in 100 ml. of ether; hydride, 9.5 g. (0.25 mole) in 200 ml. of ether. The volatility of the product and the tenacity with which it was adsorbed on the lithium aluminate seriously hindered the isolation and purification of the product. From the final distillation there was obtained 0.92 g. (10%) of clear liquid distilling at 62–63° (753 mm.), $n^{24}D$ 1.4035. The reported b.p. and index of refraction of trimethylhydrazine[4] are 58.8–60.1° (735 mm.) and $n^{20}D$ 1.4039.

Anal. Calcd. for $C_3H_{10}N_2$: neut. equiv., 74. Found: neut. equiv., 76, 77 (potentiometric titration).

Twenty per cent. of the ethyl 2,2-dimethylcarbazate was recovered. It was identified by conversion to the methiodide which did not depress the m.p. of an authentic specimen.

Attempted Reductions of 1,2-Dibenzoylhydrazine, 1,2-Diformylhydrazine and 1-Benzoyl-2,2-dimethylhydrazine.—From the treatment of each of these substances with the hydride only starting material was recovered. No alkylhydrazine could be detected.

Dimethylhydrazine Picrate.—This compound, which has not been reported previously, was prepared for comparison with some of the picrates described above. After one recrystallization from absolute ethanol the golden flakes melted at 145–146° dec.

Anal. Calcd. for $C_8H_{11}N_5O_7$: C, 33.22; H, 3.83. Found: C, 33.60; H, 4.06.

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

Reactions with Diazoalkanes. VI. Action of 9-Diazofluorene on 2-Arylideneindane-1,3-diones

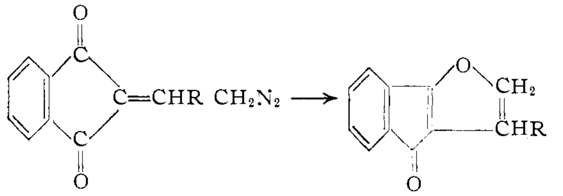
BY AHMED MUSTAFA AND ABDEL HAMID ELSAYED HARHASH

RECEIVED SEPTEMBER 7, 1955

The intensely colored 2-arylideneindane-1,3-diones, listed in Table II, react with 9-diazofluorene to give colorless products believed to have the cyclopropane structure (III).

9-Diazofluorene reacts with unsaturated compounds to form cyclopropane derivatives. Thus with acenaphthylene,[1a] ω-nitrostyrenes,[1b] acrylonitrile,[1c] α,β-unsaturated ketones,[1c,1d] α,β-unsaturated esters,[1d,1e] azo compounds, *e.g.* diethylazodicarboxylate[1e] and with *p*-quinonedibenzenesulfonimides,[1f] the corresponding cyclopropane derivatives are obtained.

2-Arylideneindane-1,3-diones (I) have been found to react with ethereal diazomethane solution in the presence of methyl alcohol to yield colorless substances, believed to be furanoindenones (II).[2] We have now found that when the intensely colored compounds Ia-g are allowed to react with 9-diazofluorene in benzene solution at room temperature (except in the case of If-g where the reaction is brought to the boiling point of the benzene solution) the deep color of the reaction mixture faded and colorless or substantially colorless products (III) are obtained.



Ia, R = C_6H_5, b, R = $C_6H_4NO_2$-*o*, II
c, R = $C_6H_4NO_2$-*m*, d, R = $C_6H_4NO_2$-*p*,
e, R = $C_6H_4OCH_3$-*p*, R = $C_6H_3:O_2CH_2$-3,4 (piperonyl),
g, R = C_4H_3S (2-thienyl)

In view of the well established mechanism for the addition of 9-diazofluorene to analogous α,β-unsaturated compounds[1] (α,β-unsaturated ketones[1e] and α,β-unsaturated esters),[1e] the addition products of the same reagent to Ia-g have, probably, the cyclopropane structure III. It is improbable that the products IIIa-g are of the furanoindenone structure (*cf.* II), since IIIa, c and d give the corresponding diphenylhydrazone derivatives and IIIa forms phthalic on treatment with chromic acid. IIIa gives the correct molecular weight and analytical values. When an alcoholic solution of IIIa and/or d is treated with hydroxylamine hydrochloride in presence of aqueous potassium hydroxide[3] or in presence of pyridine, 1,3-indandione dioxime is obtained, together with an oily substance which is under further investigation. The behavior of Ia toward hydroxylamine hydrochloride in the presence of pyridine simulates that of IIIa toward the same reagent in the presence of pyridine, yielding 1,3-indandione dioxime. Such a reaction would lend additional support to the theory that the three-membered ring can react in a manner analogous to a carbon–carbon double bond when conjugated with a carbonyl group.[4,5] IIIa is thermolabile and undergoes isomerization by the action of heat at 220° for one hour in a vacuum, to an isomer having the molecular formula $C_{29}H_{18}O_2$; the structure of this isomer is under further investigation.

Evidence for the formation of IIIa in the reaction of Ia and 9-diazofluorene has been obtained from the vibrational spectrum.

The infrared spectra of compounds IIIa and 1,3-indanedione (IV) exhibit a single sharp medium intensity band in the region 1690 to 1550 cm.$^{-1}$.

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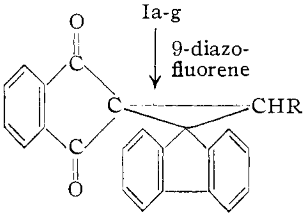
[1] (a) A. Schönberg, A. Mustafa and N. Latif, THIS JOURNAL, **75**, 2267 (1953); (b) A. Mustafa and A. H. E. Harhash, *ibid.*, **76**, 1383 (1954); (c) L. Horner and E. Lingnau, *Ann.*, **573**, 30 (1951); (d) H. Staudinger and A. Gaule, *Ber.*, **49**, 1956 (1916); (e) L. Horner and E. Lingnau, *Ann.*, **591**, 21 (1955); (f) A. Mustafa and M. Kamel, THIS JOURNAL, **75**, 2939 (1953).

[2] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952).

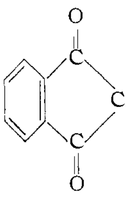
[3] *Cf.* the ready isomerization of cyclopropane-bis-indandione-1,2,2,2-dispiran by the action of 5% sodium hydroxide solution (*C. A.*, **21**, 3203 (1927)).

[4] *Cf.* the behavior of 2-arylidene-3-phenylindan-1-ones, *e.g.*, 2-benzylidene-3-phenylindan-1-one and of alkylated 2-arylidene-3-phenylidan-1-ones (aryl-radical = $C_6H_4OCH_3$-*p*) toward the action of hydroxylamine hydrochloride in presence of aqueous sodium hydroxide solution (W. S. Johnson and W. S. Shelberg, THIS JOURNAL, **67**, 1758 (1945)).

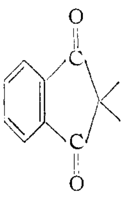
[5] *Cf.* the behavior of 2-benzylideneindan-1,3-dione (Ia) toward the action of dilute alkali (W. Wislicenus and A. Kötzle, *Ann.*, **252**, 72 (1889)) and toward phenylhydrazine (W. Wislicenus and F. Reitzenstein, *Ann.*, **277**, 362 (1893)).



III



IV



V

This band can be assigned unambiguously to the aromatic carbon–carbon stretching frequency. In compound Ia, however, the infrared spectrum of this region reveals a very intense doublet with band centers at 1620 and 1600 cm.$^{-1}$. These bands have been assigned, respectively, to C=C stretching and aromatic carbon–carbon stretching frequencies. The intensity of the absorption results from the presence of the heavily conjugated system. The absence of the 1620 cm.$^{-1}$ band in IIIa may be accepted as definite proof that the double bond content in Ia has been destroyed in the reaction.

TABLE I

INFRARED ABSORPTION IN THE 1750 TO 1550 CM.$^{-1}$ REGION

Compound	Frequency assignment –C=O	C=O	C=C	C_6H_6	C_6H_6
IIIa	1735s	1709vs	...	1600m	....
Ia	1737s	1696vs	1620s	1600s	1575m
IV	1750s	1710vs	...	1600m	....

TABLE II

I	III	M.p.,[f] °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia[a]	IIIa	216	88	$C_{29}H_{18}O_2$[g]	87.44	87.27	4.52	4.45		
Ib[b]	IIIb	186	81	$C_{29}H_{17}NO_4$	78.55	78.46	3.84	3.77	3.16	3.10
Ic[c]	IIIc	214	82	$C_{29}H_{17}NO_4$	78.55	78.39	3.84	3.75	3.16	2.96
Id[d]	IIId	196	89	$C_{29}H_{17}NO_4$	78.55	78.47	3.84	3.69	3.16	3.10
Ie[e]	IIIe	199	87	$C_{30}H_{20}O_3$	84.11	83.92	4.67	4.57		
If[d]	IIIf	224	65	$C_{30}H_{18}O_4$	81.45	81.36	4.07	4.00		
Ig[e]	IIIg	191	63	$C_{27}H_{16}O_2S$[h]	80.19	80.08	3.96	3.85		

[a] W. Wislicenus and A. Kötzle, *Ann.*, **252**, 72 (1889). [b] D. Radulescu and M. V. Ionescu, *Bul. soc. stiinte Cluj*, **2**, 155 (1924). [c] V. Petrow, J. Saper and B. Sturgeon, *J. Chem. Soc.*, 2134 (1949). [d] M. V. Ionescu, *Bull. soc. chim.*, **47**, 210 (1930). [e] Ng. Ph. Buu-Hoï, Ng. Hoán and D. Lavit, *J. Chem. Soc.*, 2130 (1950). [f] All melting points are with decomposition. [g] Mol. wt., 398; found: mol. wt. (Rast), 392. [h] Calcd., S, 7.92. Found: S, 7.84.

The proposed configuration IIIa contains a highly substituted cyclopropane ring. The infrared data tentatively support this structure. Derfer, Pickett and Boord[6] have shown that a breathing vibration of the three-membered ring occurs characteristically between 1020 to 1000 cm.$^{-1}$. Normally this band is relatively intense; however, heavy substitution may weaken the intensity considerably, as in the case of 1,1,2,2-tetramethylcyclopropane. A weak band does occur in the spectrum at 1013 cm.$^{-1}$. The assignment of this band to the cyclopropane ring system is, nevertheless, only tentative. In this highly complex region of the spectrum the occurrence of absorption cannot be accepted as definite evidence, whereas the absence of a band in this case might well have been considered as fairly good proof against the presence of the cyclopropane ring.

The spectra of compounds, IIIa, Ia and IV contain two carbonyl bands in each case (see Table I). The splitting of the carbonyl absorption results from the coupling of the two ketone groups, an effect similar to that found in anhydrides. As this splitting is still present in the product (IIIa), it provides additional evidence that the residue V has survived the reaction.

Experimental

The infrared spectra of compounds Ia, IIIa and IV were recorded with a Perkin-Elmer model 21 spectrophotometer in the region of 5000–650 cm.$^{-1}$ employing sodium chloride optics. The spectrum was obtained on the pressed potassium bromide suspension.

Action of 9-Diazofluorene on 2-Arylideneindane-1,3-diones (I).—To 0.7 g. of the dione I was added 1.5 g. of 9-diazofluorene in 30 ml. of dry benzene. The deep color of the reaction mixture faded after standing at room temperature overnight in all cases except those of If and Ig where it was necessary to reflux the reaction mixture for three hours. Except in the case of IIIc, d and e, the solution was concentrated to one-third of its volume, about 30 ml. of petroleum ether (b.p. 40–60°) added, and the mixture left to cool and the pale-yellow crystals that separated collected by filtration, washed with a few ml. of ether and recrystallized from benzene as colorless crystals. In case of IIIc, d and e, the crystals that separated directly from the reaction mixture on cooling were filtered off and recrystallized from benzene.

All the products IIIa–g give an olive-green color with concentrated sulfuric acid which changes to violet on standing. They are almost insoluble in aqueous sodium hydroxide solution (10%). In general, they are soluble in chloroform or hot benzene but are sparingly soluble in ethyl alcohol.

Action of Phenylhydrazine on IIIa, c and d.—To a suspension of 0.5 g. of each of IIIa, c and d in 30 ml. of ethyl alcohol was added one ml. of phenylhydrazine and a few drops of acetic acid. The reaction mixture was refluxed for two hours, and all the solid went into the solution, which became orange-red in color. The reddish crystals that separated on cooling were collected by filtration and recrystallized from glacial acetic acid.

The diphenylhydrazone derivative of IIIa forms deep yellow crystals, m.p. 222° dec.

Anal. Calcd. for $C_{41}H_{30}N_4$: C, 85.12; H, 5.19; N, 9.69. Found: C, 84.92; H, 4.96; N, 9.53.

The diphenylhydrazone derivative of IIIc forms deep-yellow crystals, m.p. 229–230° dec.

Anal. Calcd. for $C_{41}H_{29}N_5O_2$: C, 78.97; H, 4.65; N, 11.23. Found: C, 78.73; H, 4.61; N, 10.94.

The diphenylhydrazone derivative of IIIb forms orange crystals, m.p. 238° dec.

Anal. Calcd. for $C_{41}H_{29}N_5O_2$: C, 78.97; H, 4.65; N, 11.23. Found: C, 78.69; H, 4.45; N, 11.12.

All the above mentioned hydrazone derivatives give a brown color with concentrated sulfuric acid and are almost insoluble in aqueous sodium hydroxide solution.

Action of Hydroxylamine Hydrochloride on (a) IIIa.—To a suspension of 0.7 g. of IIIa in 30 ml. of ethyl alcohol, was added a solution of hydroxylamine hydrochloride (0.5 g.) in one ml. of water and one ml. of pyridine (or a solution of 0.5 g. of potassium hydroxide in one ml. of water) and the

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[6] J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949).

reaction mixture was refluxed for six hours. The resulting reddish solution, after being cooled, was poured into ice-cold water; the solid that separated was collected, crystallized from ethyl alcohol and proved to be the dioxime of 1,3-indandione (identification was carried out by m.p. and mixed m.p. determination with an authentic sample prepared by the action of hydroxylamine hydrochloride on Ia as described above[7]).

Anal. Calcd. for $C_9H_8N_2O_2$: C, 61.36; H, 4.55; N, 15.91. Found: C, 61.25; H, 4.37; N, 15.76.

(b) **IIId.**—Similarly the action of hydroxylamine hydrochloride on IIId yields the dioxime of 1,3-indandione (m.p. and mixed m.p.) together with an oily substance which is under further investigation.

Oxidation of IIIa with Chromic Acid.—IIIa (0.5 g.) was boiled with 50 ml. of glacial acetic acid, 1.5 g. of finely powdered chromic acid was then added and boiling was continued for two hours. The green solution was poured into ice-cold water and, upon standing, a pale-yellow precipitate separated. The precipitate was collected, crystallized from hot water and proved to be phthalic acid.

Action of Heat on IIIa.—IIIa (0.7 g.) was heated for two hours at 220° (bath-temp.) in a test-tube shaped vessel (Pyrex glass) which was connected during pyrolysis to a working oil vacuum pump. The reaction vessel was then allowed to cool in a vacuum. The bottom of the reaction vessel contained a brownish-red residue which upon treatment with a few ml. of cold ether turned into a pale-yellow solid. It was crystallized from benzene as pale-yellow crystals or faint yellow (*ca.* 0.2 g.), m.p. 176°.

Anal. Calcd. for $C_{29}H_{18}O_2$: C, 87.44; H, 4.52. Found: C, 87.34; H, 4.50.

It gives a brown color with concentrated sulfuric acid and is almost insoluble in aqueous sodium hydroxide solution (10%). It is sparingly soluble in cold ethyl alcohol and glacial acetic acid. It is unaffected when treated with hydroxylamine bydrochloride under the same conditions described above.

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[7] W. Wislicenus and A. Kötzle, *Ann.*, **252**, 72 (1889), gave m.p. 225° for the same dioxime. When their experiment was repeated and the product was crystallized from alcohol, colorless substances, m.p. 238°. was obtained.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY, AND THE FRANCIS DELAFIELD HOSPITAL]

Some 4,5- and 5,6-Substituted Benzothiazoles

BY H. B. GILLESPIE, MORRIS ENGELMAN AND SAMUEL GRAFF

RECEIVED OCTOBER 15, 1955

Some substituted benzotriazoles are effective growth inhibitors in certain biological systems. Several new benzotriazoles have been prepared and the structure of the previously reported 5-methoxy-6-nitrobenzotriazole has been shown to be 5-methoxy-4-nitrobenzotriazole. The reduction of β-[4,6-dinitro-3-methoxyphenyl]-hydroxylamine by ammonium sulfide resulted in a *p*-diamine rather than an *o*-diamine as reported in the literature.

The synthesis and some results of preliminary biological assay of several 4,6-substituted benzimidazoles and benzotriazoles has been reported previously.[1] This report describes the preparation of some 4,5- and 5,6-substituted benzotriazoles. In an attempt to obtain 5-methoxy-6-nitrobenzotriazole (II), the nitration of 1-acetyl-5-methoxybenzotriazole (I) was repeated according to Fel'dman and Usovskaya.[2] It seemed to us unlikely that the nitro group should enter the 6-position since halogenation and nitration of 5-hydroxybenzotriazole yield compounds with the entering group in the 4-position and nitration of benzotriazole results in the 4-nitro derivative. On the basis of such evidence, Fries[3] suggested that the benzotriazoles were naphthenoid in character. This idea was supported by the synthesis, from 5-hydroxybenzotriazole, of the 4-carboxylic acid derivative by the Kolbe reaction.[4]

Assuming random nitration, three isomers are possible. These are 5,4- (III), 5,6- (II) and 6,4-methoxynitrobenzotriazole (IV). The latter compound, prepared by an unambiguous synthesis by the action of nitrous acid on 3,4-diamino-5-nitroanisole (V), was found to differ in its properties from the nitration product. To distinguish between the 4,5- and the 5,6-isomers, the preparation of 4-methoxy-5-nitro-*o*-phenylenediamine (VII), from which the 5-methoxy-6-nitrobenzotriazole (VI) could be formed by ring closure, was attempted by the method of Borsche and Feske.[5] These workers reported that the reduction of β-[4,6-dinitro-3-methoxyphenyl]-hydroxylamine (VIII) by ammonium sulfide resulted in an *o*-diamine. On repeating this work, we have found that the product was indeed a diamine IX which formed a diacetyl derivative X. However, it failed to yield a quinoxaline derivative with benzil. The same diamine was synthesized from the corresponding amine, 3-amino-4,6-dinitroanisole (XI), by ammonium sulfide reduction. The diacetyl derivative was the same as that prepared from Borsche and Feske's diamine and treatment of the diamine with benzil did not yield a quinoxaline. However, catalytic reduction converted the nitrodiamine into a triamine which reacted readily with benzil to form 6-amino-2,3-diphenyl-7-methoxyquinoxaline. In addition, 2,5-diacetamido-4-nitroanisole (X) was synthesized by an independent method,[6] and shown by analysis and mixed melting point determination to be identical with the diacetyldiamine of Borsche and Feske. The action of ammonium sulfide on β-[4,6-dinitro-3-methoxyphenyl]-hydroxylamine (VIII) did not result in an *o*-diamine (VII) as reported but in the *p*-diamine, namely, 2,5-diamino-4-nitroanisole (IX).

An investigation of the isomeric 4,5- (VI) and 5,6-aminomethoxybenzotriazoles (XIV) was resorted to for the elucidation of the structure of the

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[1] H. Gillespie, M. Engelman and S. Graff, THIS JOURNAL, **76**, 3531 (1954).

[2] I. Kh. Fel'dman and V. S. Usovskaya, *J. Gen. Chem.* (*USSR*), **19**, 356 (1949); *C. A.*, **43**, 7016d (1949).

[3] K. Fries, H. Guterbock and H. Kuhn, *Ann.*, **511**, 213 (1934).

[4] M. Scalera and F. H. Adams, THIS JOURNAL, **75**, 715 (1953).

[5] W. Borsche and E. Feske, *Ber.*, **59**, 816 (1926).

[6] French Patent 966,799, Oct. 18, 1950; *C. A.*, **46**, 6396*g* (1952).