place also through an other, preferable free radical mechanism.

EXPERIMENTAL

Thermal decomposition of aryldiazonium tetrachloroborates and tetrabromoborates. The diazonium complex (0.05 mole) was suspended in 80 g. of ligroin (b.p. 110–115°) in a 150 ml. flask equipped with a reflux condenser and closed with a calcium chloride tube to exclude atmospheric moisture. Decomposition of the material was carried out slowly by heating the flask to a temperature slightly above the decomposition point of diazonium complex. After complete decomposition was achieved, which could be noticed by the lack of evolution of boron halide on further heating, the dark solution was diluted with 120 ml. of benzene and poured on ice. The organic layer was isolated and washed with distilled water until neutral. The benzene-ligroin solution was dried with calcium chloride and fractionally distilled at atmospheric pressure.

Arylation of fluorobenzene with aryldiazonium tetrachloroborates and tetrabromoborates. Aryldiazonium tetrahaloborate (0.1 mole) was suspended in 200 ml. of fluorobenzene at room temperature in a 500-ml. flask, equipped with magnetic stirrer, thermometer, reflux condenser, and calcium chloride tube. With constant agitation the mixture was heated to a temperature 10–15° below the thermal decomposition point of the diazonium salt, or, in the case of more stable complexes (decomposition point above 95°), to the boiling point of fluorobenzene in the course of 1 hr. The mixture was then kept at that temperature with continuous agitation until all the solid material dissolved (6 to 48 hr.) yielding a clear brown-red solution. The solution was poured on ice, the organic layer washed with distilled water until it was neutral and dried with calcium chloride. After the removal of fluorobenzene by distillation at atmospheric pressure, the higher boiling reaction products were separated by fractionation at a reduced pressure and analysed by gas-liquid chromatography.

Arylation of fluorobenzene with phenyldiazonium chloride. Phenyldiazonium chloride (25 g.) was suspended in 200 g. of fluorobenzene at 10° in a 500-ml. flask equipped as in the previous experiment. The temperature of the mixture was allowed to rise to 25° in 0.5 hr. with constant agitation and kept at 25° until completion of the reaction (indicated by the disappearance of solid diazonium chloride). Further treatment of the solution was as previously described. Analysis of the fluorobiphenyl isomers was carried out by gas-liquid chromatography. A Perkin-Elmer, Model 154C Vapor Fractometer fitted with a 4 m. × $^1/_4$-in. stainless steel column using polypropylene glycol (UCON LB 550-X) supported on diatomaceous earth was used at a temperature maintained at 195°. Hydrogen (or helium) flowing at 60 cc./min. was utilized as carrier gas.

From the areas of individual peaks mole % figures were calculated for each product after first determining relative response data obtained from pure fluorobiphenyls following the method of Messner, Rosie, and Argabright.[8] Individual peaks of the isomeric fluorobiphenyls were identified with the retention times determined on pure isomers used and also checked by their infrared spectra.

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(8) A. E. Messner, D. M. Rosie, and D. A. Argabright, *Anal. Chem.*, 31 (2), 230 (1959).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

Studies of the Friedel Crafts Reaction on Unsaturated Azlactones

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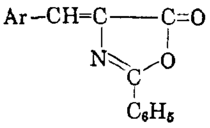
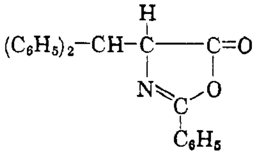
2-Phenyl-4-benzylidene-5(4H)-oxazolone reacts with benzene, toluene, *m*-xylene and chlorobenzene in the presence of anhydrous aluminum chloride to give ω-benzamidoacetophenone derivatives. 2-Benzamidoindenone and 2-acetamidoindenone are prepared by the action of anhydrous aluminum chloride on the corresponding benzylideneoxazolone in carbon tetrachloride. The constitution of the products is discussed.

On attempting to prepare 2-phenyl-4-diphenylmethyl-5-(4H)-oxazolone (II) (yellow crystals, m.p. 158–159°) by the action of anhydrous aluminum chloride on a mixture of benzene and 2-phenyl-4-benzylidene-5(4H)-oxazolone (Ia),[1] we obtained instead a colorless compound, m.p. 123–124°. The same compound was obtained when Ia was replaced by Ib.



I



II

Ia. Ar = C_6H_5
Ib. Ar = *p*-Cl C_6H_4

This indicates that the reaction cannot take place by 1,4-addition of the benzene molecule as proposed by Filler and Hebron,[1] but by the elimination of the arylidene group.

The fact that when benzene was replaced by toluene, *m*-xylene, or chlorobenzene a different product was obtained indicates that the solvent is involved in the reaction. The similarity of the melting point of the products obtained from benzene and toluene with ω-benzamidoacetophenone (IVa), and ω-benzamino-4-methylacetophenone (IVb).[2-5] respectively, indicates that the reaction proceeds according to the following scheme.

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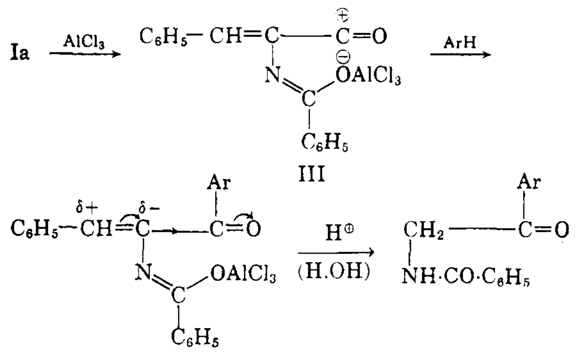
(1) Robert Filler and Lourdes M. Hebron, *J. Org. Chem.*, 23, 1815 (1958).

(2) Robinson, *Beil.*, 14, 54 (1931).

(3) Pictet and Gams, *Beil.*, 14, I, 372 (1933).

(4) Ruggeri and Rigoli, *Beil.*, 14, 37 (1951).

(5) Rüdenburg, *Beil.*, 14, *I*, 380 (1933).



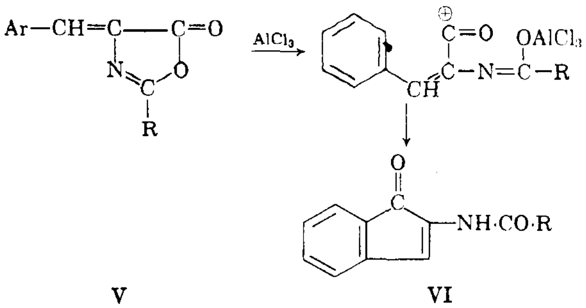
IVa. Ar = C_6H_5
IVb. Ar = $p\text{-}CH_3\ C_6H_4$
IVc. Ar = $3,5\text{-}(CH,)_2\ C_6H_3$
IVd. Ar = $p\text{-}Cl\ C_6H_4$

It seems that the presence of two groups (>C=O and —NHCO C_6H_5) with —T effect attached to the unsaturated carbon of the benzylidene facilitates hydrolysis of the double bond in the acid medium of the reaction mixture.

This structure is further supported by: (1) the interaction of 2-phenyl-5-oxazolone with benzene, toluene, *m*-xylene, and chlorobenzene in the presence of anhydrous aluminum chloride to give the corresponding derivative of IV; (2) infrared spectra (The infrared measurements were carried out in a Perkin-Elmer infracord model 137 in carbon tetrachloride solution. Cell thickness 0.5 mm.) showed in all cases an —NH stretching frequency, amide I, and amide II stretching frequency (*cf.* experimental part); (3) analytical data.

Oxidation of IVd with chromic anhydride yields *p*-chlorobenzoic acid (melting point and mixture melting point experiment), indicating that IVd is a *p*-chloro derivative.

Filler and Hebron[1] stated that no 2-benzamidoindenone (VIa) could be obtained from that reaction. We have now obtained such a compound by intramolecular cyclization of the corresponding benzylideneoxazolone,[6] in acetylene tetrachloride at 60° according to the following scheme.



V VI

Va. Ar = R = C_6H_5 VIa. R = C_6H_5
Vb. Ar = C_6H_5, R = CH_3 VIb. R = CH_3

Structure VI is based upon: (1) oxidation with sulfuric acid and mercuric sulfate to give phthalic acid[7,8]; (2) infrared spectra (*cf.* experimental part); (3) they are all deep red in color; (4) analytical data.

It should be noticed that a colorless compound is also obtained together with the red 2-benzamidoindenone, described in the above reaction. However, its yield increases when the volume of acetylene tetrachloride solvent is reduced. It gave analytical data similar to VIa (*cf.* experimental part) and we believe that this compound is a polymer of VIa.

The previous reactions indicate clearly that the oxazolone ring reacts as a cyclic anhydride.

EXPERIMENTAL[9]

Reaction of 2-phenyl-4-benzylidene-5(4H)-oxazolone (I) *with:* (a) *Benzene.* In a 1-l., round-bottom flask, fitted with a mechanical stirrer, dropping funnel, and reflux condenser, was placed 9.5 g. (0.072 mole) of anhydrous aluminum chloride in 125 ml. of dry, thiophene free benzene. The mixture was cooled to 10° and stirred for 1 hr. To this solution was added dropwise with stirring a solution containing 6.0 g. (0.024 mole) of 2-phenyl-4-benzylidene-5(4H)-oxazolone (Ia) in 125 ml. of dry benzene, the temperature being maintained at 10–20° during the addition. The mixture turned brick-red, when all the oxazolone had been added; the mixture was stirred for 3 hr. at room temperature. The complex was decomposed with 250 ml. of dilute (1:15) hydrochloric acid, and two clear layers were obtained. The benzene layer was separated, the aqueous layer extracted with benzene and the combined extracts washed with dilute hydrochloric acid, then with water until neutral to litmus. The benzene was dried over anhydrous sodium sulfate and removed by evaporation on a steam bath to give a brown oil. It was dissolved in ether and on addition of petroleum ether (b.p. 40–60°) a colorless substance separated. It was filtered off and crystallized from petroleum ether (b.p. 60–80°) as colorless crystals, m.p. 123–124° (Robinson,[2] stated the m.p. for ω-benzamidoacetophenone is 123°; Pictet and Gams,[3] stated m.p. 124°; Ruggeri and Rigoli,[4] gave m.p. 125° for the same compound); yield (1.8 g.).

Anal. Calcd. for $C_{15}H_{13}N\ O_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 74.95; H, 5.47; N, 6.08.

Infrared spectrum: —NH stretching frequency at 3571 cm.$^{-1}$; amide I, 1666 cm.$^{-1}$; and amide II, 1618 cm.$^{-1}$ The mother-liquor was concentrated, to give an oily residue which could not be solidified.

(b) *Toluene.* The experiment was carried out as described in (a), using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 6.0 g. (0.024 mole) of the oxazolone (Ia), and 250 ml. of dry toluene. After hydrolysis with dilute hydrochloric acid (1:15) 250 ml., the toluene layer was separated, washed with water until neutral to litmus, and the toluene was steam distilled. The residue thus obtained was extracted with ether, the ether dried over anhydrous sodium sulfate and distilled. A colorless substance separated, which was filtered off and crystallized from benzene as colorless needles, m.p. 118° (Rüdenberg,[5] stated that m.p. for ω-benzamino-4-methylacetophenone is 118–119°) (yield 4.9 g.).

Anal. Calcd. for $C_{16}H_{15}N\ O_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 76.26; H, 5.84; N, 5.64.

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[6] M. S. Newman and L. M. Joshel, *J. Am. Chem. Soc.*, **62,** 972 (1940).

[7] A. Schönberg, W. I. Awad, and G. A. Mousa, *J. Am. Chem. Soc.*, **77,** 3850 (1955).

[8] W. I. Awad and M. S. Hafez, *J. Org. Chem.*, **25,** 1180 (1960).

[9] Microanalyses are carried out by Alfred Bernhardt, in Max Planck Institut, Mülheim (Ruhr), Germany. The melting points are not corrected.

Infrared spectrum: —NH stretching frequency at 3571 cm.$^{-1}$; amide I, 1666 cm.$^{-1}$; amide II, 1618 cm.$^{-1}$

(c) *m-Xylene.* The experiment was carried out as described before in (b), using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 6.0 g. (0.024 mole) of the oxazolone (Ia), and 250 ml. of dry *m*-xylene. The product thus obtained crystallized from benzene as colorless crystals, m.p. 129° (yield 5.7 g.).

Anal. Calcd. for $C_{17}H_{17}N\ O_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.63; H, 6.45; N, 5.24.

Infrared spectrum: —NH stretching frequency at 3597 cm.$^{-1}$; amide I, 1689 cm.$^{-1}$; amide II, 1622 cm.$^{-1}$.

(d) *Chlorobenzene.* The experiment was carried out as described before in (b), using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 6.0 g. (0.024 mole) of the oxazolone (Ia), and 250 ml. of dry chlorobenzene. The product thus obtained crystallized from benzene as colorless needles, m.p. 160° (yield 5.9 g.).

Anal. Calcd. for $C_{15}H_{12}N\ Cl\ O_2$: C, 65.81; H, 4.38; N, 5.11; Cl, 12.98. Found: C, 65.99; H, 4.27; N, 4.91; Cl, 12.85.

Infrared spectrum: —NH stretching frequency at 3508 (weak) cm.$^{-1}$; amide I, 1689 cm.$^{-1}$; amide II, 1562 cm.$^{-1}$ (broad).

Reaction of 2-phenyl-4(2-chlorobenzylidene)5(4H)-oxazolone with benzene. The experiment was carried out as described before in the case of (2-phenyl-4-benzylidene-5(4H)-oxazolone (Ia) with benzene), using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 6.8 g. (0.024 mole) of the oxazolone (Ib), and 250 ml. dry, thiophene free benzene. The product crystallized from petroleum ether (b.p. 60–80°) as colorless crystals, m.p. 123–124° (yield 0.95 g.). It was proved to be IVa (melting point and mixture melting point).

Reaction of 2-phenyl-5-oxazolone with: (a) *Benzene.* The experiment was carried out as described before in the case of (2-phenyl-4-benzylidene-5(4H)-oxazolone with benzene), using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 3.9 g. (0.024 mole) of the oxazolone, and 250 ml. dry thiophene free benzene. The product crystallized from petroleum ether (b.p. 60–80°) as colorless crystals, m.p. 123–124°, (yield 3.55 g.). It was proved to be IVa (melting point and mixture melting point).

(b) *Toluene.* The experiment was carried out as described before in the case of (2-phenyl-4-benzylidene-5(4H)-oxazolone with toluene), using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 3.9 g. (0.024 mole) of the oxazolone, and 250 ml. of dry toluene. The product crystallized from benzene as colorless needles, m.p. 118° (yield 3.7 g.). It was proved to be IVb (melting point and mixture melting point).

(c) *m-Xylene.* The experiment was carried out as described in (b), using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 3.9 g. (0.024 mole) of the oxazolone, and 250 ml. of dry *m*-xylene. The product crystallized from benzene as colorless crystals, m.p. 129° (yield 3.4 g.). It was proved to be IVc (melting point and mixture melting point).

(d) *Chlorobenzene.* The experiment was carried out as described in (b), using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 3.9 g. (0.024 mole) of the oxazolone, and 250 ml. of dry chlorobenzene. The product crystallized from benzene as colorless needles, m.p. 160° (yield 3.85 g.). It was proved to be IVd (melting point and mixture melting point).

Oxidation of IVd. A mixture of 2 g. of IVd, 6.0 g. of chromic anhydride and 100 ml. of glacial acetic acid, was placed in a round bottomed flask (150 ml. capacity). The mixture was then heated on a water bath for 30 min., then the acetic acid was distilled under reduced pressure; the residue thus obtained was poured on an ice water mixture and extracted with ether. The ether layer was separated and washed with water (100-ml. portions) three times. The ether was then extracted with 200 ml. of a 5% solution of sodium bicarbonate. The bicarbonate layer was separated and acidified with dilute hydrochloric acid, to give a colorless substance. It was filtered off, washed with water and sublimed, m.p. 242–243° (yield 0.80 g.). It was proved to be *p*-chlorobenzoic acid (melting point and mixture melting point).

Preparation of 2-benzamidoindenone. In a 1-l., round-bottom flask, fitted with a mechanical stirrer, dropping funnel and reflux condenser, was placed 9.5 g. (0.072 mole) of anhydrous aluminum chloride in 125 ml. of dry acetylene tetrachloride. The mixture was stirred for 1 hr. at room temperature. To this was added with stirring a solution containing 6.0 g. (0.024 mole) of 2-phenyl-4-benzylidene-5(4H)-oxazolone (Ia) in 125 ml. of dry acetylene tetrachloride. When all the oxazolone had been added, the reaction mixture was stirred at 60° (by heating on a water-bath) for 1 hr., then stirring was continued for 2 hr. at room temperature. The complex was decomposed with 250 ml. of dilute (1:15) hydrochloric acid and two clear layers were obtained. The acetylene tetrachloride layer was separated, washed with dilute hydrochloric acid, then with water until neutral to litmus. The acetylene tetrachloride was steam distilled. The residue thus obtained was extracted with ether, the ether layer separated, dried over anhydrous sodium sulfate and the ether was distilled; the volume was reduced to 50 ml. A red substance separated which was filtered off and crystallized from benzene-petroleum ether (40–60°) as dark red needles, m.p. 140° (yield 4.3 g.). It gave a brown-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{16}H_{11}N\ O_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 76.93; H, 4.37; N, 5.81.

Infrared spectrum: —NH stretching frequency at 3496 cm.$^{-1}$; amide I, 1686 cm.$^{-1}$; amide II, 1607 cm.$^{-1}$, and a frequency at 1724 cm.$^{-1}$ for a cyclic five-membered ketone.[10]

The mother-liquor was concentrated to give a colorless substance, which was filtered and crystallized from ethyl alcohol as colorless needles, m.p. 219° (yield 0.53 g.).

Anal. Found: C, 77.25; H, 4.47; N, 5.63.

The above reaction was repeated using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 6.0 g. (0.024 mole) of the oxazolone (Ia), and a total volume of acetylene tetrachloride (100 ml.). The reaction was carried out as described before, where 0.9 g. indenone and 3.7 g. of the colorless substance were obtained.

Preparation of 2-acetamidoindenone. The experiment was carried out as described before in the case of 2-benzamidoindenone, using 9.5 g. (0.072 mole) of anhydrous aluminum chloride, 4.5 g. (0.024 mole) of 2-methyl-4-benzylidene-5(4H)-oxazolone (Vb), and 250 ml. of dry acetylene tetrachloride. The product thus obtained was crystallized from benzene in dark red needles, m.p. 163° (yield 3.3 g.). It gave an orange color with concentrated sulfuric acid.

Anal. Calcd. for $C_{11}H_9N\ O_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 71.01; H, 4.59; N, 7.64.

Infrared spectrum: —NH stretching frequency at 3546 cm.$^{-1}$; amide I, 1724 cm.$^{-1}$; amide II, 1615 cm.$^{-1}$

Oxidation of VIa. A mixture of VIa (0.5 g.), mercuric sulfate (0.3 g.), and concd. sulfuric acid (4 ml.), was placed in a glass retort (100-ml. capacity). The mixture was then heated in a metal bath for 10 min. at 250° (bath temperature), then for 50 min. at 300–310° (bath temperature), when colorless needles were observed on the colder part of the retort tube. The crystals were scratched out of the tube and sublimed to give characteristic needles of phthalic anhydride (melting point and mixture melting point and positive fluorescein test).

Acknowledgment. The authors wish to express their thanks to Professor F. G. Baddar, Professor of Organic Chemistry, Faculty of Science, A'in Shams University, for his kind discussions during this work.

ABBASSIA, CAIRO, EGYPT, U.A.R.

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(10) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, First Edition, reprinted 1956, London, Methuen, p. 128.