195. *Experiments with Diazomethane and its Derivatives. Part XIII.* Action of Diazomethane on Hydroxyanils.*

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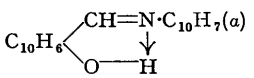
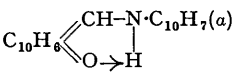
The *o*-hydroxyanils listed in Table I are *stable* or very resistant towards *ethereal* diazomethane solution, but, reacting in the ketonic form, they yield coumaran derivatives (listed in Table II) when treated with diazomethane *in the presence of methyl alcohol*; scheme (C) illustrates the proposed reaction mechanism. The stability towards ethereal diazomethane is believed to be due to the fact that in ethereal solution the anils do not contain a free hydroxyl group, but a chelate ring system (I or II), and that they react with methyl alcohol with formation of an intermolecular hydrogen bridge and the opening of the chelate ring system (III).

The importance of the above findings for the theory of chelation is stressed.

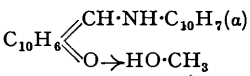
THIS paper deals with the remarkable behaviour of a number of anils (see Table I) derived from *o*-hydroxyaldehydes which were found to be stable towards diazomethane in ethereal solution, but reacted with it in the presence of methyl alcohol. By analogy with our previous findings (Schönberg and Mustafa, *J.*, 1946, 746), this is ascribed to the fact that these *o*-hydroxyanils are not true *o*-hydroxy-compounds but resonance hybrids having the hydrogen bridge (see I and II); when, however, methyl alcohol is present, the six-membered ring is opened and the ketonic



(I; no reaction with diazomethane.)



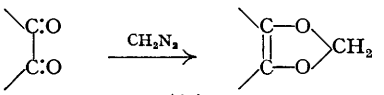
(II; no reaction with diazomethane.)



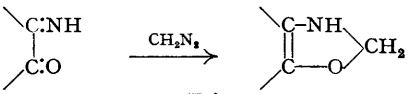
(III; reacts with diazomethane.)

form (III) is established. The differential behaviour of substances listed in Table I towards diazomethane in ethereal and in methyl-alcoholic solution thus constitutes an additional criterion for the existence of chelation.

The anils mentioned above, in the presence of methyl alcohol, have the nature of compounds related to *o*-quinones and *o*-quinoneimines, which react with diazomethane to form five-membered heterocyclic compounds [see Arndt, Amende, and Ender, *Monatsh.*, 1932, **59**, 202; Fieser and Hartwell, *J. Amer. Chem. Soc.*, 1935, **57**, 1479; Schönberg and Mustafa, *loc. cit.*, in the case of (A), and Schönberg and Awad, *loc. cit.*, in the case of (B)]. By analogy, it would



(A.)

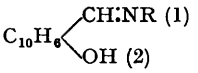


(B.)

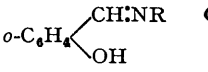
be expected that benzocoumaran derivatives should be obtained when (III) and its analogues are treated with diazomethane in the presence of methyl alcohol, and this is indeed the case (*e.g.*, formation of VII*a*).

* For earlier papers (not numbered) by Schönberg and his co-workers on the action of diazomethane and its derivatives on organic substances, see *Ber.*, 1929, **62**, 440, 1663; 1930, **63**, 3102; 1931, **64**, 1390, 2324, 2577; 1932, **65**, 289; 1933, **66**, 246; *Annalen*, 1930, **483**, 176; *J.*, 1941, 348; *J.*, 1946, 746; this vol., in the press.

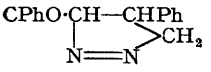
TABLE I.



[IV*a*, R = $C_{10}H_7(\alpha)$; IV*b*, R = $C_{10}H_7(\beta)$; IV*c*, R = $C_6H_3Me_2(2:3)$; IV*d*, R = $C_6H_3Me_2(2:4)$; IV*e*, R = $C_6H_3Me_2(2:5)$.]

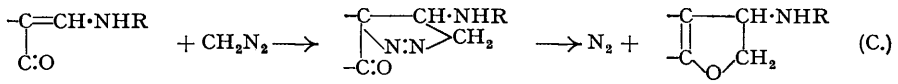


[V; R = $C_6H_3Me_2(2:5)$.]



(VI.)

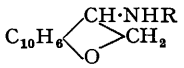
Mechanism of the Formation of the Coumaran Derivatives.—We believe that reaction occurs according to (C): similar schemes are proposed for the above-mentioned actions of diazomethane



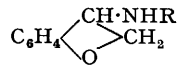
(C.)

on *o*-quinones (1 : 2-diketones; *e.g.*, benzil) or *o*-quinoneimines; compare also the formation of (VI) from benzylideneacetophenone and diazomethane (Smith and Prings, *J. Org. Chem.*, 1937, **2**, 23).

TABLE II.



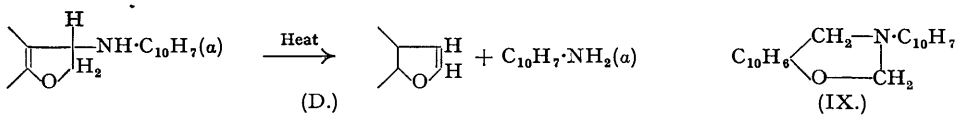
[VII *a*, *b*, *c*, *d*, *e*; R as in corresponding (IV).]



[VIII; R as in (V).]

Constitution of the Products listed in Table II.—These products are of an analogous structure; 3-(α-*naphthylamino*)-4 : 5-*benzocoumaran* (VII*a*) is taken as an example. Its constitution is based on three facts: (*a*) the analogy of its formation (see A and B); (*b*) its properties; (*c*) the fact that no other formula can be proposed which fits the physical and chemical properties of the substance.

In contrast to (IV*a*), (VII*a*) is colourless, in agreement with the proposed formula [reaction has taken place involving the chromophoric system in (III)]; (VII*a*) has no methoxyl group and has one active hydrogen atom (the same holds true for all substances listed in Table II). When it is heated at 250°, it affords α-naphthylamine in addition to a resin, believed to be the polymerisation product of benzocoumarone (see D); the reaction product from (IV*a*) and diazomethane cannot therefore contain a tertiary nitrogen atom, for such a compound (*e.g.*, IX) cannot give α-naphthylamine on pyrolysis.



(D.) (IX.)

The compound (VII*a*) was recovered unchanged when treated with phenylmagnesium bromide followed by hydrolysis; it does not react with diazomethane. The substances listed in Table II have basic properties; *e.g.*, 3-(*p*-2-xylidino)coumaran (VIII) reacts with gaseous hydrogen chloride to form the corresponding hydrochloride. (VII*a*) is completely different from the yellow 2-methoxynaphthylmethylene-α-naphthylamine (*O*-methyl ether of IV*a*); the nature of the latter is established by the fact that it is obtained by the action of methyl sulphate on the sodium salt of 2-hydroxynaphthylmethylene-α-naphthylamine (IV*a*) and by condensation of 2-methoxy-1-naphthaldehyde with α-naphthylamine. The same is true in the case of the β-naphthyl derivative (IV*b*). The substances listed in Table II are all solids, except (VIII), which was analysed as its *hydrochloride*.

Action of Diazomethane on the Anils of p-*Hydroxyaldehydes.*—It was found that 4-hydroxynaphthylmethylene-α-naphthylamine and the corresponding β-naphthyl derivative react with diazomethane to form the known 4-methoxyl derivatives. This action took place even in ethereal diazomethane solution, which was to be expected since in these *p*-hydroxy-compounds the hydroxyl groups are free, no chelation being possible.

EXPERIMENTAL.

The ethereal diazomethane solution was prepared by the action of aqueous potassium hydroxide on nitrosomethylurethane followed by distillation (*Org. Synth.*, Vol. 15, p. 3).

Action of Ethereal Diazomethane Solution on p-*Hydroxybenzylidene-α- and -β-naphthylamine.*—These compounds (Senier and Forster, *J.*, 1914, **105**, 2470) were converted into the corresponding *O*-methyl ethers by the action of an ethereal diazomethane solution in the cold (Found, respectively: C, 82·3;

H, 5·9; N, 5·7; and C, 82·5; H, 5·8; N, 5·8. Calc. for $C_{18}H_{15}ON$: C, 82·8; H, 5·7; N, 5·4%). Further identification was carried out by mixed m. p. determination with authentic specimens of *p*-methoxybenzylidene-α- (Pope and Fleming, *J.*, 1908, **93**, 1916) and -β-naphthylamine (Steinhart, *Annalen*, 1887, 241, 341), respectively.

2-*Hydroxy*-1-*naphthylmethylene*-o-3-*xylidine* (IV*c*) was obtained by the condensation of equimolecular amounts of 2-hydroxy-1-naphthaldehyde and *o*-3-xylidine in yellow needles; m. p. 153° (Found: C, 83·1; H, 6·2; N, 5·3. $C_{19}H_{17}ON$ requires C, 82·9; H, 6·2; N, 5·1%). The condensation was carried out as described by Senier and Clarke (*J.*, 1911, **99**, 2084) for the synthesis of (IV*d*).

o-*Hydroxyanils which resist the Action of an Ethereal Solution of Diazomethane.*—Ethereal solutions of 1 g. each of (IV*a*) (Bartsch, *Ber.*, 1903, **36**, 1975), (IV*b*) (*idem*, *ibid.*), (IV*c*), (IV*d*) (Senier and Clarke, *loc. cit.*), (IV*e*) (*idem*, *loc. cit.*), and (V) were treated with excess of cold diazomethane (prepared from nitrosomethylurethane, 8 g.), and the mixture left for 48 hours at 0°. The ether was then evaporated off, and in every case the crude products showed the properties of the starting materials and after recrystallisation showed the same m. p. and mixed m. p.

Action of Diazomethane on o-*Hydroxyanils in the Presence of Methyl Alcohol.*—(*a*) 2-Hydroxy-1-naphthylmethylene-α-naphthylamine (IV*a*) (Bartsch, *loc. cit.*) (1 g.) in cold methyl alcohol (10 c.c.) was treated as in the preceding paragraph, fresh amounts of ethereal diazomethane being added during the 48 hours. The methyl alcohol and ether were evaporated off, and the solid residue was crystallised from benzene–light petroleum (b. p. 30—50°), forming colourless crystals, m. p. 169°. 3-(α-*Naphthylamino*)-4 : 5-*benzocoumaran* (VII*a*) is insoluble in hot water, soluble in hot benzene, hot ethyl alcohol, and cold ether, and gives a yellow colour with concentrated sulphuric acid (Found: C, 85·4; H, 5·5; N, 4·2; active hydrogen, 0·34. $C_{22}H_{17}ON$ requires C, 84·9; H, 5·5; N, 4·5; active hydrogen, 0·32%). When crystallised from hot glacial acetic acid, it gave colourless crystals of the *acetyl* derivative, m. p. 225° (Found: C, 77·4; H, 5·9. $C_{24}H_{21}O_3N$ requires C, 77·6; H, 5·6%); when the solution of this derivative in hot water was treated with aqueous ammonia, (VII*a*) was recovered (m. p. and mixed m. p.).

(*b*) Similarly, 3-(β-*naphthylamino*)-4 : 5-*benzocoumaran* (VII*b*) was obtained from 2-hydroxy-1-naphthylmethylene-β-naphthylamine (IV*b*) in almost colourless crystals, m. p. 190°. It is soluble in hot benzene and ethyl alcohol and gives a yellowish-green colour when treated with concentrated sulphuric acid (Found: C, 84·8; H, 5·7; N, 4·5%). It was crystallised from benzene–light petroleum (b. p. 30—50°).

(*c*) The action of ethereal diazomethane in the presence of methyl alcohol on 2-hydroxy-1-naphthylmethylene-*o*-3-xylidine (IV*c*) gave colourless crystals of 3-(o-3-*xylidino*)-4 : 5-*benzocoumaran* (VII*c*), readily crystallised from benzene, m. p. 173°; soluble in ether and hot ethyl alcohol, difficultly soluble in light petroleum (b. p. 50—60°) (Found: C, 83·1; H, 6·6; active hydrogen, 0·36. $C_{20}H_{19}ON$ requires C, 83·0; H, 6·6; active hydrogen, 0·35%).

(*d*) Similarly, 2-hydroxy-1-naphthylmethylene-*m*-4-xylidine (IV*d*) was treated with ethereal diazomethane in the presence of methyl alcohol, and 3-(m-4-*xylidino*)-4 : 5-*benzocoumaran* (VII*d*) obtained in colourless crystals; it is readily crystallised from benzene or methyl alcohol, m. p. 200°, difficultly soluble in ether, soluble in hot benzene (Found: C, 82·7; H, 6·2; N, 4·9. $C_{20}H_{19}ON$ requires C, 83·0; H, 6·6; N, 4·8%).

(*e*) In the usual manner (IV*e*) was converted into 3-(p-*xylidino*)-4 : 5-*benzocoumaran* (VII*e*), which formed colourless crystals from benzene–light petroleum (b. p. 50—70°), m. p. 162—163° (yellow-brown melt), readily soluble in ether and benzene and difficultly soluble in light petroleum (b. p. 50—70°) (Found: C, 82·8; H, 6·1; N, 5·3; active hydrogen, 0·36%).

(*f*) Salicylidene-*p*-xylidine (V) (Senier and Shepheard, *J.*, 1909, **95**, 443) was treated similarly; evaporation of the ether and methyl alcohol gave an oily product. Its ethereal solution on treatment with a stream of dry hydrogen chloride gave the *hydrochloride* of 3-(*p*-xylidino)-4 : 5-coumaran (VIII) in colourless crystals, m. p. 183° (not sharp); difficultly soluble in benzene and cold ethyl alcohol, soluble in hot water (Found: C, 69·9; H, 6·7; N, 5·1; Cl, 12·8. $C_{16}H_{18}ONCl$ requires C, 69·8; H, 6·5; N, 5·1; Cl, 12·8%).

Preparation of o-*Methoxyanils.*—The following *O*-methyl ethers of *o*-hydroxyanils were prepared by condensation of equimolecular amounts of 2-methoxy-1-naphthaldehyde (Barger and Starling, *J.*, 1911, **99**, 2032) and the corresponding aromatic amine (cf. Steinhart, *loc. cit.*). The reaction mixture in alcohol was heated under reflux for 2 hours; on cooling, and if necessary on concentration, the methyl ethers of the hydroxyanils separated out. Colours obtained with concentrated sulphuric acid are given in parenthesis after the m. p.

2-*Methoxy*-1-*naphthylmethylene*-α-*naphthylamine* was obtained in brownish-yellow crystals from ethyl alcohol, m. p. 143—144° (red); it is readily crystallised from hot benzene (Found: C, 84·3; H, 5·6; N, 4·9; OMe, 9·4. $C_{22}H_{17}ON$ requires C, 84·9; H, 5·5; N, 4·5; OMe, 9·9%). The β-*naphthyl* analogue formed yellow crystals, readily crystallised from ethyl alcohol, m. p. 123° (reddish-orange) (Found: C, 84·3; H, 5·0; N, 4·8%). The o-3-*xylidine* compound formed yellow crystals from ethyl alcohol, m. p. 120° (orange-yellow), soluble in hot ethyl alcohol and benzene (Found: C, 83·2; H, 6·8; N, 4·7. $C_{20}H_{19}ON$ requires C, 83·0; H, 6·6; N, 4·8%). The m-4-*xylidine* analogue crystallised from methyl alcohol in yellow crystals, m. p. 71° (orange), easily soluble in benzene (Found: C, 83·1; H, 6·4; N, 4·8%). The p-*xylidine* compound formed yellow crystals from methyl alcohol, m. p. 117° (orange) (Found: C, 82·4; H, 6·8; N, 4·9%).

Action of Methyl Sulphate on 2-*Hydroxy*-1-*naphthylmethylene*-β-*naphthylamine* (IV*b*).—A suspension of (IV*b*) (1 g.) in hot methyl alcohol (15 c.c.) was treated gradually with methyl sulphate (about 2 c.c.), followed by addition of a methyl-alcoholic solution of potassium hydroxide till alkaline. The mixture was set aside at room temperature for 2 hours, poured into water, extracted with ether, and crystallised from ethyl alcohol; it formed yellow crystals, m. p. 123° (red-brown melt), not depressed when admixed with a specimen of 2-methoxy-1-naphthylmethylene-β-naphthylamine prepared as above. The α-analogue was similarly obtained in yellow crystals, m. p. 143°, not depressed when admixed with a specimen of 2-methoxy-1-naphthylmethylene-α-naphthylamine prepared as above.

Phenylmagnesium Bromide and 3-(α-*Naphthylamino*)-4 : 5-*benzocoumaran.*—The benzocoumaran

(VII*a*) was treated with excess of phenylmagnesium bromide in ether–benzene, heated under reflux for 2 hours, and left overnight at room temperature. On hydrolysis, the starting substance was obtained unchanged or almost unchanged.

Action of Heat on 3-(α-*Naphthylamino*)-4 : 5-*benzocoumaran*.—The coumaran (VII*a*) (1 g.) was heated in a stream of dry carbon dioxide for ½ hour (bath temp., 250°). An almost colourless oil distilled over, which, on cooling, followed by extraction with hot light petroleum (b. p. 30—50°) and evaporation of the latter, gave colourless crystals of α-naphthylamine (m. p. and mixed m. p.). The part insoluble in the light petroleum was a resin which could not be identified.

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