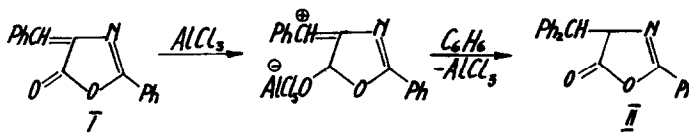


INFLUENCE OF WATER IN THE $AlCl_3$ -CATALYSED REACTION
OF UNSATURATED AZLACTONES WITH AROMATICS

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(Received 22 March 1962)

FILLER and HEBRON reported¹ that unsaturated azlactones (I) react with aromatic hydrocarbons in the presence of aluminium chloride yielding azlactones of type (II). The reaction consists formally in the addition of benzene to the exocyclic double bond of (I); analogous additions are well known, for instance to unsaturated acids.^{2,3}



We found that in the presence of aluminium chloride, saturated azlactones (III) may undergo intramolecular condensations to cyclic α -acylaminoketones⁴ or may react intermolecularly with various aromatic compounds yielding acylaminoketones (IV).^{5,6} This reaction does not require extremely anhydrous conditions.

¹ R. Filler and L.M. Hebron, *J. Org. Chem.* **23**, 1815 (1958).

² C.D. Nenitzescu and I.G. Gavat, *Ber. Dtsch. Chem. Ges.* **70**, 1883 (1937).

³ C.D. Nenitzescu and A.M. Glatz, *Bull. Soc. Chim. Fr.* 218 (1961).

⁴ E. Ciorănescu and L. Bîrlădeanu, *Izv. Akad. Nauk, Otdel. khim. Nauk* 149 (1961).

⁵ E. Ciorănescu, L. Bîrlădeanu and R. Sternberg, *Izv. Akad. Nauk, Otdel. khim. Nauk* 144 (1961).

⁶ P.T. Frangopol, A.T. Balaban, L. Bîrlădeanu and E. Ciorănescu, *Tetrahedron* **16**, 59 (1961).

In a recent attempt to reproduce the preparation of azlactone (III), Awad and Hafez⁷ obtained in place of this product only acylaminoketones (IV) and explained this result by admitting that the unsaturated azlactone (I) is split and that the saturated azlactone (III) thus produced reacts to give the observed product (IV). However these authors make no statement about the other fragment formed by this splitting.

Assuming that the difference between the results of the American¹ and Egyptian⁷ authors may be due to an effect of water observed earlier in our laboratory,⁸ we performed the reaction described by Filler and Hebron in the presence and in the absence of water.

From 2-phenyl-4-benzylidene-5-oxazolone (I) and benzene, in the presence of freshly sublimed aluminium chloride, we obtained in 63 per cent yield azlactone (II), m.p. 157° (lit.¹ m.p. 158°-159°), benzylamine derivative m.p. 261° (lit.¹ m.p. 260°-261°). Thus perfectly anhydrous AlCl₃ is necessary in the reaction of Filler and Hebron.

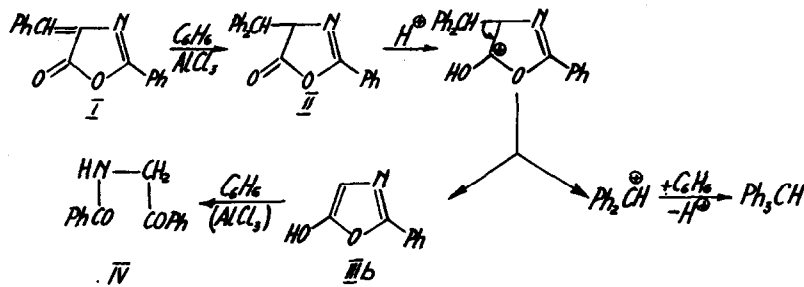
Employing the same conditions but using water-containing aluminium chloride (by exposure of the finely ground anhydrous catalyst, in thin layer, to the atmosphere for five minutes) we obtained from the same reagents the product reported by Awad and Hafez: the residue left after steam-distillation of the reaction mixture consisted in α -benzoylaminoacetophenone (IV) m.p. 124°-125°, yield 61 per cent. A second product obtained in this reaction was triphenylmethane, m.p. 89°, which was carried off by steam. Both products were identified by mixed m.p. with authentic

⁷ W.I. Awad and M.S. Hafez, *J. Org. Chem.* **26**, 2055 (1961).

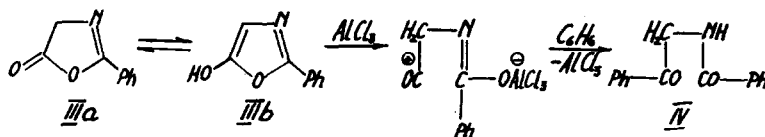
⁸ C.D. Nenitzescu and I.P. Cantuniari, *Ber. Dtsch. Chem. Ges.* **65**, 1449 (1932).

samples.

In order to get an insight into the mechanism of this reaction we treated the azlactone (II) with water-activated aluminium chloride in benzene, and we again obtained after fractionate crystallizations α -benzoylaminoacetophenone (IV) in 65 per cent yield and triphenylmethane in 41 per cent yield. Therefore the reaction can be described by the following sequence:



The addition compound (II) is formed from the unsaturated azlactone and benzene in the presence of either anhydrous or moist aluminium chloride. In the latter case the reaction does not stop here, since under the influence of the strong acid H[AlCl₃OH]^{9,10} this azlactone (II) undergoes a splitting¹¹ into azlactone (IIIb) and a diphenylmethyl carbonium ion, both resonance-stabilized. The reaction of these two fragments with benzene accounts for the formation of triphenylmethane and benzoylaminoacetophenone.



⁹ C.D. Nenitzescu, M. Avram and E. Sliam, *Bull. Soc. Chim. Fr.* 1266 (1955).

¹⁰ J. Miliotis, *C.R. Acad. Sci., Paris* 245, 1314 (1957).

¹¹ D. Fles, M. Dadić, A. Markovac-Prpić and M. Fles, *J. Org. Chem.* 26, 4838 (1961).