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

Action of Grignard Reagents. VIII. Action of Organomagnesium and Lithium Compounds on Benzo-, Naphtho-(2′,3′)-oxazol-2-ones and their N-Substituted Derivatives

BY AHMED MUSTAFA, WAFIA ASKER AND ORKEDE HASSAN HISHMAT

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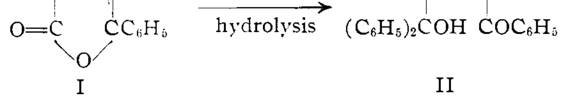
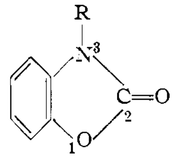
Treatment with Grignard reagents, followed by hydrolysis, caused the opening of the hetero ring in benzo- and in naphtho-(2′,3′)-oxazol-2-ones and their N-aroyl- and N-arylsulfonyl derivatives to give the corresponding N-aroyl- and N-arylsulfonyl derivatives of *o*-aminophenol and of 3-amino-2-naphthol. Similar results were obtained with phenyllithium. Similarly, the action of phenylmagnesium bromide yields 3-keto-1-phenyl-1-hydroxyisoindoline and triphenylcarbinol in the case of N-benzoylphthalimide, benzotriazole and triphenylcarbinol in the case of 1-benzoylbenzotriazole and $\alpha,\alpha,\delta,\delta$-tetraphenylbutylene glycol and *p*-toluenesulfonamide in the case of N-*p*-toluenesulfonylsuccinimide. Phenylmagnesium bromide also brought out the cleavage of N–C bond in N-benzenesulfonylbenzanilide to give benzenesulfonanilide and triphenylcarbinol.

Recently it was shown that phenylmagnesium bromide cleaves the oxazolone ring[1] in 4-methyl-2-phenyl-5-oxazolone (I), forming 2-benzoylamino-1,1-diphenylcarbinol (II).

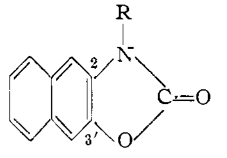


I II

We now have investigated the action of Grignard reagents on benzoxazol-2-one (IIIa), naphtho-(2′,3′)-oxazol-2-one (IVa),[2] their aroyl- (IIIc) and (IVb), arylsulfonyl derivatives (IIId, IIIe and IVc) and 3-acetylbenzoxazol-2-one (IIIb), respectively.

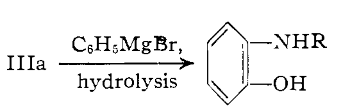


IIIa, R = H; b, R = $COCH_3$
c, R = COC_6H_5; d, R = $SO_2C_6H_5$
e, R = $SO_2C_6H_4CH_3$-*p*

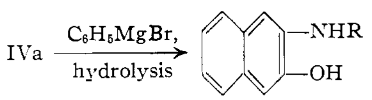


IVa, R = H
b, R = COC_6H_5
c, R = $SO_2C_6H_5$

When IIIa is treated with an excess of phenylmagnesium bromide and the product hydrolyzed, N-benzoyl-*o*-aminophenol (Va) is obtained. Similarly, N-benzoyl-3-amino-2-naphthol (VIa) has been prepared by the action of the same reagent on IVa.



Va, R = COC_6H_5; b, R = $COC_6H_4CH_3$-*p*;
c, R = $COC_{10}H_7$-1
d, R = $SO_2C_6H_5$; e, R = $SO_2C_6H_4CH_3$-*p*

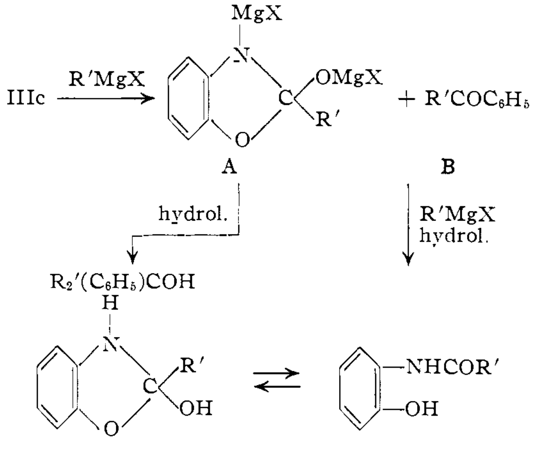


VIa, R = COC_6H_5; b, R = $COC_{10}H_7$-1; c, R = $SO_2C_6H_5$

3-Benzoylbenzo- (IIIc) and 3-benzoylnaphtho-(2′,3′)-oxazol-2-one (IVb), on treatment with excess of phenylmagnesium bromide both by the normal or the inverse addition,[3] give Va and VIa, respectively, together with triphenylcarbinol. Similarly, N-(*p*-toluoyl)- (Vb) and N-(1-naphthoyl)-*o*-aminophenol (Vc) are obtained by the action of *p*-tolyl-, and of 1-naphthylmagnesium halides together with di-(*p*-tolyl)-phenylcarbinol and di-(1-naphthyl)-phenylcarbinol, respectively, on IIIc. The action of 1-naphthylmagnesium bromide on IVb gives rise to N-(1-naphthoyl)-3-amino-2-naphthol (VIb) and di-(1-naphthyl)-phenylmethylcarbinol.

Va similarly is obtained together with diphenylmethylcarbinol by the action of phenylmagnesium bromide on 3-acetylbenzoxazol-2-one (IIIb).

It is believed that the formation of the N-aroyl derivatives Va-c and VIa-b proceeds *via* the sequence of reactions indicated in the scheme



Likewise, treatment of IIIc with phenyllithium gave results which are similar to those obtained with phenylmagnesium bromide.

Whereas arylmagnesium halides effect the elimination of the benzoyl group in IIIc and IVb, methylmagnesium iodide reacts with IIIc, producing fission of the hetero ring with the formation of Va and *t*-butyl alcohol.

3-Benzenesulfonyl- (IIId), 3-*p*-toluenesulfonylbenzoxazol-2-one (IIIe) and 3-benzenesulfonylnaphtho-(2′,3′)-oxazol-2-one (IVc) undergo hetero ring fission by the action of phenylmagnesium bromide, yielding N-benzenesulfonyl- (Vd), N-*p*-tolu-

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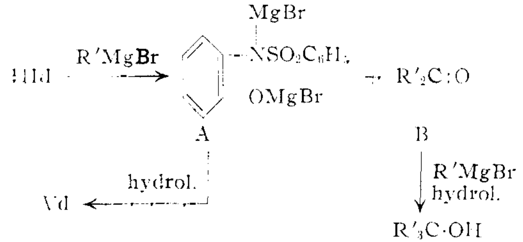
(1) *Cf.* "The Chemistry of Penicillin," H. T. Clarke, J. H. Johnson and R. Robinson, eds., Princeton University Press, Princeton, N. J., 1949, p. 738.

(2) *Cf.* the formation of 3-phenyl-2-benzylbenzothiazolenium perchlorate by the action of benzylmagnesium chloride on 3-phenylbenzothiazol-2-one, followed by the addition of perchloric acid (H. Passing, *J. prakt. Chem.*, **153**, 5 (1939).

(3) *Cf.* the normal and inverse addition of Grignard reagents to 2-methyl-3,1,4-benzoxaz-4-one (W. C. Lothrop and P. A. Goodwin, THIS JOURNAL, **65**, 363 (1943)).

enesulfonyl-*o*-aminophenol (Ve) and N-benzenesulfonyl-3-amino-2-naphthol (VIc), respectively, together with triphenylcarbinol. Similarly, Vd and tri-1-naphthylmethylcarbinol are obtained by the action of 1-naphthylmagnesium bromide on IIId (*cf.* scheme A).

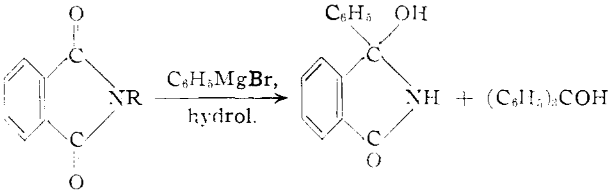
The stability of the N-arylsulfonyl linkage toward the Grignard reagent is contrasted with the ready elimination of the aroyl group attached to the nitrogen atom by this reagent.



Scheme A

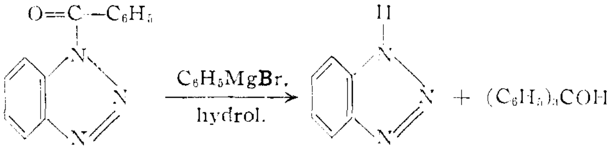
The action of phenyllithium on IIId led to results which are similar to those obtained with phenylmagnesium bromide.

For a further study of the effect of the aroyl- and of the arylsulfonyl group attached to a heterocyclic nitrogen compound on the hetero ring opening with Grignard reagents, the action of phenylmagnesium bromide on N-benzoylphthalimide (VIIa) and on 1-benzoylbenzotriazole (IX) now has been investigated. Thus, whereas N-benzenesulfonylphthalimide (VIIb) undergoes ring fission with phenylmagnesium bromide yielding *o*-bis-(diphenylhydroxymethyl)-benzene (XI) together with benzenesulfonamide and diphenyl,[4] VIIa undergoes elimination of the benzoyl group by the action of the same reagent, forming 3-keto-1-phenyl-1-hydroxyisoindoline (VIII)[5] together with triphenylcarbinol.



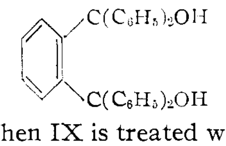
VIIa, R = COC_6H_5
b, R = $SO_2C_6H_5$

VIII



IX

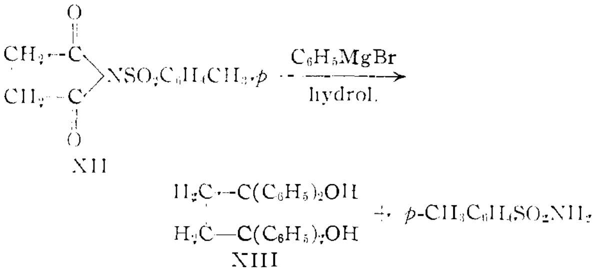
X



XI

Similarly, when IX is treated with phenylmagnesium bromide, triphenylcarbinol and benzotriazole (X) are obtained.[6] The behavior of IX toward Grignard reagents may be compared with its behavior toward lithium aluminum hydride.[7]

N-*p*-Toluenesulfonylsuccinimide (XII), which is closely related to VIIb, reacts analogously with Grignard reagents. Thus XII undergoes ring opening by the action of phenylmagnesium bromide, yielding α,α,δ,δ-tetraphenylbutylene glycol (XIII) together with *p*-toluenesulfonamide. XIII is dehydrated readily by the action of glacial acetic acid and hydrochloric acid to α,α,δ,δ-tetraphenylbutadiene.



Recently Mustafa and co-workers[8] have shown that phenylmagnesium bromide effects the cleavage of the N–S and N–C linkages in N-dibenzenesulfonyl- and N-dibenzoyl derivatives of aniline, yielding benzenesulfonamide together with diphenylsulfone and benzanilide together with triphenylcarbinol, respectively. We now have found that when the mixed aroyl arylsulfonyl derivative, namely, N-benzenesulfonylbenzanilide (XIV) is treated with the same reagent, the latter brings out N–C bond cleavage only, yielding benzenesulfonanilide and triphenylcarbinol. The elimination of the benzoyl group and not the benzenesulfonyl group in the case of XIV with phenylmagnesium bromide may be compared with the results obtained in the case of IIId, IVd, IIc, VIIa and VIIb when treated with the same reagent.

$$C_6H_5N(COC_6H_5)SO_2C_6H_5 \xrightarrow[\text{hydrolysis}]{C_6H_5MgBr} C_6H_5NHSO_2C_6H_5 + (C_6H_5)_3COH$$

Experimental

Action of Phenylmagnesium Bromide on (A) Benzoxazol-2-one (IIIa).—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 1 g. of IIIa[9,10] in 30 ml. of dry benzene. The water was removed from the reflux condenser and the ether evaporated from the reaction mixture, which then was heated for three hours on a steam-bath. After the mixture had stood overnight at room temperature, it was poured slowly in 100 ml. of saturated aqueous ammonium chloride solution and extracted with ether. The ether benzene mixture was dried over sodium sulfate and evaporated. The solid, so ob-

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[4] A. Mustafa and O. H. Hishmat, THIS JOURNAL, **75**, 4647 (1953); compare also the hetero ring opening of 2-(phenylsulfonyl)-1,2-benzisothiazol-3-one with phenylmagnesium bromide, yielding 2-phenylmercaptotriphenylcarbinol (ref. 4).

[5] *Cf.* the formation of 3-keto-1,2-diphenyl-1-hydroxyisoindoline by the action of phenylmagnesium bromide on N-phenylphthalimide C. Beis, *Compt. rend.*, **143**, 432 (1 906)).

[6] This experiment was carried out with Ahmed Fathy Abdel Maugoud Shalaby.

[7] N. G. Gaylord, THIS JOURNAL, **76**, 285 (1954); compare also the analogy between the action of Grignard reagents and of lithium aluminum hydride on N-acetylcarbazole (K. Banholzer, T. W. Campbell and H. Schmid, *Helv. Chim. Acta*, **35**, 1577 (1952)) and N-benzoylcarbazole (A. Mustafa, W. Asker and co-workers, THIS JOURNAL, **76**, 5447 (1954)).

[8] A. Mustafa, W. Asker, O. H. Hishmat and A. F. A. Shalaby, *ibid.*, **76**, 5447 (1954).

[9] H. Lindemann and W. Schultheis, *Ann.*, **451**, 253 (1927).

[10] One gram of the starting material was used unless otherwise stated.

tained, was crystallized from benzene as colorless crystals (*ca.* 0.58 g.), m.p. 164°, identified as N-benzoyl-*o*-aminophenol (Va) (m.p. and mixed m.p.,[11] solubility in alkali and development of greenish-brown color with ferric chloride solution).

(B) **Naphtho-(2',3')-oxazol-2-one (IVa).**—A solution of IVa[12] in 40 ml. of benzene was added to phenylmagnesium bromide (prepared as above). The reaction mixture was worked up; the solid obtained was washed with light petroleum[13] (*ca.* 25 ml.) and crystallized from ethyl alcohol as colorless crystals (*ca.* 0.72 g.), m.p. 233°, which were identified as N-benzoyl-3-amino-2-naphthol (VIa) (m.p. and mixed m.p. determination and formation of 3-benzoylamino-1-(*p*-nitrobenzeneazo)-2-naphthol[14]).

Action of Grignard Reagents on: (A) 3-Benzoylbenzoxazol-2-one (IIIc). (a) **Phenylmagnesium Bromide. Normal Addition.**—A solution of IIIc[15] in 30 ml. of benzene was added portionwise to a solution of phenylmagnesium bromide (prepared as described above). The reaction mixture was refluxed for four hours and kept aside overnight at room temperature, during which yellow solid separated, which went into solution after some time with a brown color changing to green. The reaction mixture was decomposed, extracted with ether and evaporated. The solid residue so obtained was washed with cold light petroleum (*ca.* 20 ml.) and extracted with hot petroleum ether (b.p. 80–100°). The insoluble part was crystallized from benzene as colorless crystals (*ca.* 0.51 g.), identified as Va.

The petroleum ether extract gave on concentration colorless crystals (*ca.* 0.28 g.), m.p. 163°, which proved to be triphenylcarbinol (m.p. and mixed m.p. and color reaction with sulfuric acid).

Inverse Method.—To a solution of IIIc in 50 ml. of benzene was added slowly a solution of phenylmagnesium bromide in a nitrogen atmosphere under a positive pressure of 7 mm. When the reaction mixture was refluxed for three hours and then worked up as described above Va (0.46 g.), and triphenylcarbinol (*ca.* 0.25 g.) were obtained.

(b) ***p*-Tolylmagnesium Iodide.**—To a solution of *p*-tolylmagnesium iodide (prepared from 0.8 g. of magnesium and 7.5 g. of *p*-iodotoluene in 40 ml. of ether) was added a solution of IIIc in 40 ml. of benzene. The reaction mixture was worked up as described in the case of IIIa. The ether–benzene mixture was washed with cold aqueous sodium hydroxide solution (10%, *ca.* 45 ml.), dried and evaporated. The oily residue, so obtained, gave on scratching and cooling colorless crystals mixed with an oily substance. These crystals were separated from the oil by washing with light petroleum (*ca.* 15 ml.) and identified as di-*p*-tolyl.

The light petroleum washing gave, upon concentration and cooling, colorless crystals (*ca.* 0.16 g.), m.p. 75°, identified as di-*p*-tolylphenylcarbinol (m.p. and mixed m.p.[16] and the formation of yellowish-green color when its solution in glacial acetic acid is treated with sulfuric acid).

The alkali washings were acidified, extracted with ether, dried and evaporated. The solid, so obtained, was crystallized from benzene as colorless crystals (*ca.* 0.44 g.), m.p. 135°. N-(*p*-Toluoyl)-*o*-aminophenol (Vb) is soluble in alcohol and benzene, but sparingly soluble in light petroleum; it gives a green color with sulfuric acid and an orange-brown color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 74.0; H, 5.7; N, 6.2. Found: C, 73.8; H, 5.6; N, 6.0.

(c) **1-Naphthylmagnesium Bromide.**—A mixture of 1-naphthylmagnesium bromide (prepared from 1.2 g. of magnesium, 10.4 g. of 1-bromonaphthalene and 40 ml. of ether) and 1.5 g. of IIIc in 40 ml. of benzene was refluxed for three hours and then worked up as described above. The ether–benzene solution was evaporated, and the solid so obtained was crystallized from glacial acetic acid as colorless crystals (*ca.* 0.58 g.), m.p. 165°, which were identified as di-(1-naphthyl)-phenylcarbinol (m.p. and mixed m.p.[17] and the formation of deep violet color with sulfuric acid).

The alkali extract gave, upon acidification with cold dilute hydrochloric acid, followed by extraction with ether and evaporation, colorless crystals (*ca.* 0.87 g.) from benzene, m.p. 192°. It was identified as N-(1-naphthoyl)-*o*-aminophenol (Vc) (m.p. and mixed m.p.[18]). It is easily soluble in hot ethyl alcohol, but sparingly soluble in light petroleum. It gives a green color with sulfuric acid which changes to brown on addition of a crystal of potassium nitrate.

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.6; H, 4.9; N, 5.3. Found: C, 77.5; H, 4.7; N, 5.1.

When 0.5 g. of Vc is treated with 1 ml. of benzoyl chloride in presence of 10 ml. of aqueous sodium hydroxide (15%), it gives colorless crystals from glacial acetic acid (*ca.* 0.61 g.), m.p. 174°. It does not depress the melting point of an authentic specimen of *o*-benzoyl-N-(1-naphthoyl)-*o*-aminophenol.[18]

Anal. Calcd. for $C_{24}H_{17}NO_3$: C, 78.5; H, 4.6; N, 3.8. Found: C, 78.3; H, 4.5; N, 3.7.

Action of Phenyllithium on IIIc.—A cold clear solution of phenyllithium (prepared from 1.2 g. of lithium, 12 g. of bromobenzene and 38 ml. of ether) was added dropwise to a solution of 1.2 g. of IIIc in 35 ml. of benzene. The reaction mixture was refluxed for a half-hour and kept aside for one hour at room temperature, during which the color of the solution changed from green to yellow and finally yellowish-brown. The experiment was carried out in a nitrogen atmosphere under a positive pressure of 7 mm. The reaction mixture was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution, extracted with ether and the ethereal layer was washed with aqueous sodium hydroxide (8%, 40 ml.), then with water, dried and evaporated. The material that separated was recrystallized from petroleum ether (b.p. 80–100°) as colorless crystals (*ca.* 0.47 g.), m.p. 163°, identified as triphenylcarbinol.

The alkali washings, on acidification and extraction with ether, gave 0.72 g. of Va (identification as above).

(B) **3-Benzoylnaphtho-(2',3')-oxazol-2-one (IVb).** (a) **Phenylmagnesium Bromide.**—IVb was prepared by the action of benzoyl chloride on IVa (*cf.* IIIc) and was obtained as colorless crystals from chloroform, m.p. 226° in almost quantitative yield. It is easily soluble in benzene, but difficultly soluble in cold ethyl alcohol and gives a pale-yellow color with sulfuric acid.

Anal. Calcd. for $C_{18}H_{11}NO_3$: C, 74.7; H, 3.8; N, 4.8. Found: C, 74.6; H, 3.8; N, 4.6.

A solution of IVb in 40 ml. of benzene was treated with phenylmagnesium bromide as described in the case of IIIc. The ether benzene solution was evaporated and the solid residue that was obtained was extracted with cold benzene (*ca.* 25 ml.) and the insoluble part was crystallized from hot alcohol as colorless crystals (*ca.* 0.42 g.), m.p. 232°, identified as VIa.[14]

The benzene extract gave, on concentration and cooling, colorless crystals (*ca.* 0.39 g.) which were proved to be triphenylcarbinol.

(b) **1-Naphthylmagnesium Bromide.**—Similarly, the action of 1-naphthylmagnesium bromide on 1.5 g. of IVb was carried out as described in the case of IIIc. Di-(1-naphthyl)-phenylcarbinol (*ca.* 0.51 g.) and VIa (*ca.* 0.88 g.) were obtained (identification as above).

Action of Phenylmagnesium Bromide on 3-Acetylbenzoxazol-2-one (IIIb).—Similarly, the action of phenylmagnesium bromide on a solution of 1.5 g. of IIIb[19] in 40 ml. of benzene was worked up as described in the case of IIIc. Va (*ca.* 0.83 g.) and diphenylmethylcarbinol (*ca.* 0.58 g.) were obtained. The carbinol melted, after washing with light petroleum (b.p. 80–100°), at 82–83° (m.p. and mixed m.p.[20] and the formation of a red color with sulfuric acid).

Action of Phenylmagnesium Bromide on (a) 3-Benzenesulfonylbenzoxazol-2-one (IIId).—A solution of IIIa (1 g.) in 10 ml. of freshly distilled pyridine was treated with 1.5 g. of benzenesulfonyl chloride and the reaction mixture was heated (steam-bath) for a half-hour and kept aside overnight at room temperature. The solid that separated was collected, washed with cold ethyl alcohol (*ca.* 10 ml.) and crystallized from hot alcohol as colorless crystals (*ca.* 1.32 g.), m.p. 144°. IIId, easily soluble in benzene but sparingly soluble in light petroleum, is insoluble in aqueous sodium hydroxide solution (10%) even on boiling.

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[11] H. Hubner, *Ann.*, **210**, 387 (1891).

[12] K. Fries, *Ber.*, **58**, 2849 (1925).

[13] Light petroleum is the fraction boiling at 40–60° and petroleum ether 60–80°; the boiling range of the other fractions is specified.

[14] E. Jusa and E. Riesz, *Monatsh.*, **58**, 137 (1931).

[15] E. von Meyer, *J. prakt. Chem.*, **92**, 257 (1915).

[16] A. Kliegl, *Ber.*, **38**, 86 (1905).

[17] C. S. Schoepfle, THIS JOURNAL, **44**, 188 (1922).

[18] F. Bell, *J. Chem. Soc.*, 1981 (1930).

[19] F. A. Kalckhoff, *Ber.*, **16**, 1828 (1883).

[20] A. Klages, *ibid.*, **35**, 2646 (1902).

Anal. Calcd. for $C_{13}H_9NO_4S$: C, 56.7; H, 3.3; N, 5.1; S, 11.6. Found: C, 56.6; H, 3.1; N, 4.9; S, 11.5.

A mixture of 1.5 g. of IIId and phenylmagnesium bromide was worked up as described in the case of IIIc. The ethereal solution was washed several times with cold aqueous sodium hydroxide solution (40 ml.), then with water, dried and evaporated. Triphenylcarbinol (*ca.* 0.46 g.) was obtained.

The alkali washings gave on acidification, extraction with ether and evaporation colorless crystals (*ca.* 0.78 g.) from benzene, m.p. 140–141°; identified as N-benzenesulfonyl-*o*-aminophenol (Vd) (m.p. and mixed m.p.[21] and the formation of an olive-green color with alcoholic ferric chloride solution).

When 0.5 g. of Vd, prepared as above, was treated with 1 ml. of benzenesulfonyl chloride in the presence of aqueous sodium hydroxide (15%, 20 ml.) and the reaction mixture was heated (steam-bath) for two hours, colorless solid was obtained. This was crystallized from alcohol, m.p. 164°.[21] O,N-Dibenzenesulfonyl-*o*-aminophenol is easily soluble in hot benzene, but sparingly soluble in petroleum ether; yield *ca.* 64%.

Anal. Calcd. for $C_{18}H_{15}NO_5S_2$: C, 55.5; H, 3.9; N, 3.6; S, 16.4. Found: C, 55.2; H, 3.7; N, 3.5; S, 16.3.

(b) **3-*p*-Toluenesulfonylbenzoxazol-2-one (IIIe).**—Similarly, phenylmagnesium bromide and IIIe[22] gave triphenylcarbinol (*ca.* 0.46 g.) and N-*p*-toluenesulfonyl-*o*-aminophenol (Ve) (*ca.* 0.58 g.) (m.p. and mixed m.p.[23]) which crystallized readily from ethyl alcohol and gives a pale-green color with alcoholic ferric chloride solution. It is converted to N-*p*-toluenesulfonyl-O-benzoyl-*o*-aminophenol by the action of benzoyl chloride on Ve in presence of aqueous sodium hydroxide solution (m.p. and mixed m.p.[22]).

(c) **3-Benzenesulfonylnaphtho-(2′,3′)-oxazol-2-one (IVc).**—IVc was prepared similarly by the action of benzenesulfonyl chloride on IVa as described in the case of IIId and was obtained in colorless crystals from a mixture of ethyl alcohol and chloroform, m.p. 204°, in most quantitative yield. IVc is soluble in benzene, but sparingly soluble in alcohol, gives no color either with an alcoholic ferric chloride solution nor with sulfuric acid.

Anal. Calcd. for $C_{17}H_{11}NO_4S$: C, 62.8; H, 3.4; N, 4.3; S, 9.8. Found: C, 62.6; H, 3.3; N, 4.1; S, 9.7.

A mixture of 0.7 g. of IVc and phenylmagnesium bromide was worked up as described above. Triphenylcarbinol (*ca.* 0.18 g.) and N-benzenesulfonyl-3-amino-2-naphthol (VIc) (*ca.* 0.27 g.) were obtained. VIc crystallizes readily from benzene, melts at 166°, gives an olive-green color with alcoholic ferric chloride solution and is soluble in aqueous alkali solution.

Action of 1-Naphthylmagnesium Bromide on IIId.—The action of 1-naphthylmagnesium bromide on IIId was carried out as described in the case of IIIc. The ethereal solution was washed with aqueous sodium hydroxide solution, then with water, dried and evaporated. The oily residue, so obtained, was treated with 20 ml. of fuming nitric acid, then poured into cold water and the yellow powder collected. It was washed with acetic acid and melted at 241° dec. and proved to be hexanitro-α,α,α-trinaphthylcarbinol.[24]

The alkali washings gave, on acidification, Vd (0.38 g.) (identified as above).

Action of Phenyllithium on IIId.—A mixture of phenyllithium and 1.5 g. of IIId was worked up as described in the case of IIIc. Triphenylcarbinol (*ca.* 0.54 g.) and Vd (*ca.* 0.51 g.) were obtained.

Action of Phenylmagnesium Bromide on: (a) **N-Benzoylphthalimide (VIIa).**—A solution of VIIa[25] in 50 ml. of benzene was treated with phenylmagnesium bromide in the usual manner. The ethereal solution of the reaction products was evaporated and the oily residue, so obtained, was washed several times with hot petroleum ether when it turned into solid powder. This was collected and crystallized from a mixture of benzene and light petroleum as colorless crystals (*ca.* 0.38 g.), m.p. 163°, identified as 3-keto-1-phenyl-1-hydroxyisoindoline (VIII) (m.p. and mixed m.p.[5]). VIII is easily soluble in alcohol, but sparingly soluble in light petroleum and gives red color with sulfuric acid.

The petroleum ether washings gave, on concentration, colorless crystals (*ca.* 0.21 g.) of triphenylcarbinol.

(b) **1-Benzoylbenzotriazole (IX).**—Similarly, IX was treated with phenylmagnesium bromide and the ether-benzene mixture, containing the reaction products, was evaporated. The solid residue so obtained was washed several times with cold carbon tetrachloride (25 ml.) and was then crystallized from chloroform as colorless crystals (*ca.* 0.62 g.) identified as triphenylcarbinol.

The carbon tetrachloride washings were evaporated to yield colorless crystals, which upon recrystallization from a mixture of benzene and petroleum ether (b.p. below 40°) gave the product, m.p. 98°, which was not depressed on admixture with authentic benzotriazole. It gave 1-benzoyl benzotriazole on treatment with benzoyl chloride.[7]

The carbon tetrachloride washings were treated with a concentrated ethereal solution of picric acid to give benzotriazole picrate (m.p. and mixed m.p.[7]).

(c) **N-*p*-Toluenesulfonylsuccinimide (XII).**—A mixture of XII[26] and phenylmagnesium bromide was worked up as described above. The ethereal solution of the reaction products was washed twice with cold aqueous sodium hydroxide solution (10%, *ca.* 40 ml.). The ethereal layer was washed with water, dried and evaporated; the oily residue, that solidified after washing with light petroleum (*ca.* 40 ml.), was crystallized from acetone as colorless crystals (*ca.* 0.62 g.), m.p. 205–206°, identified as α,α,δ,δ-tetraphenylbutylene glycol (XIII) (m.p. and mixed m.p.[27]). XIII was converted to α,α,δ,δ-tetraphenylbutadiene by the action of acetic acid and hydrochloric acid.[28]

The alkaline extract was acidified with dilute hydrochloric acid, extracted with ether, dried and evaporated. The colorless crystals (*ca.* 0.32 g.) thus obtained, proved to be *p*-toluenesulfonamide (m.p. and mixed m.p.).

(c) **N-Benzenesulfonylbenzanilide (XIV).**—To a phenylmagnesium bromide solution was added XIV[29] and 30 ml. of benzene. The reaction mixture was refluxed for five hours and kept aside overnight at room temperature, during which the color of the reaction mixture changed from red to green and finally brown. It was decomposed with aqueous ammonium chloride solution and extracted with ether. The ethereal layer was washed with cold aqueous sodium hydroxide (35 ml., 10%), then with water and evaporated. The oily residue, so obtained, was solidified on washing with cold light petroleum and was crystallized from chloroform as colorless crystals (*ca.* 0.53 g.) which were identified as triphenylcarbinol.

The alkali washings gave on acidification, extraction with ether and evaporation, colorless crystals (0.21 g.) of benzenesulfonanilide (m.p. and mixed m.p.).

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