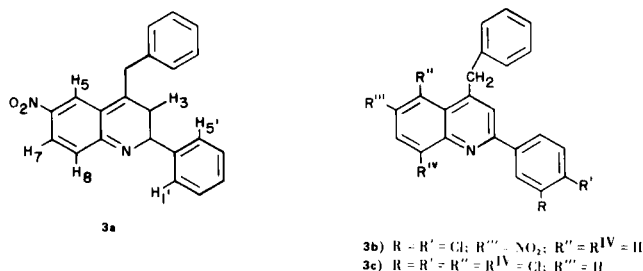


propargyl aldehyde **2**, was thought to represent a route to the unknown class of compounds of yne-analogs of deoxybenzoines. The reaction between the carbanion and

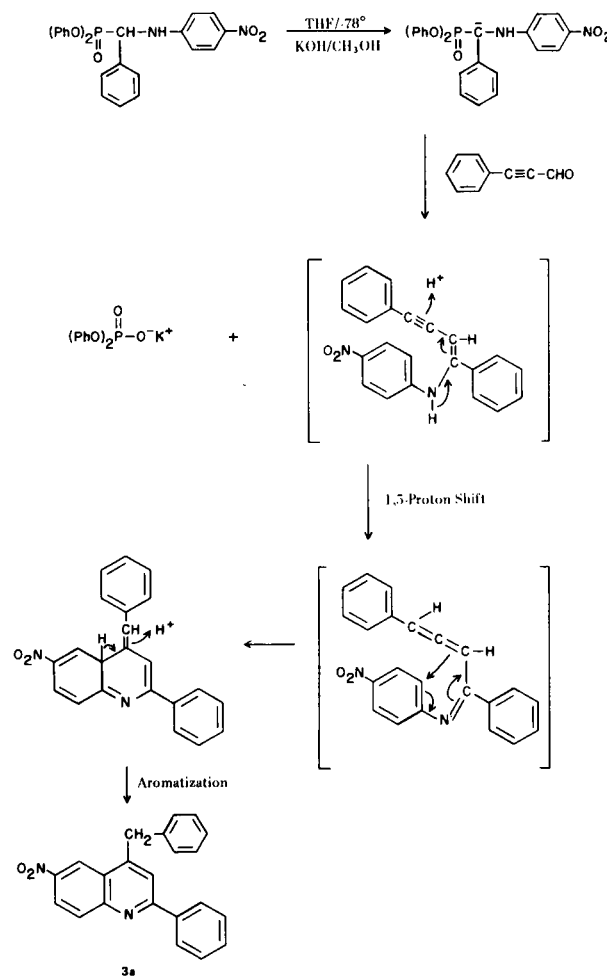


2 proceeded as usual. The color due to the carbanion disappeared. The material isolated in the largest amount, however, could not be hydrolyzed. Also, the ir spectrum did not show a peak due to an N-H group; the nmr spectrum exhibited no peak which disappeared upon shaking the sample with deuterium oxide. In contrast, the N-H proton of literally dozens of enamines prepared by us so far were all exchangeable with deuterium oxide. In addition, the compounds isolated from the reactions involving **2** were almost colorless, whereas the enamines obtained thus far were all deeply colored.

An extensive ¹H-nmr and ¹³C-nmr spectroscopical investigation revealed that these compounds were 2-phenyl-4-benzylquinolines (**3a-3c**). The most revealing feature of the ¹H-nmr spectrum (deuteriochloroform, TMS) for **3a** besides the chemical shift of the benzylic



Scheme 1



protons ($\delta = 4.55$, s) is the splitting pattern of the protons of the benzene ring of the quinoline system. As expected, H₅ has the lowest chemical shift position ($\delta = 9.1$). It is coupled with H₇ ($J_m = 2.4$ Hz) and with H₈ ($J_p = 0.5$ Hz); H₇ and H₈ are spin coupled with each other ($J_o = 9.2$ Hz). The signal due to H₃ appears as a singlet at δ 7.8. The signals for the protons of the two phenyl groups with the exception of H_{1'} and H_{5'} appear as a multiplet between δ 7-7.6. The most useful feature of ¹³C-nmr spectrum is the peak due to the benzylic C-atom at 40.2 ppm (deuteriochloroform).

The mechanism of the formation of these quinolines has not been established. The following scheme serves, however, as a guideline for designing additional experiments to elucidate the mechanism.

Establishing the structures of several compounds isolated in smaller amounts as well as establishing the scope and limitation of this novel reaction is being pursued presently.

EXPERIMENTAL

General Procedure for Preparing the Novel Quinolines.

4-Benzyl-2-phenyl-6-nitroquinoline (3a).

In a three neck flask was placed 2.3 g. (0.005 mole) of diphenyl-1-[(4-nitroanilino)]-1-phenylmethanephosphonate dissolved in 250-300 ml. of tetrahydrofuran and the solution was kept at -78°. This solution was treated with 0.005 mole of a 10% solution of potassium hydroxide in methanol. A deep orange color was generated indicating formation of the carbanion. To this solution was added 0.65 g. (0.005 mole) of freshly distilled

phenylpropargyl aldehyde and the reaction mixture was stirred for 3-4 hours at -78° and another 8-10 hours at room temperature. The progress of reaction was monitored by tlc. Disappearance of one of the two or both spots due to starting materials was, with appearance of a new spot, considered to be the end point of the reaction. The tetrahydrofuran was evaporated under vacuum and the oily residue was treated with 200-300 ml. of distilled water. The aqueous solution was extracted with dichloromethane (3 X 150 ml.). The dichloromethane extracts were dried and evaporated under vacuum. The resulting red oil was taken up in approximately 75 ml. of ethanol brought to boiling and stored in a refrigerator. After cooling overnight, yellow crystals of 3a, C₂₂H₁₆N₂O₂, m.p. 187-188° (ethanol), yield 30%.

Compound 3b.

This compound (C₂₂H₁₄Cl₂N₂O₂) had m.p. 188-189° (methanol), yield 37%.

Compound 3c.

This compound (C₂₂H₁₃Cl₄N) had m.p. 214-215° (ligroin, 60-90°), yield 40%.

All C, H, N, (Cl) analysis agreed within 0.4% with the calculated values.

Acknowledgment.

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REFERENCES AND NOTES

- (1) Paper VII of this series: P. D. Seemuth and H. Zimmer, *J. Org. Chem.*, in press.
- (2) H. Zimmer and D. M. Nene, ACS-Meeting, New Orleans, March 1977, Abstract of papers, Org. Division, 13N.
- (3) H. Zimmer and D. M. Nene, *Chimia*, **31**, 330 (1977) and additional references therein.