The fresh activation of alumina was carried out by heating it in a small test-tube, using a free flame until the formation of water drops on the cooler parts of the tube ceased (about one minute); the drops were then evaporated by heating with a free flame, and the alumina allowed to cool (*ca.* one minute) and used directly.

In all cases, decolorization was effected by treating the colored surface active material, wet with benzene, with methyl alcohol or with ethyl alcohol in the case of V and VI (elution).

(b) **Experiments with Thermochromic Substances.**—Ethyl benzoate (Schering-Kahlbaum) was purified by shaking it with sodium carbonate for 24 hours, followed by filtration and distillation.

CAIRO, EGYPT

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

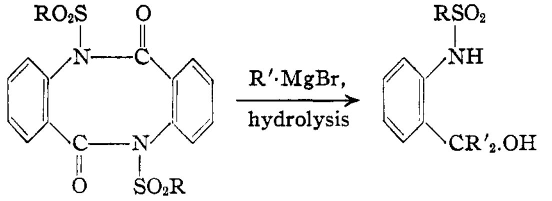
Action of Grignard Reagents. V. Action of Grignard Reagents on N-(Phenylsulfonyl) Derivatives of 1,2-Benzisothiazolone, Phthalimide and Naphthosultam

BY AHMED MUSTAFA AND ORKEDE HASSAN HISHMAT

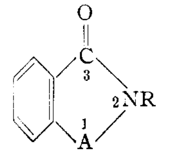
RECEIVED APRIL 16, 1953

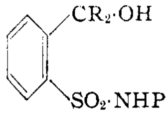
2-(Phenylsulfonyl)-1,2-benzisothiazol-3-one by the action of phenylmagnesium bromide, followed by hydrolysis, undergoes hetero ring opening to give 2-phenylmercaptotriphenylcarbinol and benzenesulfonamide. Similarly, the action of phenylmagnesium bromide yields *o*-bis-(diphenylhydroxymethyl)-benzene and benzenesulfonamide in the case of N-phenylsulfonylphthalimide, and 8-phenylsulfonyl-1-phenylsulfonylnaphthylamine in the case of phenylsulfonylnaphthosultam.

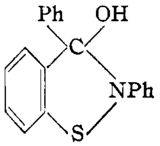
In parts I and IV,[1] Mustafa and co-workers have shown that Grignard reagents cleave the C–N linkage of N,N'-diarylsulfonyldianthranilide (I) and 2-phenyl-1,2-benzisothiazol-3-one-1,1-dioxide (IIIa), giving the corresponding *o*-arylsulfonamidotriarylcarbinols (II) and the N-substituted *o*-sulfamylcarbinols (IV), respectively.



I II

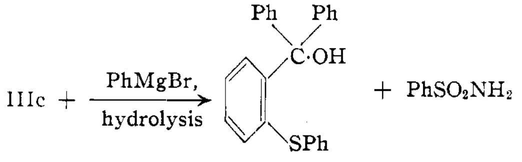




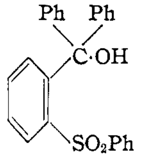


IIIa, A = SO_2, R = Ph IV V
IIIb, A = S, R = Ph
IIIc, A = S, R = SO_2Ph

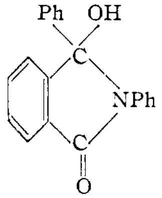
In contrast to the behavior of 2-phenyl-1,2-benzisothiazol-3-one (IIIb) toward phenylmagnesium bromide[1b] which is added in the usual manner to the carbonyl group,[2] yielding 3-phenyl-3-hydroxy-2-phenyl-1,2-benzisothiazole (V), 2-(phenylsulfonyl)-1,2-benzisothiazol-3-one (IIIc), by the action of phenylmagnesium bromide, followed by hydrolysis, undergoes the hetero ring opening[3] with the formation of 2-phenylmercaptotriphenylcarbinol (VI) together with benzenesulfonamide. The structure of VI is inferred from the facts that it is colorless, contains active hydrogen, gives the expected molecular weight and is identical with a synthetic specimen, prepared by the action of phenylmagnesium bromide on the ethyl ester of phenylthiosalicylic acid.[4] When a solution of VI in acetic acid is treated with hydrogen peroxide solution 2-phenylsulfonyltriphenylcarbinol (VII) is obtained and proved to be identical with a sample prepared according to Cobb.[5]



VI



VII



VIII

We have also investigated the action of phenylmagnesium bromide on N-phenylsulfonylphthalimide (IX). Thus whereas N-phenylphthalimide which is closely related to 2-phenyl-1,2-benzisothiazol-3-one-1,1-dioxide (IIIa) reacts with phenylmagnesium bromide to give 3-keto-1,2-diphenyl-1-hydroxyisoindoline (VIII), *o*-dibenzoylbenzene and aniline[6] IX undergoes hetero ring fission only with

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(1) (a) A. Mustafa and A. M. Gad, *J. Chem. Soc.*, 384 (1949); (b) A. Mustafa and M. K. Hilmy, *ibid.*, 1339 (1952).

(2) *Cf.* the action of Grignard reagents on 1,2-benzisothiazol-3(2H)-one-1,1-dioxide (B. Oddo and Q. Mingoia, *Gazz. chim. ital.*, **57**, 465 (1927)).

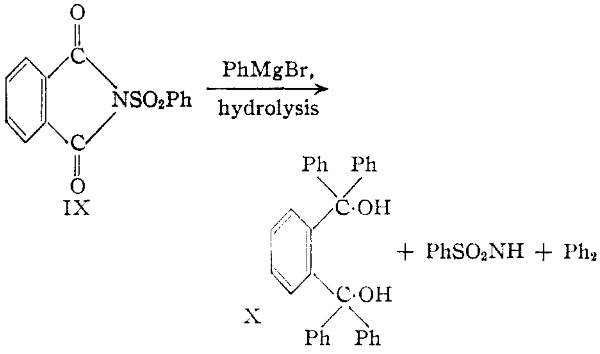
(3) *Cf.* the 2-arylsulfonyl-1,2-benzisothiazol-3-ones (*cf.* IIIc) are less stable than the 2-aryl derivatives (*cf.* IIIb). For example IIIc undergoes hetero ring fission with aniline (E. W. Bartlett, L. E. Hart and E. W. McClelland, *J. Chem. Soc.*, 760 (1939), and E. W. McClelland and R. H. Peters, *ibid.*, 1229 (1947)), whereas IIIb is stable toward the same reagent (E. W. McClelland and A. J. Gait, *ibid.*, 921 (1926)).

(4) *Cf.* C. Graebe and O. Schultefs (*Ann.*, **263**, 5 (1891)) who reported the preparation of the ethyl ester of phenylthiosalicylic acid, giving m.p. 151° for the ester and 166° for the acid. The ethyl ester has now been prepared, using Graebe's method (action of ethyl iodide on the silver salt of phenylthiosalicylic acid) and by the action of ethereal diazoethane solution on the acid and is found, in both cases, to melt at 38°. It is readily hydrolyzed by aqueous sodium hydroxide (25%) to the corresponding acid and gives the hydroxamic test for esters (*cf.* A. I. Vogel, "A Text-Book of Practical Organic Chemistry," Longmans, Green and Co., London, p. 991).

(5) P. H. Cobb, *Am. Chem. J.*, **35**, 486 (1906).

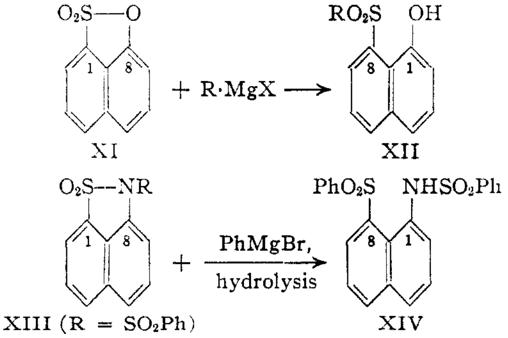
(6) C. Beis, *Compt. rend.*, **143**, 432 (1906).

phenylmagnesium bromide, yielding *o*-bis-(diphenylhydroxymethyl)-benzene (X) together with benzenesulfonamide and diphenyl. The constitution of X is based on its identity with an authentic specimen, prepared by the action of phenyllithium on ethyl phthalate.[7] It contains two active hydrogen atoms and gives the expected molecular weight.



IX
X

Recently, Mustafa[1b,8] has shown that by the action of Grignard solutions on 1,8-naphthosultone (XI) or its substitution products, the sultone ring is opened, thus introducing a new method of preparing peri-hydroxydiarylsulfones (XII). We have now found that, whereas the sultam ring in the case of naphthosultam (XIII, R = H) and N-methylnaphthosultam (XIII, R = CH_3) is stable or almost stable toward phenylmagnesium bromide, it is opened in the case of N-phenylsulfonylnaphthosultam (XIII, R = SO_2Ph) by the action of phenylmagnesium bromide, yielding 8-phenylsulfonyl-1-phenylsulfonylnaphthylamine (XIV). The constitution of XIV is based on the facts that it is colorless, contains an active hydrogen atom, is soluble in aqueous alkali,[9] gives the expected molecular weight, and reacts with ethereal diazomethane.[1b]



XI XII
XIII (R = SO₂Ph) XIV

Experimental

Action of Phenylmagnesium Bromide on: (A) 2-Phenylsulfonyl-1,2-benzisothiazol-3-one (IIIc).—Two grams of (IIIc)[3] was added to an ethereal solution of phenylmagnesium bromide (prepared from 1 g. of magnesium and 9 g. bromobenzene in 50 ml. of dry ether), followed by addition of 30 ml. of dry benzene. The reaction mixture was heated (water-bath) for two hours and then set aside overnight at room temperature. It was decomposed with cold saturated aqueous ammonium chloride solution and extracted with ether. The ethereal solution was extracted with cold aqueous sodium hydroxide solution (8%, *ca.* 40 ml.), washed with water, dried with sodium sulfate and evaporated. The oily residue was washed twice with cold light-petroleum (b.p. below 40°) and the solid so obtained was crystallized from petroleum ether (b.p. 80–100°) (*ca.* 0.9 g.) as colorless crystals, m.p. 140°. *Anal.* Calcd. for $C_{25}H_{20}OS$: C, 81.5; H, 5.4; S, 8.7; active hydrogen, 0.27; mol. wt., 365. Found: C, 81.4; H, 5.4; S, 8.6; active hydrogen, 0.26; mol. wt. (micro Rast), 354. 2-Phenylmercaptotriphenylcarbinol (VI) is easily soluble in benzene, alcohol and acetic acid, but difficultly soluble in light-petroleum (b.p. 50–60°). It gives a deep-green color which turns brown and finally red after half an hour when treated with concentrated sulfuric acid. The same color changes are observed when a few drops of concentrated sulfuric acid are added to an acetic acid solution of VI.

The alkaline extract was acidified with dilute hydrochloric acid, extracted with ether and the ethereal solution was dried, evaporated and the solid residue (*ca.* 0.6 g.) was crystallized from benzene and proved to be benzenesulfonamide (m.p. and mixed m.p.).

2-Phenylsulfonyltriphenylcarbinol (VII).—A solution of 1 g. of VI in 15 ml. of glacial acetic acid was treated with 1.5 ml. of hydrogen peroxide solution (90/100 volumes) and the reaction mixture was heated (water-bath) for half an hour. On cooling, the crystals that separated were recrystallized from acetic acid as colorless crystals, m.p. 182°. *Anal.* Calcd. for $C_{25}H_{20}O_3S$: C, 75.0; H, 5.0; S, 8.0; active hydrogen, 0.25. Found: C, 75.0; H, 4.8; S, 7.9; active hydrogen, 0.24. VII does not depress the melting point of an authentic specimen of 2-phenylsulfonyltriphenylcarbinol[5]; it gives a red color when its solution in concentrated sulfuric acid is treated with a few drops of concentrated nitric acid.[5] It is insoluble in aqueous potassium hydroxide. The yield is almost quantitative.

Synthesis of VI. (a) **The ethyl ester of phenylthiosalicylic acid** was prepared by the action of ethereal diazoethane solution[10] (from 8 g. of nitrosoethylurea) on a partially dissolved and partially suspended sample of 1 g. of phenylthiosalicylic acid[4] in 40 ml. of ether. The reaction mixture was kept at 0° (ice-bath) for 24 hours. The colorless ethereal solution was washed with cold aqueous sodium carbonate, then with cold water, dried and evaporated. The oily residue was dissolved in 30 ml. of light-petroleum (b.p. below 40°) and the colorless crystals that separated on cooling, were recrystallized from light-petroleum (b.p. 50–60°), m.p. 38°. *Anal.* Calcd. for $C_{15}H_{14}O_2S$: C, 69.8; H, 5.4; S, 12.4. Found: C, 69.6; H, 5.4; S, 12.2. The yield was *ca.* 82%. The ethyl ester, prepared by the above method, proved to be identical (m.p. and mixed m.p.) with that prepared by refluxing a mixture of 10 ml. of ethyl iodide, 2 g. of the dry silver salt of phenylthiosalicylic acid and 50 ml. of dry ether for four hours.[4]

When 1 g. of the ethyl ester was refluxed with 30 ml. of aqueous sodium hydroxide solution (25%) for two hours and the reaction mixture was cooled, acidified with dilute hydrochloric acid, phenylthiosalicylic acid was obtained (m.p. and mixed m.p.) in almost quantitative yield.

(b) **2-Phenylmercaptotriphenylcarbinol** was obtained by the action of phenylmagnesium bromide (prepared from 1 g. of magnesium, 9 g. of bromobenzene and 40 ml. of dry ether) on a solution of 2 g. of the ethyl ester of phenylthiosalicylic acid in 30 ml. of dry benzene as described above. The reaction mixture was decomposed with cold aqueous ammonium chloride solution, extracted with ether, dried and evaporated. The oily residue, on washing with 40 ml. of cold light-petroleum (b.p. 50–60°), gave a solid which was crystallized from petroleum ether (b.p. 80–100°) as colorless crystals, m.p. 139–140° (not depressed when admixed with a sample of (VI) prepared by the action of phenylmagnesium bromide on (IIIc) and gave the same color reaction when treated with concentrated sulfuric acid). *Anal.* Calcd. for $C_{25}H_{20}OS$: C, 81.5; H, 5.4; S, 8.7. Found: C, 81.3; H, 5.3; S, 8.5. The yield was *ca.* 71%. It is readily oxidized to VII (m.p. and mixed m.p.) by the action of hydrogen peroxide as described above.

(B) **N-Phenylsulfonylphthalimide (IX).**—A solution of 2 g. of IX[11] in 50 ml. of dry benzene was added to a solution of phenylmagnesium bromide (prepared as above); the

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[7] G. Wittig, and M. Lee, *Ber.*, **64**, 2395 (1931).

[8] A. Mustafa, *J. Chem. Soc.*, 2151 (1949).

[9] *Cf.* H. Gilman, "Organic Chemistry," 2nd. ed., Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 901.

[10] E. A. Werner, *J. Chem. Soc.*, **115**, 1093 (1919).

[11] T. W. Evans and W. M. Dehn, THIS JOURNAL, **51**, 3651 (1929).

reaction mixture was refluxed for two hours (water-bath) and kept aside overnight at room temperature. It was decomposed with aqueous ammonium chloride solution, extracted with ether and the ethereal solution was extracted twice with cold aqueous sodium hydroxide solution (8%, *ca.* 40 ml.). The ethereal layer was washed with water, dried and evaporated and the oily residue, which solidified after washing with 40 ml. of light-petroleum (b.p. 50–60°), was recrystallized from petroleum ether (b.p. 80–100°) as colorless crystals, m.p. 201°. *Anal.* Calcd. for $C_{32}H_{26}O_2$: C, 86.9; H, 5.9; active hydrogen (two atoms), 0.45; mol. wt., 442. Found: C, 86.8; H, 5.9; active hydrogen, 0.43; mol. wt. (micro Rast), 436. The yield was *ca.* 1.2 g. It was identified as *o*-bis-(diphenylhydroxymethyl)-benzene (X)[7] (m.p. and mixed m.p. and color reaction with concentrated sulfuric acid which is yellow, turning to reddish-brown).

The light-petroleum (b.p. 50–60°) washings gave, after slow evaporation, colorless crystals (*ca.* 0.36 g.), of biphenyl (m.p. and mixed m.p.).

The aqueous alkaline extract was acidified with dilute hydrochloric acid, extracted with ether, dried and evaporated. The colorless crystals (*ca.* 0.64 g.) thus obtained proved to be benzenesulfonamide (m.p. and mixed m.p.).

(C) **N-Phenylsulfonylnaphthosultam** (XIII, R = SO_2Ph) was prepared as follows: the yellow solution of 1 g. of naphthosulfam[12] (XIII, R = H) in 30 ml. of aqueous potassium hydroxide (25%), was treated with 3 ml. of benzenesulfonyl chloride with continuous stirring. A vigorous reaction took place with the disappearance of the yellow color and the separation of a colorless solid. The reaction mixture was heated (water-bath) for 15 minutes, cooled and filtered and the solid was crystallized from acetic acid and then from benzene as colorless crystals, m.p. 196°. *Anal.* Calcd. for $C_{16}H_{11}O_4NS_2$: C, 55.7; H, 3.2; N, 4.0; S, 18.6; mol. wt., 345. Found: C, 55.6; H, 3.2; N, 3.9; S, 18.4; mol. wt. (micro Rast), 340. The yield was almost quantitative. (XIII, R = SO_2Ph) is difficultly soluble in alcohol and ether and is insoluble in aqueous sodium hydroxide.

(b) To a solution of phenylmagnesium bromide (prepared as above) was added 2 g. of XIII (R = SO_2Ph) and 40 ml. of dry benzene; a yellow precipitate formed after few minutes. The water was removed from the reflux condenser and the ether was evaporated from the reaction mixture, which was heated for three hours on a water-bath. After the mixture had stood overnight at 25°, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution, and the reaction mixture was extracted with ether. The ethereal solution was dried, evaporated and the oily residue which solidified after scratching was washed with cold ether and crystallized from chloroform as colorless crystals, m.p. 196–197° (yellow melt) (mixed m.p. with (XIII, R = SO_2Ph) gave 168°). *Anal.* Calcd. for $C_{22}H_{17}O_4NS_2$: C, 62.4; H, 4.0; N, 3.3; S, 15.1; active hydrogen, 0.24; mol. wt., 423. Found: C, 62.3; H, 4.0; N, 3.3; S, 14.9; active hydrogen, 0.22; mol. wt. (micro Rast), 421. 8-Phenylsulfonyl-1-phenylsulfonylnaphthylamine (XIV) is soluble in hot benzene, but difficultly soluble in alcohol; it dissolves in hot aqueous potassium hydroxide solution with pale-yellow color and gives no color when treated with concentrated sulfuric acid, but on adding one crystal of potassium nitrate a red color is developed. The yield was *ca.* 64%.

A suspension of 0.5 g. of XIV in 30 ml. of ether was treated with an ethereal solution of diazomethane (prepared from 4 g. of nitrosomethylurea) and the reaction mixture was kept at 0° overnight and then treated with a fresh amount of ethereal diazomethane solution, prepared as above. The ether was allowed to evaporate slowly and the solid which separated was crystallized from chloroform–petroleum ether mixture as colorless crystals, m.p. 226°. *Anal.* Calcd. for $C_{23}H_{19}O_4NS_2$: C, 63.2; H, 4.3; N, 3.2; S, 14.6. Found: C, 63.0; H, 4.1; N, 3.1; S, 14.4. The N-methyl derivative of (XIV) is easily soluble in chloroform, but difficultly soluble in ethyl alcohol. It is insoluble in aqueous potassium hydroxide and gives no color reaction when treated with concentrated sulfuric acid. The yield was *ca.* 58%.

(D) **Naphthosultam** (XIII, R = H) **and N-Methylnaphthosultam** (XIII, R = CH_3).—Two grams of each of XIII (R = H)[12] and XIII (R = CH_3)[13] were treated with a solution of phenylmagnesium bromide under the same experimental conditions described in the case of (XIII, R = SO_2-Ph). On working up the reaction mixtures, XIII (R = H) and XIII (R = CH_3) were recovered completely or almost completely unchanged.

CAIRO, EGYPT

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[12] F. Dannerth, THIS JOURNAL, **29**, 1319 (1907).

[13] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 606 (1948).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF FORDHAM UNIVERSITY]

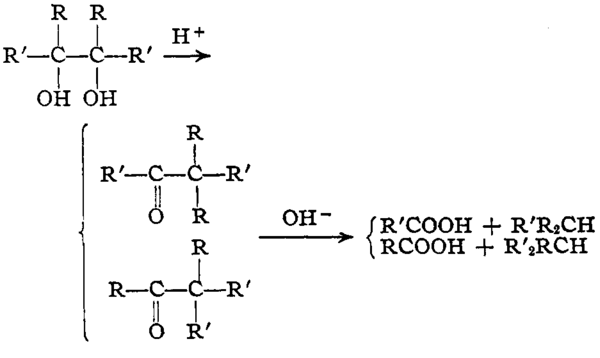
The Pinacol Rearrangement in the Heterocyclic Series. I. Pyridine Analogs of Benzopinacol

BY MATTHEW R. KEGELMAN AND ELLIS V. BROWN

RECEIVED APRIL 11, 1953

Symmetrical analogs of benzopinacol containing two phenyl groups with either two 2-pyridyl groups or two 3-pyridyl groups have been synthesized and rearranged. The structures of the products of rearrangement have been determined by characterization of their degradation products.

Investigators in the past[1] have determined relative migratory aptitudes for some twenty different aryl groups, based on a standard value of unity which was arbitrarily assigned to the phenyl group. This was accomplished by taking advantage of the scheme outlined in reaction 1. If, for example, rearrangement of the pinacol shown gave rise to two parts of the pinacolone where the group R′ has migrated for every one part of the pinacolone where the group R has migrated, then the migratory aptitude of the group R′ was said to be twice that of the



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[1] (a) J. C. Bailar, THIS JOURNAL, **52**, 3596 (1930); (b) W. E Bachmann and F. H. Moser, *ibid.*, **54**, 1124 (1932); (c) W. E. Bachmann, *ibid.*, **54**, 1967 (1932); (d) C. H. Beale and H. H. Hatt, *ibid.*, **54**, 2405 (1932); (e) W. E. Bachmann and W. Ferguson, *ibid.*, **56**, 2081 (1934); (f) W. E. Bachmann and E. Ju-Hwa Chu, *ibid.*, **57**, 1095 (1935); (g) W. E. Bachmann and E. Ju-Hwa Chu, *ibid.*, **58**, 1118 (1936); (h) H. H. Hatt, A. Pilgrim and E. F. M. Stephenson, *J. Chem. Soc.*, 478 (1941); (i) R. Gaertner, *J. Org. Chem.*, **15**, 1006 (1950).