Acridine dissolved in hexane–benzene was filtered hot; slow cooling gave hair-like, pale yellow crystals.

Anal. Calcd. for $C_{13}H_9N$: C, 87.1; H, 5.1; N, 7.8. Found: C, 87.2; H, 4.9; N, 7.5; radioassay, 0.214 mμc./mg. C.

Another sample was recrystallized first from benzene. These crystals were then recrystallized from absolute ethanol. The crystals from ethanol were then recrystallized from absolute ether. Analyses are given in corresponding order.

Anal. Found: 1. 0.220 mμc./mg. C; 2. 0.211 mμc./mg. C; 3. 0.217 mμc./mg. C.

A five-step crystallization using hexane–benzene was then carried out on sublimed material. Analyses are given for the first, third and fifth steps.

Anal. Found: 1. 0.221 mμc./mg. C; 3. 0.218 mμc./mg. C; 5. 0.217 mμc./mg. C.

Total Activity in Acridine.—The total activity in the form of acridine was estimated as follows. A minimum figure is obtained by using that weight of acridine actually recovered. These figures are A, 2.064; B, 14.02 g. Considering losses in sublimation, transfer, etc., an estimate can be made of the most probable value for recoverable acridine. These figures are A, 3.14 g.; B, 18.42 g. The maximum figure can be considered to be that ignoring any radiation damage. These figures are A, 3.674 g.; B, 24.336 g., and are useful only insofar as they place an upper limit on the total activity as acridine.

UPTON, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Action of Grignard Reagents. VII. Benzoxazones, Benzoxaz-2,4-diones and 2,3-Diphenylquinazolone-4

BY AHMED MUSTAFA, WAFIA ASKER, MOHAMED KAMEL, AHMED F. A. SHALABY AND ALAA ELDIN A. E. HASSAN

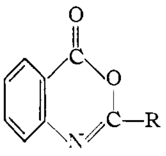
RECEIVED AUGUST 26, 1954

Treatment of benzoxazones with phenylmagnesium bromide brought about cleavage of the hetero ring in the case of 2-phenyl-3,1-benzoxaz-4-one (Ib), 2,3-benzoxaz-1-one (IVa) and its 4-aryl derivatives (IVb,c), and addition to the carbonyl group in the case of 2-phenyl-1,3-benzoxaz-4-one (VII). Addition of the Grignard also occurred with the benzoxazdiones, 1,3-benzoxaz-2,4-dione (Xa) and its benzoyl derivative Xb, which yielded a compound believed to have the structure represented by XIa, together with triphenylcarbinol in the case of Xb. Treatment with phenylmagnesium bromide, followed by hydrolysis, caused opening of the hetero ring in 2,3-diphenylquinazolone-4 (XIIb) to give III and aniline.

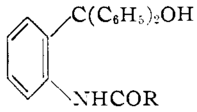
Mustafa and co-workers[1] have shown that the treatment of 1,8-naphthosultone, N-phenylsulfonylnaphthosultam, 2-phenyl-1,2-benzisothiazol-3-one-1,1-dioxide, 2-phenylsulfonyl-1,2-benzisothiazol-3-one and N-phenylsulfonylphthalimide with Grignard reagents results in opening of the hetero five-membered ring. We have now investigated the reaction of the hetero six-membered ring in benzoxazones (Ia-b, IVa-c and VII), benzoxaz-2,4-diones (Xa,b) and 2,3-diphenylquinazolone-4 (XIIb) with these reagents. It has been shown that the reactions of Grignard reagents with 2-methyl-3,1-benzoxaz-4-one (Ia)[2] and coumarin[3] are not strictly analogous. Thus, Ia reacted with phenylmagnesium bromide by the inverse method to give the acetyl derivative of *o*-aminobenzophenone (33%) and with this reagent by direct addition to give only 2-acetamidophenyldiphenylcarbinol (IIa, 23%); in the case of coumarin, the carbinol is the only product formed by either method. We obtained the carbinol IIa in almost quantitiative yield by addition of Ia to the Grignard.

Treatment of 2-phenyl-3,1-benzoxaz-4-one (Ib) with phenylmagnesium bromide, by both the inverse method and normal addition, gave only 2-benzamidophenyldiphenylcarbinol (IIb) and its dehydration product 2,4,4-triphenyl-3,1-benzoxazine (III). Treatment of Ib with phenyllithium gave results similar to those obtained with phenylmagnesium bromide.

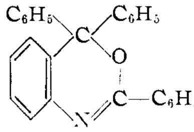
The structure of II and III was determined by the benzoylation of *o*-aminotriphenylcarbinol which yielded IIb; dehydration of IIb yielded III.[4]



Ia, R = CH_3
b, R = C_6H_5

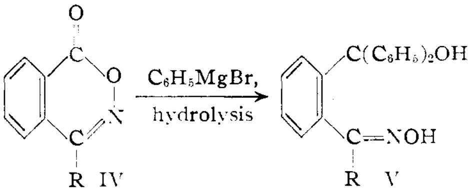


IIa, R = CH_3
b, R = C_6H_5

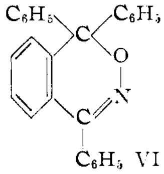


III

Treatment with phenylmagnesium bromide brought about opening of the oxazone ring in the 2,3-benzoxaz-1-ones, IVa-c, which yielded the corresponding oximes of 2-formyl- (Va), 2-benzoyl- (Vb) and 2-(α-naphthoyl)-triphenylcarbinol (Vc), respectively.



IV and V: a, R = H; b, R = C_6H_5; c, R = α-$C_{10}H_7$



VI

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[1] (a) A. Mustafa, *J. Chem. Soc.*, 2151 (1949); (b) A. Mustafa and M. K. Hilmy, *ibid.*, 1339 (1952); (c) A. Mustafa and O. H. Hishmat, THIS JOURNAL, **75**, 4647 (1953).

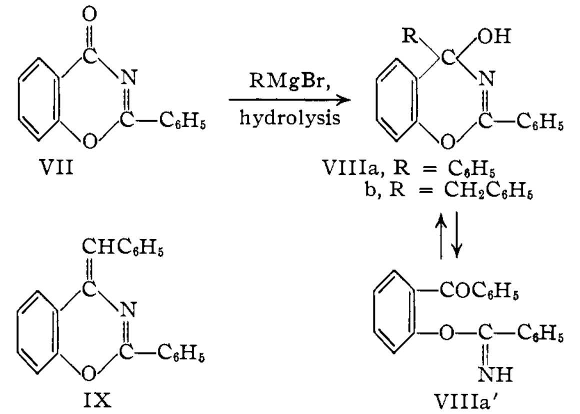
[2] W. C. Lothrop and P. A. Goodwin, *ibid.*, **65**, 363 (1943).

[3] I. M. Heilbron and D. W. Hill, *J. Chem. Soc.*, 2005 (1927).

[4] A. Baeyer and V. Villiger, *Ber.*, **37**, 3191 (1904).

The structure of Vb which was taken as an example of compounds Va-c, was inferred from the fact that it was converted readily to 1,1,4-triphenyl-2,3-benzoxazine (VI); furthermore, when the product obtained by the action of phenylmagnesium bromide on diethyl phthalate[5] was treated with hydroxylamine hydrochloride in glacial acetic acid, VI was obtained.

In contrast to I and IV, which underwent hetero ring opening with phenylmagnesium bromide, 2-phenyl-1,3-benzoxaz-4-one (VII) reacted with the Grignard to yield 2,4-diphenyl-4-hydroxy-1,3-benzoxazine (VIIIa) which could also be present in equilibrium with the open form, VIIIa′. When VII was treated with benzylmagnesium chloride and the product was hydrolyzed, 2-phenyl-4-benzal-1,3-benzoxazine (IX) was obtained rather than VIIIb.[6] That VIIIa and IX are not identical in structure is indicated by the analytical results; furthermore, VIIIa is colorless and contains an active hydrogen atom, while IX is yellow and contains no active hydrogen. The behavior of VII toward Grignard reagents is comparable to that of flavone.[7]



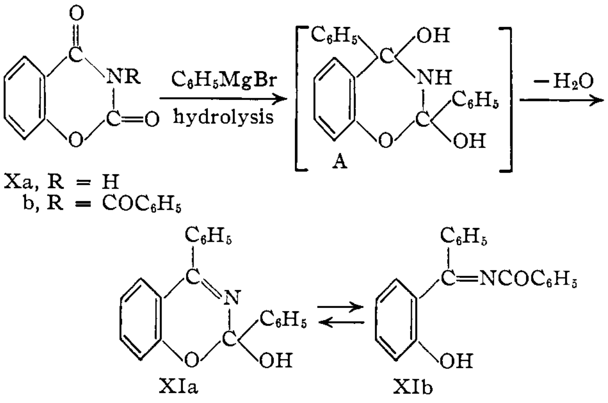
VII

VIIIa, R = C_6H_5
b, R = $CH_2C_6H_5$

IX

VIIIa′

Little is known about the action of Grignard reagents on benzoxaz-diones. When 1,3-benzoxaz-2,4-dione (Xa) was treated with phenylmagnesium bromide, addition to the carbonyl groups occurred with the formation of XIa.



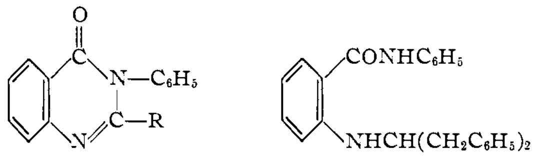
Xa, R = H
b, R = COC_6H_5

XIa XIb

The properties[8] listed in the Experimental section indicate that the product is represented by structure XIa rather than the open tautomeric form XIb. The fact that XIa is not identical with VIIIa excludes the possibility of the formation of VIIIa by dehydration of the intermediate (A).

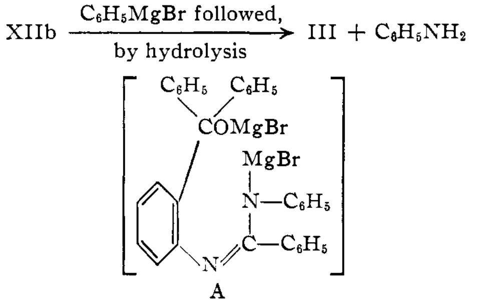
Xb reacted with phenylmagnesium bromide, with elimination of the benzoyl group and addition to the carbonyl group, to yield XIa and triphenylcarbinol.[9]

The action of Grignard reagents on substituted derivatives of quinazolone-4 has been studied by Koelsch[10] and Heilbron[11]; whereas, 3-phenylquinazolone-4 (XIIa) reacts with benzylmagnesium chloride to form XIII, 1,2-dimethylquinazolone-4 adds phenylmagnesium bromide in the usual manner to the carbonyl group.



XIIa, R = H; b, R = C_6H_5 XIII

We have found that when 2,3-diphenylquinazolone-4 (XIIb) reacted with phenylmagnesium bromide followed by hydrolysis, III and aniline were obtained. (A) is an intermediate in this reaction.



Experimental

Action of Phenylmagnesium Bromide. (a) 2-Phenyl-3,1-benzoxaz-4-one (Ib). Normal Addition.—To a solution of phenylmagnesium bromide (prepared from 0.9 g. of magnesium and 9 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1.5 g. of Ib[12] in 50 ml. of dry benzene. The ether was evaporated and the reaction mixture heated for 3 hours on a steam-bath. After the mixture had stood overnight at room temperature, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution and extracted with ether. The precipitate which separated from the ether–benzene mixture was crystallized from glacial acetic acid as colorless crystals (yield 0.9 g., m.p. 212–213°) and identified as 2,4,4-triphenyl-3,1-benzoxazine (III) by m.p. and mixed m.p. with an authentic sample prepared as described below.

Anal. Calcd. for $C_{26}H_{19}NO$: C, 86.4; H, 5.3; N, 4.4. Found: C, 86.2; H, 5.2; N, 4.2.

The filtered ether–benzene mixture was dried over sodium

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[5] L. B. Howell, THIS JOURNAL, **42**, 2333 (1920).

[6] *Cf.* the formation of 3-phenyl-2-benzalbenzothiazoline by the action of benzylmagnesium chloride on 3-phenylbenzothiazol-2-one; H. Passing, *J. prakt. Chem.*, **153**, 5 (1939).

[7] E. R. Watson, K. B. Sen and V. R. Medhi, *J. Chem. Soc.*, **107**, 1477 (1915); I. M. Heilbron, D. H. Hey and A. Lowe, *ibid.*, 1380 (1936); I. M. Heilbron and A. Zaki, *ibid.*, 1902 (1931).

[8] These properties are quite different from these of salicylidenebenzamide the structure of which is similar to XIb; A. W. Titherley and N. E. Marples, *J. Chem. Soc.*, **93**, 1933 (1908).

[9] Similarly, the benzoyl group of 9-benzoylcarbazole is split off by reaction with phenylmagnesium bromide; A. Mustafa, W. Asker, O. H. Hishmat, A. F. A. Shalaby and M. Kamel, THIS JOURNAL, **76**, 5447 (1954).

[10] C. F. Koelsch, *ibid.*, **67**, 1718 (1945).

[11] F. M. Hammer, I. M. Heilbron, J. H. Reade and H. N. Walls, *J. Chem. Soc.*, 251 (1932).

[12] G. Heller and G. Fiesselmann, *Ann.*, **324**, 118 (1902).

sulfate, filtered and evaporated. The oily residue was washed several times with cold light petroleum[13] (*ca.* 40 ml.) and the resulting solid was crystallized from glacial acetic acid as colorless crystals of 2-benzamidophenyldiphenylcarbinol (IIb), yield 0.4 g., m.p. 232°.

Anal. Calcd. for $C_{26}H_{21}NO_2$: C, 82.3; H, 5.5; N, 3.7. Found: C, 82.0; H, 5.4; N, 3.5.

IIb is easily soluble in hot benzene and acetic acid, but difficulty soluble in cold ethyl alcohol and light petroleum. It gives an orange-red color when treated with concentrated sulfuric acid. It was proved to be identical with an authentic sample (prepared as below by m.p. and mixed m.p.).

Inverse Method.—To a solution of 1.5 g. of Ib in 50 ml. of benzene was added slowly a solution of phenylmagnesium bromide in a nitrogen atmosphere under a positive pressure of 7 cm. The reaction mixture was refluxed for 3 hours, and then worked up as described above; IIb (0.15 g.) and III (0.9 g.) were obtained.

(b) **2-Methyl-3,1-benzoxaz-4-one (Ia).**—To a solution of phenylmagnesium bromide was added 1 g. of Ia[14] dissolved in 50 ml. of dry benzene. The reaction mixture was refluxed for 3 hours (steam-bath), set aside overnight at room temperature, and then worked up as described above. The solid (0.5 g.) which precipitated from the ether–benzene mixture, and the crystals (0.3 g.) which separated upon the addition of 30 ml. of light petroleum to the concentrated ether–benzene mixture were recrystallized from dilute ethyl alcohol to give colorless crystals, m.p. 198°; they were identified as 2-acetamidophenyldiphenylcarbinol (IIa) by m.p. and mixed m.p.[4]

2-Benzamidophenyldiphenylcarbinol (IIb).—A solution of 1 g. of 2-aminotriphenylcarbinol[4] in 10 ml. of freshly distilled pyridine was treated with 3 ml. of benzoyl chloride. The reaction mixture was heated (steam-bath) for 3 hours and then poured onto crushed ice. The solid was filtered, washed several times with cold dilute hydrochloric acid (*ca.* 20 ml.) and finally with water, and recrystallized from acetic acid as colorless crystals of IIb, m.p. 232°, yield 0.82 g.

Anal. Calcd. for $C_{26}H_{21}NO_2$: C, 82.3; H, 5.5; N, 3.7. Found: C, 82.2; H, 5.3; N, 3.7.

The m.p. of this sample was not depressed, when it was mixed with IIb, prepared by the action of phenylmagnesium bromide on Ib; the two preparations gave an orange-red color with concentrated sulfuric acid.

2,4,4-Triphenyl-3,1-benzoxazine (III).—A solution of 0.5 g. of IIb and 10 ml. of acetic anhydride, containing 0.5 g. of freshly fused sodium acetate, was refluxed for 3 hours. The cooled reaction mixture was poured onto crushed ice. The solid was filtered and crystallized from glacial acetic acid as colorless crystals (yield 0.30 g., m.p. 212–213°) which were identified as III by m.p. and mixed m.p. It gives an orange color with concentrated sulfuric acid.

Action on Phenyllithium on Ib.—Ib was treated with cold clear solution of phenyllithium (prepared from 10 g. of bromobenzene, 1 g. of lithium and 50 ml. of dry ether) as described for the reaction with phenylmagnesium bromide by the inverse method. The precipitate (0.8 g.) from the ether–benzene layer was identified as III by m.p. and mixed m.p. The filtered ether extract was concentrated and about 10 ml. of light petroleum added. The resulting solid was identified as IIb (m.p. and mixed m.p.).

Action of Phenylmagnesium Bromide on: (a) **4-Phenyl-2,3-benzoxaz-1-one (IVb).**—A solution of 1.5 g. of IVb[15] in 40 ml. of benzene was treated with phenylmagnesium bromide as described for Ia. The solid residue, obtained by evaporation of the ether extract, was crystallized from xylene as colorless crystals of the oxime of 2-benzoyltriphenylcarbinol (Vb), m.p. 199°, yield 0.99 g.

Anal. Calcd. for $C_{26}H_{21}NO_2$: C, 82.3; H, 5.5; N, 3.7. Found: C, 82.2; H, 5.1; N, 3.3.

Vb is difficultly soluble in alcohol and ether, and soluble in hot benzene and xylene: it gives a yellow-brown color with concentrated sulfuric acid.

A mixture of 1 g. of Vb, 15 ml. of glacial acetic acid and 2 ml. of concentrated hydrochloric acid was heated (steam-bath) for 10 hours. When the cold reaction mixture was poured onto crushed ice, a solid residue was obtained which was filtered, washed thoroughly with cold water, dried and crystallized from benzene–light petroleum as colorless crystals of VI; yield 0.74 g., m.p. 138°; admixture with a sample of VI, prepared as described below, gave no depression of m.p.

Anal. Calcd. for $C_{26}H_{19}NO$: C, 86.4; H, 5.3; N, 4.4. Found: C, 86.3; H, 5.1; N, 4.2.

1,1,4-Triphenyl-2,3-benzoxazine (VI).—Hydroxylamine hydrochloride (1.5 g.) was mixed with 2 g. of the product (obtained by the reaction of phenylmagnesium bromide on diethyl phthalate[5]) dissolved in 20 ml. of glacial acetic acid. The reaction mixture was refluxed for 6 hours, cooled and poured onto crushed ice. The resulting solid was filtered, washed thoroughly with water and crystallized from benzene–light petroleum; yield 1.1 g., m.p. 138°. It was identified as VI by m.p. and mixed m.p. with a sample prepared as described above.

(b) **2,3-Benzoxaz-1-one (IVa).**—The oxime of 2-formyltriphenylcarbinol (Va) was prepared from IVa[16] as described for IVb (yield 0.53 g., m.p. 158°).

Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.2; H, 5.6; N, 4.6. Found: C, 79.0; H, 5.6; N, 4.5.

Va dissolves readily in benzene with a pale green fluorescence, is difficultly soluble in light petroleum, and gives a pale yellow color with concentrated sulfuric acid.

(c) **4-(α-Naphthyl)-2,3-benzoxaz-1-one (IVc).**—To a solution of α-naphthylmagnesium bromide (prepared from 1.2 g. of magnesium, 10 g. of α-bromonaphthalene and 50 ml. of dry ether) was added 1 g. of IVc[17] and 50 ml. of benzene. The reaction mixture was worked up in the usual manner. The oxime of 2-(α-naphthoyl)-triphenylcarbinol (Vc) was crystallized from alcohol–benzene; yield 0.63 g., m.p. 242°.

Anal. Calcd. for $C_{39}H_{23}NO_2$: C, 83.9; H, 5.4; N, 3.3. Found: C, 83.5; H, 5.4; N, 3.3.

Vc is readily soluble in benzene, but difficultly soluble in ether and ethyl alcohol; it gives a pale yellow color with sulfuric acid.

Action of Grignard Reagents on 2-Phenyl-1,3-benzoxaz-4-one (VII). (a) **Phenylmagnesium Bromide.**—To a solution of phenylmagnesium bromide was added 1 g. of VII[18] in 30 ml. of dry benzene. The reaction mixture was worked up as described above. The oily residue, obtained on evaporation of the ethereal extract, solidified on scratching and cooling. 2,4-Diphenyl-4-hydroxy-1,3-benzoxazine (VIIIa) was crystallized from benzene–light petroleum as colorless crystals; yield 0.64 g., m.p. 125°.

Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.7; H, 5.0; N, 4.6; active H, 0.33. Found: C, 79.7; H, 4.9; N, 4.5; active H, 0.31.

VIIIa is easily soluble in benzene and hot alcohol, difficultly soluble in light petroleum and insoluble in cold aqueous sodium hydroxide solution; it gives an orange color with sulfuric acid. The alcoholic solution of VIIIa does not become colored when treated with alcoholic ferric chloride solution.

(b) **Benzylmagnesium Chloride.**—To a Grignard solution of benzylmagnesium chloride (prepared from 0.8 g. of magnesium, 5.5 g. of benzyl chloride and 50 ml. of dry ether) was added a solution of 1.5 g. of VII in 40 ml. of benzene. The reaction mixture was worked up in the usual manner. The oily product, obtained upon evaporation of the ethereal extract, solidified after washing with light petroleum and cold ethyl alcohol. 2-Phenyl-4-benzal-1,3-benzoxazine (IX) was obtained as yellow crystals from ethyl alcohol; yield 0.76 g., m.p. 127°.

Anal. Calcd. for $C_{21}H_{15}NO$: C, 84.8; H, 5.1; N, 4.7. Found: C, 84.6; H, 4.8; N, 4.6.

IX is easily soluble in chloroform and benzene, difficultly soluble in cold ethyl alcohol and insoluble in cold aqueous sodium hydroxide solution; it gives a yellow color with sulfuric acid. Its chloroform solution decolorizes a solution of bromine in chloroform.

Action of Phenylmagnesium Bromide on: (a) **1,3-Benzoxaz-2,4-dione (Xa).**—Xa[19] (1.5 g.) was treated with phenylmagnesium bromide as described for Ia. XIa was obtained

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(13) B.p. 50–60°.

(14) M. T. Bogert and H. A. Seil, This Journal, **29**, 517 (1907).

(15) F. H. Thorp, *Ber.*, **26**, 1795 (1893).

(16) O. Allendorff, *Ber.*, **24**, 2346 (1891).

(17) C. Graebe, *ibid.*, **29**, 826 (1896).

(18) A. W. Titherley, *J. Chem. Soc.*, **97**, 200 (1910).

(19) A. Einhorn and C. Mettler, *Ber.*, **35**, 3647 (1902).

as colorless crystals from ethyl alcohol; yield 1.1 g., m.p. 244°.

Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.7; H, 5.0; N, 4.6; active H, 0.33. Found: C, 79.8; H, 5.1; N, 4.6; active H, 0.30.

XIa is insoluble in aqueous sodium hydroxide solution (10%), gives no color with ferric chloride solution and develops an orange color with concentrated sulfuric acid. It is easily soluble in benzene and hot alcohol, but difficulty soluble in ether and light petroleum.

(b) **3-Benzoyl-1,3-benzoxaz-2,4-dione (Xb).**—A solution of 1.5 g. of Xb[19] in 60 ml. of benzene was added to a solution of phenylmagnesium bromide. The reaction mixture was refluxed for 5 hours and kept overnight at room temperature. It was decomposed with dilute hydrochloric acid, extracted with ether and concentrated. The colorless crystals that separated were filtered, recrystallized from alcohol and identified as XIa by m.p., mixed m.p. and color reaction with sulfuric acid; yield 0.78 g., m.p. 244°.

Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.7; H, 5.0; N, 4.6. Found: C, 79.6; H, 5.1; N, 4.4.

The ether-benzene mother liquor was evaporated and the oily residue washed twice with cold light petroleum. The resulting solid was crystallized from petroleum ether (b.p. 80–100°), containing a few ml. of benzene, as colorless crystals (yield 0.31 g., m.p. 163°) which were identified as triphenylcarbinol (m.p. and mixed m.p.).

(c) **2,3-Diphenylquinazolone-4 (XIIb).**—A solution of 1.5 g. of XIIb[20] in 50 ml. of benzene was added to a solution of phenylmagnesium bromide and the reaction mixture decomposed with 100 ml. of cold, dilute hydrochloric acid. The ethereal extract was evaporated and the oily residue, which solidified on cooling and scratching, was washed with cold light petroleum and crystallized from glacial acetic acid as colorless crystals (yield 0.68 g., m.p. 212°) identified as III (m.p. and mixed m.p.).

Anal. Calcd. for $C_{26}H_{19}NO$: C, 86.4; H, 5.3; N, 4.4. Found: C, 86.7; H, 5.3; N, 4.3.

Aniline was detected in the aqueous layer by diazotization and coupling with an alkaline solution of 2-naphthol, to form the scarlet phenyl-azo-2-naphthol dye which proved to be identical with an authentic specimen.

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(20) D. T. Zentmyer and E. C. Wagner, *J. Org. Chem.*, **14**, 967 (1949).

GIZA, CAIRO, EGYPT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

2-Pyrones. XIII.[1] The Chemistry of Coumalic Acid and its Derivatives

BY RICHARD H. WILEY AND LOUIS H. KNABESCHUH[2]

RECEIVED JULY 27, 1954

Coumalyl chloride has been converted to a variety of new compounds including four esters, ten amides and a ketone. It has been noted that the conversion of the chloride to the methyl ester is accompanied by formation of a previously unreported by-product—trimethyl trimesate. The amides are representative of a new class of such compounds and have been established as distinct from the isomeric pyridones, formed from methyl coumalate, by their chemical and physical (absorption) characteristics. The first successful Friedel–Crafts condensation of a 2-pyronecarboxylic acid chloride has provided the first known ketone in this series.

There is abundant evidence in the literature that coumalic acid and its derivatives undergo or fail to undergo reactions for reasons not always obvious from the accepted structural formula. We have commented previously on the difference in stability of the methyl esters of coumalic and isodehydroacetic acid toward pyridone formation.[3,4] Difficulties encountered in esterification of the acid are implied in the variety of reports on the preparation of the ester[5–7] and in the observation that the usual esterification procedure leads to ring fission.[8] Decarboxylation[9] likewise is not practical as it is with isodehydroacetic acid. For these reasons, additional information about the chemistry of coumalic acid and its derivatives is of particular interest.

The esterification of coumalyl chloride, prepared by a useful modification of previously described processes,[10–12] is the most satisfactory, and, in our hands, the only reproducible method of all those reported in the literature[5–8] for the preparation of methyl coumalate. The ester, which can be recrystallized from ligroin to give white crystals, m.p. 67–71°, is not stable and decomposes on attempted fractionation and on standing. The sodium bicarbonate washings of the crude ester, after acidification, slowly deposit a white crystalline solid, m.p. 145–146°, identified as trimethyl trimesate, reported m.p. 144°.[10] We also have isolated this compound as a by-product from the direct esterification of coumalic acid. Presumably the acid conditions result in partial decomposition of the methyl coumalate to methyl formylacetate which is trimerized or is extracted by bicarbonate from the crude ester and on acidification and standing is converted to trimethyl trimesate. This decomposition constitutes a reversal of the reaction by which the acid is formed and the condensation constitutes a reaction similar to mesitylene formation from acetone.

Coumalyl chloride reacts readily at 0° in ether solution to form coumalamide from ammonia or N-substituted coumalamides from primary amines. This reaction is unusual in view of the known ease with which methyl coumalate is converted to pyridones at room temperature and perhaps overemphasis of this possibility may account for the absence of previous descriptions of such amides. Aside from an early ambiguous report by von Pechmann,[12] the only previous[13] report on coumalamides

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(1) Previous paper in this series, R. H. Wiley and C. H. Jarboe, THIS JOURNAL, **77**, 403 (1955).

(2) The authors wish to acknowledge support of this research through a grant NSF-G55 from the National Science Foundation.

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