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

Some Adsorption Colors and Their Significance for Thermochromic and Tautomeric Effects. IV. Experiments with 1,3-Diketohydrindene Derivatives and with 1,4-Quinonedibenzenesulfonimides

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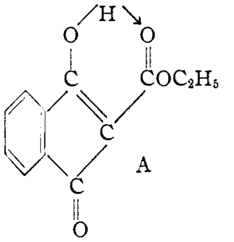
When the colorless or yellow benzene solutions of a number of 1,3-diketohydrindene derivatives are treated at room temperature with activated alumina, adsorption colors, believed to be due to the formation of the enolic forms, are produced almost immediately. 1,3-Diketo-2-phenyl-5-bromoindan exists in a light-yellow keto and a violet enolic form. The adsorption color obtained is violet. Ethyl benzoate solutions of this substance and bindone show reversible thermochromic properties believed to be due to the fact that in each case the relative concentrations of the keto and the enol forms depend on temperature. It is proposed to consider the yellow 2-carbethoxy-1,3-diketohydrindene as the corresponding aci-ester. Adsorption colors on alumina were obtained in the case of *p*-quinone- and 1,4-naphthoquinonedibenzenesulfonimides.

Recently[1] attention was drawn to 1,3-diketohydrindene (Ia) which dissolves to yield colorless solutions in acetone, but with which violet solutions are obtained in acetone–water mixtures. When activated alumina is added to the colorless cold benzene solutions, the inorganic material acquires a violet color at once. When air-dry filter paper is moistened with a colorless benzene solution of Ia and then allowed to dry, it remains colorless after evaporation of the benzene, but when the dried spot is exposed to moisture, it becomes violet.

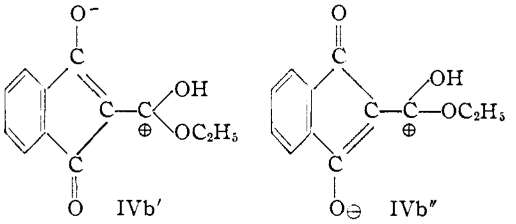
We have now carried out similar experiments (*cf.* Table I) with 2-phenyl-1,3-diketohydrindene (Ib), 2-bromo-1,3-diketohydrindene (Ic) and bindone (III), and have observed similar phenomena. We believe that the adsorption colors are due to the formation of the enolic forms II. This belief is strengthened by experiments with 1,3-diketo-2-phenyl-5-bromoindan (Id) which exists in deep violet and pale-yellowish crystalline forms. Koelsch[2] stated that by crystallization from non-polar solvents the white modification, and from polar solvents the violet-black modification, are obtained; he mentioned only acetic acid and benzene as solvents. We have treated the almost colorless benzene–petroleum ether solution of Id with activated alumina whereupon the inorganic material acquired a violet color.



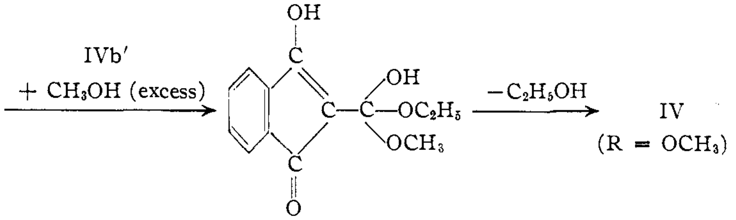
A

Constitution of the So-called 2-Carbethoxy-1,3-diketohydrindene (If) and Its Behavior Toward Alumina.—In contrast to Ia–Id, the compound described as If gives no adsorption colors with alumina or with filter paper; this and its deep yellow color can hardly be explained by formulation as If, and its transformation into the corresponding methyl ester by allowing it to stand with methyl alcohol[3] is difficult to explain. Optical measurements have shown that 2-acetyl-1,3-diketohydrindene (Ie) enolizes in alcoholic solutions yielding IVa.[4] However, a resonance hybrid structure having structure IVb[4] as the main contributing structure would explain the deep yellow color, the reaction with methyl alcohol and the behavior of the substance toward alumina and filter paper (no development of colors).

The true state of the ester If can, however, be explained by the identical resonance structures [IVb′ ↔ IV]″ which account for its differential behavior when compared with Ia, its color and its reaction toward methyl alcohol (*cf.* scheme I). The abnormal reactivity of the ester can hardly be explained by formula A which might, otherwise, be taken into serious consideration.

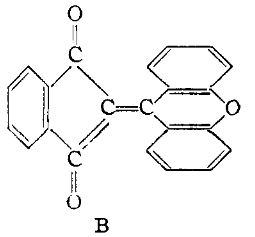


IVb′ IVb″



Scheme I.

Attention is also drawn to the abnormal reactivity of the central "double bond" of B,[5] *e.g.*, against thionyl chloride, which we explain by suggesting that the central "double bond" has in fact single bond character and the deeply colored B is in reality a resonance hybrid (*cf.* B′ ↔ B″)."



B

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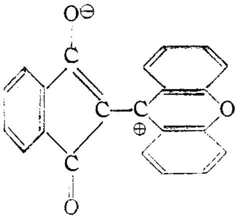
[1] A. Schönberg, A. Mustafa and W. Asker, THIS JOURNAL, **73**, 2876 (1951).

[2] C. F. Koelsch, *ibid.*, **58**, 1328 (1936).

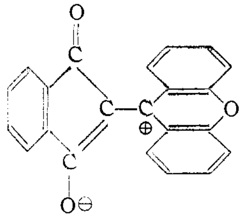
[3] F. Adickes, F. Plessmann and P. Schmidt. *Ber.*, **70**, 2119 (1937).

[4] J. Scheiber and G. Hopfer, *Ber.*, **53**, 697 (1920).

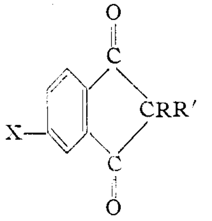
[5] *Cf.* A. Schönberg, A. Mustafa and M. E. Sobhy, THIS JOURNAL, 3377 (1953).

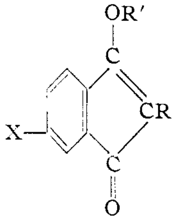


B'



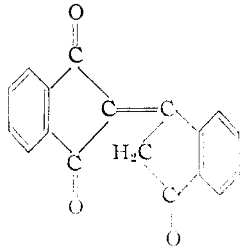
B''



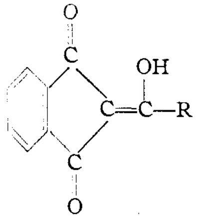


Ia, R = R' = X = H
Ib, R = Ph, R' = X = H
Ic, R = Br, R' = X = H
Id, R = Ph, R' = H, X = Br
Ie, R = $COCH_3$, R' = X = H
If, R = $COOC_2H_5$, R' = X = H

IIa, R = $COCH_3$, R' = X = H
IIb, R = $COOC_2H_5$, R' = X = H

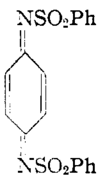


III

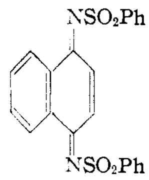


IVa, R = CH_3;
IVb, R = $-OC_2H_5$

Adsorption Colors Shown by 1,4-Quinonedibenzenesulfonimides.—In any explanation of the observed adsorption colors of *p*-quinonedibenzenesulfonimide (V) and 1,4-naphthoquinonedibenzenesulfonimide (VI)[6] (*cf.* Table I), the thermo-instability of the substances should be taken into consideration. Thus, V melts unsharply at about 178° giving a deep red-brown melt. It seems possible that the adsorption colors are due to thermo-decomposition of the substances V and VI when adsorbed (heat of adsorption). Reference is made to the behavior of 10-hydroxy-10-phenylmercaptophenanthrone which shows an adsorption color[7] which was explained similarly.



V



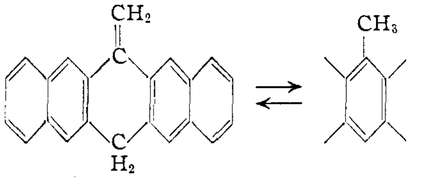
VI

Thermochromism Based on Keto–Enol Tautomerism.—The observed changes which are summarized in Table II are explained on the basis of changes of the concentrations of the enol and the keto forms with temperature. Thus, it is believed that in ethyl benzoate solutions of Id the enol form is more predominant in the cold than in the hot, whereas, in the case of III the reverse is the case. The change in relative amount of enol form with temperature is known. Thus, formylphenylethylacetate, heated to 230° shows, when quickly cooled, an enolic percentage of about 80% which returns at normal temperature gradually to 90%.[8] An advantage of optical investigations based on thermochromism is that the velocity of the keto–enol changes may be ascertained.

TABLE I

Formulas	Color of benzene soln.	Adsorption colors on freshly activated alumina[i]	Elution using methyl alcohol	Filter-paper expt.[j]	Color of 96% alcoholic soln.
Ib[a]	Colorless	Orange	+	Deep-or.	Deep-or.[h]
Ic[b]	Yellow	Orange	+	Orange	Orange
Id[c]	Pale-yell.	Violet	+	Violet	Violet[k]
III[d]	Yellow	Deep-viol.	+	Violet	Violet[j]
If[e]	Yellow	....	...	......	Yellow
V[f]	Yellow	Viol.-br.	+	......	Yellow
VI[g]	Yellow	Or.-red	+	......	Yellow

[a] W. Dieckmann, *Ber.*, **47**, 1435 (1914). [b] W. Roser and E. Haselhoff, *Ann.*, **247**, 138 (1888). [c] C. F. Koelsch, ref. 2. [d] v. W. M. Fischer and G. Wanag, *Ann.*, **489**, 97 (1931). [e] W. O. Teeters and R. L. Shriner, THIS JOURNAL, **55**, 3026 (1933). [f] R. Adams and A. S. Nagarkatti, *ibid.*, **72**, 4601 (1950). [g] R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951). [h] F. Nathanson, *Ber.*, **26**, 2576 (1893). [i] In the case of "not freshly" activated alumina, the same adsorption colors are produced after some hours, whereas, in the case of freshly activated alumina, the adsorption colors are produced almost immediately. [j] The filter paper was Whatman, W. & R. Balston, Ltd., No. 1 and No. 44. The filter paper was moistened with the benzene solution of the substance, allowed to dry and then the colorless spot was exposed to steam. A. Hantzsch and J. Zortman, *Ann.*, **392**, 322 (1912). [k] The same color is developed when the colorless dioxane solution is treated with a few drops of conductivity water.



VIIa VIIb

The thermochromism based on keto–enol changes is similar to thermochromic effects based on reversible methyl–methylene changes (*cf.* VIIa and VIIb (abbreviated formula)) discovered by Clar[9]

TABLE II[a]

Formulas	Ethyl benzoate solutions[b] Cold (−10°)	Hot (boiling point)
Id	Orange	Pale-yellow
III	Yellow	Intense yellow with orange tint

[a] The changes of the volume of the solutions with temperature were taken into consideration. [b] Experiments were carried out using dilute solutions.

Experimental

General Remarks. (a) Experiments Leading to Adsorption Colors.—The experiments were carried out by adding the adsorbents to the dilute benzene solutions of the substance under investigation.

The benzene was dried over metallic sodium; the alumina was obtained from Peter Spence and Sons, Ltd., London. When used as such it is described as "not freshly activated."

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(6) These experiments were carried out with M. Kamel.

(7) A. Schönberg, A. Mustafa and W. Asker, THIS JOURNAL, **74**, 5640 (1952).

(8) W. Dieckmann, *Ber.*, **50**, 1376 (1917).

(9) E. Clar, *Chem. Ber.*, **82**, 508 (1949).

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.

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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

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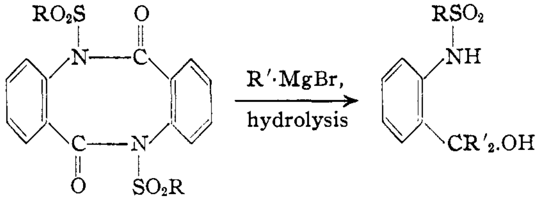
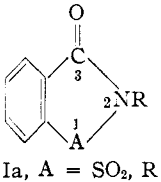
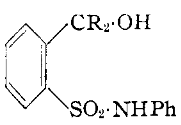
2-(Phenylsulfonyl)-1,2-benzisothiazol-3-one by the action of phenylmagnesium bromide, followed by hydrolysis, undergoes hetero ring opening to give 2-phenylmercaptotriphenylcarbinol and benzenesulfonamide. Similarly, the action of phenylmagnesium bromide yields *o*-bis-(diphenylhydroxymethyl)-benzene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

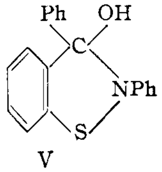
In parts I and IV,[1] Mustafa and co-workers have shown that Grignard reagents cleave the C–N linkage of N,N'-diarylsulfonyldianthranilide (I) and 2-phenyl-1,2-benzisothiazol-3-one-1,1-dioxide (IIIa), giving the corresponding *o*-arylsulfonamidotriarylcarbinols (II) and the N-substituted *o*-sulfamylcarbinols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



I II

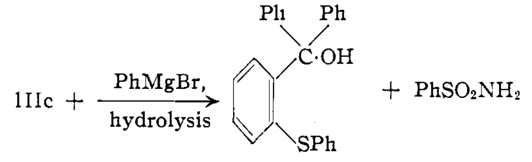




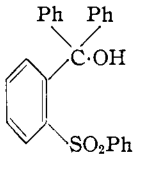


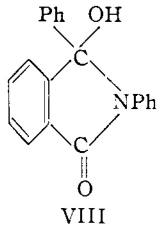
IIIa, A = SO$_2$, R = Ph IV V
IIIb, A = S, R = Ph
IIIc, A = S, R = SO$_2$Ph

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).