18. *Experiments with Diazomethane and its Derivatives. Part XV. Action of Diazomethane on* o*-Quinone Monoximes.*

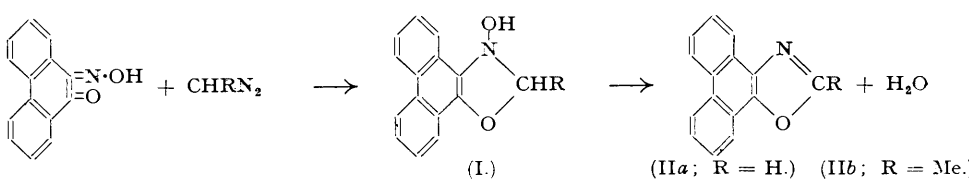
By Alexander Schönberg and William Ibrahim Awad.

Reaction of the monoximes of phenanthraquinone, retenequinone, and chrysenequinone with diazomethane or diazoethane leads to oxazole derivatives. Oxazoline derivatives corresponding to the intermediate (I) were found in the case of acenaphthenequinone monoxime, triketoindane-2 oxime, and 2-oximino-3 : 3-diphenylindan-1-one.

A scheme is advanced showing the similarity of the action of diazomethane on diketones, *o*-quinones, α-keto-lactones, *o*-quinone imines and monoximes, ketomethylene derivatives, and thiourea.

Very little is known about the action of diazomethane on *o*-quinone monoximes. It is stated, however, that oximinocamphor (stable or unstable form) gives, with diazomethane, the *N*-methyl ether (Forster and Holmes, *J.*, 1908, **93**, 247).

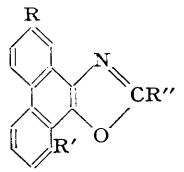
When phenanthraquinone monoxime was treated with diazomethane, phenanthroxazole (II*a*) was obtained by loss of water from an intermediate product (I), which was not isolated. The action of diazoethane led to 2-methylphenanthroxazole (II*b*).

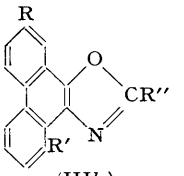


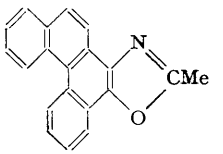
(I.) (II*a*; R = H.) (II*b*; R = Me.)

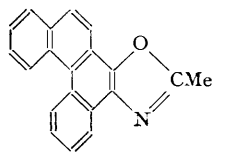
Diazomethane with retenequinone monoxime yielded reteno-oxazole (III*a* or *b*; R = Me, R′ = Pr^{i}, R″ = H), the uncertainty being caused by lack of knowledge of the position of the oximino-group present in retenequinone monoxime. Diazoethane similarly yields 2-methyl-

reteno-oxazole (III*a* or *b*; R = Me, R′ = Pr^{i}, R″ = Me). The products (III) are identical with those previously obtained from retenequinone imine. Schönberg and Awad (*J.*, 1947, 651)

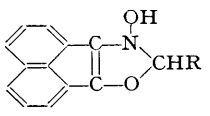

(III*a*.)

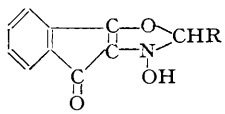

(III*b*.)

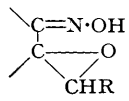

(IV*a*.)

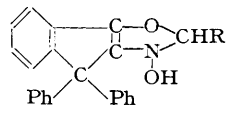

(IV*b*.)

pointed out the uncertainty concerning the structure of reteno-oxazoles, but defined it incorrectly in formulæ (II)—(IV) of that paper.


(V*a*; R = H.)
(V*b*; R = Me.)

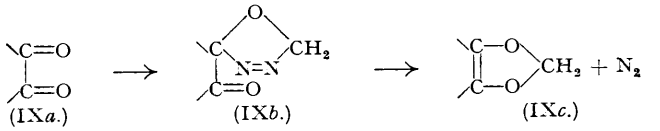

(VI*a*; R = H.)
(VI*b*; R = Me.)

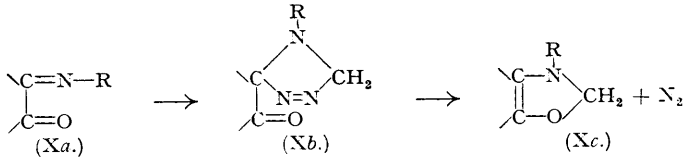

(VII.)

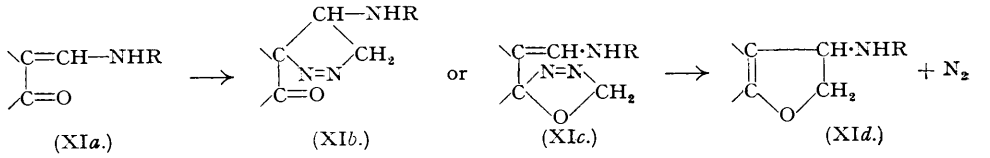

(VIII*a*; R = H.)
(VIII*b*; R = Me.)

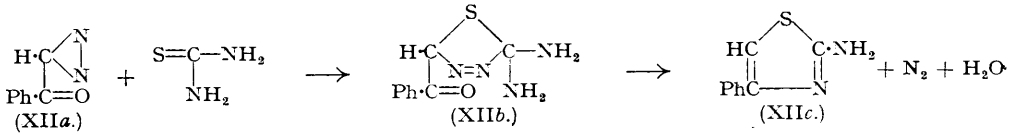
Diazoethane and chrysenequinone monoxime similarly give the 2-methylchryseno-oxazole (IV*a* or *b*).

Diazomethane and acenaphthenequinone monoxime or triketoindane-2 oxime give *3-hydroxy-acenaphthyleno*(7′ : 8′-4 : 5)*oxazoline* (V*a*) or *3-hydroxy-1′-ketoindeno*(2′ : 3′-4 : 5)*oxazoline* (VI*a*). (V*a*) and (VI*a*) are pale yellow substances. They contain no methoxy-group and only one active hydrogen atom (Zeisel's method). Acid hydrolysis of (V*a*) gives acenaphthenequinone, probably owing to the oxidation of the intermediate 1 : 2-dihydroxyacenaphthylene. (VI*a*) similarly yields triketoindane hydrate (ninhydrin). The results of hydrolysis make it improbable that the heterocyclic rings in (V*a*) and (VI*a*) can be replaced by (VII), since such substances are not expected to be hydrolysed in acid to acenaphthenequinone and triketoindane which would necessitate the rupture of a C–C linkage. According to Wanag and Lode (*Ber.*, 1939, **72**, 49) triketoindane 2-oxime is to be formulated as 2-nitrosoindane-1 : 3-dione but in our opinion its pale yellow colour is not in agreement with this hypothesis. (V*b*) and (VI*b*) were obtained by use of diazoethane.


(IX*a*.) (IX*b*.) (IX*c*.)

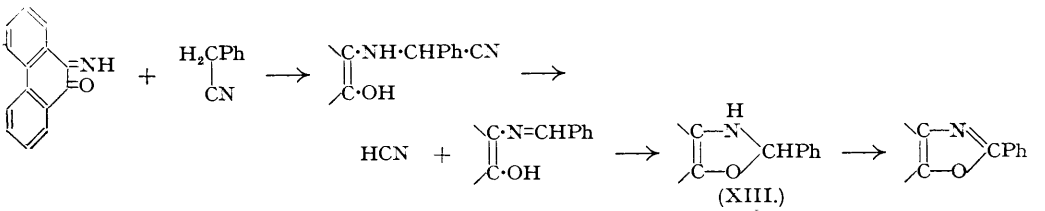

(X*a*.) (X*b*.) (X*c*.)


(XI*a*.) (XI*b*.) (XI*c*.) (XI*d*.)


(XII*a*.) (XII*b*.) (XII*c*.)

The action of diazomethane on 2-oximino-3 : 3-diphenylindan-1-one yielded 3-*hydroxy*-1′ : 1′-*diphenylindeno*(2′ : 3′-4 : 5)*oxazoline* (VIII*a*), a pale yellow substance containing one active hydrogen atom; with diazoethane the 2-*methyl* derivative (VIII*b*) was obtained.

The formation of five-membered ring compounds by the action of diazomethane and its derivatives on 1 : 2-diketones, *o*-quinones, α-keto-lactones (cf. IX*a* ⟶ IX*c*), *o*-quinone imines and monoximes (cf. X*a* ⟶ X*c*; R = H or OH), ketomethylene derivatives (cf. XI*a* ⟶ XI*d*), and thiourea (cf. XII*a* ⟶ XII*c*) may all be regarded as proceeding according to the same scheme, *i.e.*, addition of diazomethane to the >C═O, >C═N—, >C═C<, or >C═S group (cf. IX*b* and XI*c*, X*b*, XI*b*, and XII*b*), followed by the elimination of nitrogen.



(XIII.)

For the action of diazomethane on 1 : 2-diketones, *o*-quinones, coumarandiones, and thiocoumarandiones see Biltz and Paetzold (*Annalen*, 1923, **433**, 71), Arndt, Amende, and Ender (*Monatsh.*, 1932, **59**, 202), Fieser and Hartwell (*J. Amer. Chem. Soc.*, 1935, **57**, 1479), and Schönberg, Moubasher, and Mostafa (*J.*, 1941, 348). For the action on quinone imines (X*a*; R = H) see Schönberg and Awad (*loc. cit.*); the products actually obtained (*e.g.*, II*a* in the case of phenanthraquinone-imine and diazomethane) are oxazole derivatives formed by dehydrogenation of the intermediate products (*e.g.*, XIII, but with H replacing Ph). Reaction (X*a* ⟶ X*c*; R = OH) is described in this paper. For (XI*a* ⟶ XI*d*) see Schönberg, Mustafa, and Hilmy (*J.*, 1947, 1946). For the formation of (XII*c*) see King and Miller (*J. Amer. Chem. Soc.*, 1949, 367), who however do not discuss the formation of (XII*b*).

In connection with the synthesis of the phenanthroxazole derivatives, we have obtained 2-phenylphenanthroxazole (II, R = Ph) by the action of benzyl cyanide or deoxybenzoin on phenanthraquinone imine. In the case of benzyl cyanide the reaction is believed to proceed according to to the scheme above, and a similar one is proposed for the action of deoxybenzoin. The dehydrogenation required in the last step may be due to the oxidation by atmospheric oxygen or a second molecule of phenanthraquinone imine (Schönberg and Awad, *loc. cit.*). The action of *p*-nitrobenzyl cyanide leads to the formation of 2-*p*-nitrophenylphenanthroxazole.

Experimental.

The ethereal solution of diazomethane (diazoethane) was prepared according to *Org. Synth.*, Vol. 15, p. 3 (Werner, *J.*, 1919, **115**, 1093).

Action of Diazomethane on Oximes.—(a) *Phenanthraquinone monoxime* (Goldschmidt, *Ber.*, 1883, **16**, 2178). The oxime (0·5 g.) was suspended in ether and treated with an excess of ethereal diazomethane as usual for 6 hours. The solution was evaporated to dryness *in vacuo*, and the residue recrystallised from methyl alcohol; phenanthroxazole (II*a*) was obtained in light-yellow crystals, m. p. 152° (Found : C, 81·8; H, 4·0; N, 6·4. Calc. for $C_{15}H_9ON$: C, 82·2; H, 4·1; N, 6·4%). A mixed-m. p. determination with phenanthroxazole prepared according to Schönberg and Awad (*loc. cit.*) gave no depression; both samples gave the same colour with concentrated sulphuric acid.

(b) *Retenequinone monoxime* (Bamberger and Hooker, *Annalen*, 1885, **299**, 102). Reteno-oxazole (III*a* or III*b*; R = Me, R′ = Pr^i, R″ = H) recrystallised from methyl alcohol in yellow crystals, m. p. 108°, undepressed on admixture with an authentic specimen (Schönberg and Awad, *loc. cit.*) (Found : C, 82·7; H, 6·1; N, 5·2. Calc. for $C_{19}H_{17}ON$: C, 82·9; H, 6·2; N, 5·1%).

(c) *Acenaphthenequinone monoxime* (Francesconi and Pirazzoli, *Gazzetta*, 1903, **33**, I, 36). 3-*Hydroxyacenaphthyleno*(7′ : 8′-4 : 5)*oxazoline* (V*a*) recrystallised from methyl alcohol in yellow crystals, m. p. 163°. It gives a yellowish-orange colour in concentrated sulphuric acid, is insoluble in concentrated aqueous sodium hydroxide solution, and sublimes *in vacuo* (boiling ethyl cinnamate bath) (Found : C, 73·4; H, 4·3; N, 6·8; active H, 0·58; OMe, nil. $C_{13}H_9O_2N$ requires C, 73·9; H, 4·3; N, 6·6; one active H, 0·47%).

(d) 2-*Oximino*-3 : 3-*diphenylindan*-1-*one* (Koelsch and Le Claire, *J. Org. Chem.*, 1941, **6**, 531). 3-*Hydroxy*-1′ : 1′-*diphenylindeno*(2′ : 3′-4 : 5)*oxazoline* (VIII*a*) recrystallised from methyl alcohol in light-yellow crystals, m. p. 178° (Found : C, 80·0; H, 5·1; N, 4·5; active H, 0·3. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2; N, 4·3; one active H, 0·3%). It gave a yellowish-orange colour in concentrated sulphuric acid.

(e) *Triketoindane* 2-*oxime* (Teeters and Shriner, *J. Amer. Chem. Soc.*, 1933, **55**, 3026). 3-*Hydroxy*-1′-*ketoindeno*(2′ : 3′-4 : 5)*oxazoline* (VI*a*) was obtained in a way similar to that described previously, but ½ hour after the addition of the diazomethane solution a green deposit was formed which was filtered off. After recrystallisation twice from ethyl alcohol (96%) and then from methyl alcohol, yellow crystals of (VI*a*)

were obtained, having m. p. 247° (to a reddish-brown melt; shrinking before melting) (Found : C, 63·4; H, 4·0; N, 7·87; OMe, nil. $C_{19}H_7O_3N$ requires C, 63·5; H,3·7; N, 7·4%). It gave a yellowish-orange colour with concentrated sulphuric acid.

Hydrolysis of 3-*Hydroxyacenaphthyleno-oxazoline.*—The substance (0·2 g.) was dissolved in hot methyl alcohol (10 c.c.), and then concentrated hydrochloric acid (10 c.c.) was added. The mixture was refluxed for 2 hours and left to cool; the brown precipitate recrystallised from glacial acetic acid in yellow crystals which proved to be acenaphthenequinone, the m. p. being undepressed on admixture with an authentic specimen; both samples gave the same colour with concentrated sulphuric acid.

Hydrolysis of (VI*a*).—The substance (VI*a*) (0·1 g.) was dissolved in glacial acetic acid (15 c.c.), and an equal volume of concentrated hydrochloric acid was added. The mixture was refluxed for 4 hours. The solution was evaporated under normal pressure till a solid began to appear, and then cooled and filtered. The product was impure ninhydrin, as it gave a violet colour on the skin in the presence of water. The substance when treated with concentrated sodium hydroxide solution gave the blue colour reaction of ninhydrin.

Action of Diazoethane on Oximes.—(a) *Phenanthraquinone monoxime.* The oily residue obtained after the ether had been distilled off was cooled and scratched, with a little dilute methyl alcohol; it solidified to a brownish amorphous mass, which crystallised from methyl alcohol in light-yellow crystals, m. p. 145°, undepressed on admixture with an authentic specimen of 2-methylphenanthroxazole (II*b*), prepared according to Schönberg and Awad (*loc. cit.*) (Found : C, 82·6; H, 4·8; N, 5·7. Calc. for $C_{16}H_{11}ON$: C, 82·4; H, 4·7; N, 6·0%).

(b) *Retenequinone monoxime.* 2-Methylreteno-oxazole (III; R = Me, R′ = Pr^i, R″ = Me) recrystallised from dilute methyl alcohol (80%) in light-yellow crystals, m. p. 135°, undepressed on admixture with an authentic specimen prepared according to Schönberg and Awad (*loc. cit.*) (Found : C, 83·4; H, 6·7; N, 4·7. Calc. for $C_{20}H_{19}ON$: C, 83·0; H, 6·6; N, 4·8%).

(c) *Chrysenequinone monoxime* (Graebe and Hönigsberger, *Annalen*, 1900, **311**, 272). 2-*Methylchryseneoxazole* (IV*a* or *b*) recrystallised from methyl alcohol in yellow crystals, m. p. *ca.* 223° (Found : C, 84·9; H, 4·9; N, 4·5. $C_{20}H_{13}ON$ requires C, 84·8; H, 4·6; N, 4·9%).

(d) *Acenaphthenequinone monoxime.* 3-*Hydroxy*-2-*methylacenaphthylene*(7′ : 8′-4 : 5)*oxazoline* (V*b*) recrystallised from methyl alcohol in yellow crystals, m. p. 93°, and gave an orange colour in concentrated sulphuric acid (Found : N, 6·4; active H, 0·48. $C_{14}H_{11}O_2N$ requires N, 6·2; one active H, 0·44%).

(e) 2-*Oximino*-3 : 3-*diphenylindan*-1-*one.* 3-*Hydroxy*-1′ : 1′-*diphenyl*-2-*methylindeno*(2′ : 3′-4 : 5)-*oxazoline* (VIII*b*) crystallised from methyl alcohol in yellow crystals, m. p. 152° (Found : C, 80·7; H, 5·6; N, 3·9. $C_{23}H_{19}O_2N$ requires C, 80·9; H, 5·6; N, 4·1%). It gave an orange colour with concentrated sulphuric acid.

(f) *Triketoindane* 2-*oxime.* 3-*Hydroxy*-1′-*keto*-2-*methylindeno*(2′ : 3′-4 : 5)*oxazoline* (VI*b*) crystallised from methyl alcohol in yellow crystals, m. p. 160°, insoluble in cold sodium hydroxide solution (Found : C, 64·9; H, 4·5. $C_{11}H_9O_3N$ requires C, 65·0; H, 4·4%).

Action of (a) *Benzyl Cyanide,* (b) *Deoxybenzoin, and* (c) p-*Nitrobenzyl Cyanide on Phenanthraquinone Imine.*—(a) The imine (0·5 g.) and benzyl cyanide (0·3 g.) in anisole (5 c.c.) were refluxed for 1 hour, after which the anisole was evaporated off. The residual brown oil was cooled in an ice–salt mixture and triturated with alcohol (98%) at that temperature, whereby a yellow solid was formed. The product (II; R = Ph), crystallised from ethyl alcohol, had m. p. 202°, undepressed on admixture with an authentic specimen of 2-phenylphenanthroxazole prepared according to Stein and Day (*J. Amer. Chem. Soc.*, 1942, **64**, 2567) (Found : C, 85·1; H, 4·5; N, 4·6. Calc. for $C_{21}H_{13}ON$: C, 85·4; H, 4·4; N, 4·8%).

(b) The reaction was carried out as above, and the 2-phenylphenanthroxazole produced, after crystallisation from ethyl alcohol, had m. p. 202°, undepressed on admixture with the product obtained in (a) (Found : C, 85·4; H, 4·8; N, 4·8%).

(c) p-*Nitrobenzyl cyanide.* The reaction was carried out as in (a) with the imine (0·5 g.) and *p*-nitrobenzyl cyanide (0·5 g.). 2-*p*-Nitrophenylphenanthroxazole (II; R = *p*-$NO_2{\cdot}C_6H_4$) obtained on cooling the mixture was crystallised from chloroform as yellow crystals, m. p. 268° (Found : C, 74·1; H, 3·6; N, 7·8. Calc. for $C_{21}H_{12}O_3N_2$: C, 74·3; H, 3·5; N, 8·2%). Schiedt (*J. pr. Chem.*, 1941, **157**, 203) gives m. p. 272°.

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