

NITRO GROUP PARTICIPATION IN LEUCKART REACTION-I*

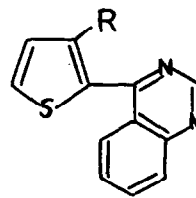
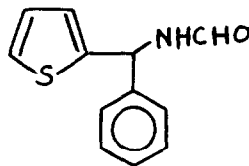
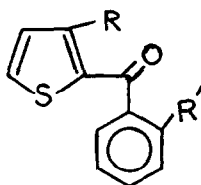
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Recently it was shown that 2-propionylthiophene gives thienyl substituted pyrimidines¹, an anomalous Leuckart product in addition to the expected 1-(2-thienyl)-1, aminopropane^{2,3}. We came across yet another interesting observation which we report below.

Leuckart reaction⁴ on simple benzoylthiophene(Ia) leads to the normal N-formyl product II⁵. However, when there is a nitro group β -to the carbonyl group as in Ib⁶ or Ic, the nitro group participates in the Leuckart reaction and a quinazoline derivative(IIIa or IIIb) was obtained in excellent yield (overall yield 76%) in one step.

The ketones had strong carbonyl I.R. absorption. [1650 cm^{-1} (Ib) and 1660 cm^{-1} (Ia & c)]. However the expected N-formyl carbonyl absorption was not seen in the case of the nitro ketones Leuckart product, nor was the NH absorption seen. Both IIIa and IIIb had a very sharp singlet at 9.2δ (1H) not exchangeable with D_2O in the 60 MHz NMR spectrum, characteristic of the quinazoline proton. The UV absorption spectra of the two compounds were identical and were also similar to the quinazoline spectrum.



Ia $R = R' = \text{H}$
b $R = \text{H}; R' = \text{NO}_2$
c $R = \text{CH}_3; R = \text{NO}_2$

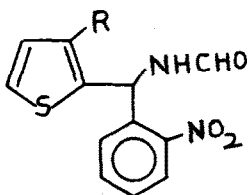
II

IIIa $R = \text{H}$
b $R = \text{CH}_3$

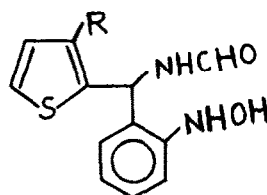
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The elemental analyses and high resolution mass spectra indicated the assigned formulae and the m.p. of IIIa was identical to that reported^{7***}. In this connection we are tempted to believe that the first stage in this two step synthesis may be the formation of the N-formyl compound IV which must afterwards undergo reduction to the N-formylhydroxylamine V followed by dehydrocyclisation to give the totally aromatic quinazolones IIIa or IIIb.

We find this method superior to the method reported for the above and other thienoquinazolines both in yields and in general procedure. We are currently studying the generality of this reaction on several systems and complete details will be reported elsewhere.



IVa R = H
b R = CH₃



V

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