356. *The Beckmann Rearrangement of the Dioximes of Anthraquinone and* 1 : 5-*Dichloroanthraquinone.*

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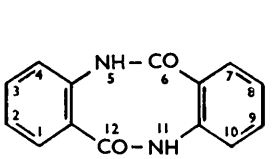
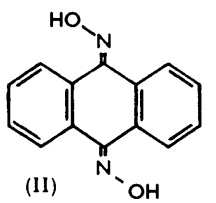
The Beckmann rearrangement of anthraquinone dioxime with polyphosphoric acid gives dianthranilide (I), in good yield; the dioxime therefore has the *anti*-configuration. 1 : 5-Dichloroanthraquinone yields a mixture of two dioximes which are shown, on the basis of the products they give on Beckmann rearrangement, to be the *trans-trans*- and *cis-trans*-compounds. Both oximes are cyclised by alkali, at approximately equal rates, to the bis*iso*-oxazole (VII), and it is shown that this cyclisation is accompanied by stereochemical inversion; the general validity of such cyclisations for the assignment of oxime configurations is questioned.

Dianthranilide * (I), a nitrogen analogue of disalicylide, the parent of a series extensively investigated by Baker and his colleagues,[1] was prepared, in poor yield, by Schroeter and Eisleb [2] by a five-stage process from anthranilic acid. A much simpler route appeared to be by the Beckmann rearrangement of anthraquinone *anti*-dioxime (II). A dioxime of anthraquinone, of unknown stereochemical configuration, was prepared by Meisenheimer and Mahler [3] by the pyridine method, but there is no record of its having been subjected to the Beckmann rearrangement. Beckmann and Liesche [4] carried out such a



(I)



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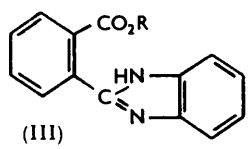


(III)

rearrangement with anthraquinone monoxime and obtained a keto-lactam, the oxime of which, on further Beckmann rearrangement, afforded 2-*o*-carboxyphenylbenziminazole (III ; R = H), no doubt by way of *NN'*-phthaloyl-*o*-phenylenediamine.

In view of the failure of Beckmann and Liesche [4] to bring about the Beckmann rearrangement of benzoquinone dioxime with the usual reagents, we subjected anthraquinone dioxime to the action of hot polyphosphoric acid, which has been shown [5] to be remarkably effective for the rearrangement of ketoximes. The product, obtained in good yield, was shown to be dianthranilide (I) by comparison with a specimen prepared by the method of Schroeter and Eisleb; [2] no trace of the benziminazole (III; R = H) or of the derived tetracyclic lactam (*iso*indolobenziminazole) could be found in the reaction product. This result establishes the *anti*-configuration (II) for the anthraquinone dioxime obtained by the pyridine procedure.[3]

We next turned our attention to the dioximes of 1 : 5-dichloroanthraquinone. Three

* The Ring Index names for (I) (No. 2093) are phenhomazine-6 : 12-dione or, more systematically, dibenzo[*b*,*f*][1, 5]diazocine-6 : 12-dione, but we prefer dianthranilide as being both more intelligible and more euphonious; we have adopted the Ring Index numbering.

[1] Baker, McOmie, and Ollis, *J.*, 1951, 200; Baker, Ollis, and Zealley, *ibid.*, p. 201; Baker, Gilbert, Ollis, and Zealley, *ibid.*, p. 209; Baker, Gilbert, and Ollis, *J.*, 1952, 1443; Baker, El-Nawawy, and Ollis, *ibid.*, p. 3163; Baker, Harborne, Price, and Rutt, *J.*, 1954, 2042.

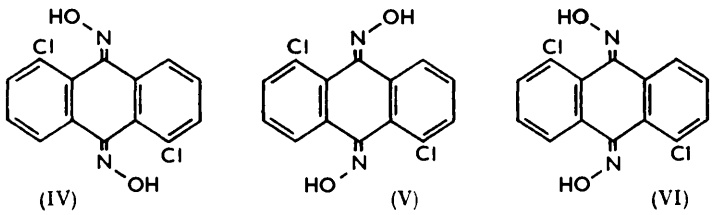
[2] Schroeter and Eisleb, *Annalen*, 1909, **367**, 101.

[3] Meisenheimer and Mahler, *ibid.*, 1934, **508**, 191.

[4] Beckmann and Liesche, *Ber.*, 1923, **56**, 1.

[5] Horning and Stromberg, *J. Amer. Chem. Soc.*, 1952, **74**, 2680; Horning, Stromberg, and Lloyd, *ibid.*, p. 5153.

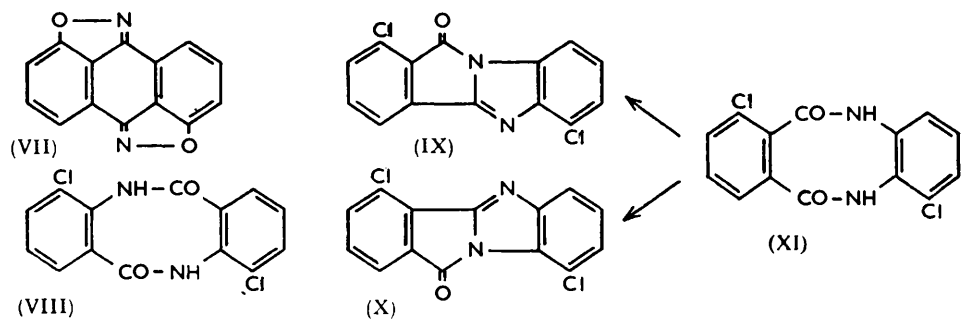
stereoisomerides are possible; two of these are *anti*-forms, which we designate * as *cis-cis*- (IV), and *trans-trans*- (V), the third, *syn*, form being the *cis-trans*-compound, (VI):



(IV) (V) (VI)

1 : 5-Dichloroanthraquinone forms a dioxime more readily than does anthraquinone, and Freund and Achenbach [6] subjected a mixture of dioximes obtained by the action of hydroxylamine on 1 : 5-dichloroanthraquinone to the action of hot alkali, obtaining the bis*iso*oxazole (VII), and a dioxime, m. p. 245°, which they found to be unaffected by alkali and to which they accordingly ascribed the *trans-trans*-configuration (V); the bis*iso*-oxazole was regarded as having been formed from the *cis-cis*-dioxime (IV), which was, however, not isolated.

Repetition of Freund and Achenbach's work with the mixture of 1 : 5-dichloroanthraquinine dioximes obtained by the pyridine procedure gave the bis*iso*oxazole (VII) and a dioxime, m. p. 262°; the latter was, however, not the pure *trans-trans*-compound since Beckmann rearrangement gave two products [(VIII) and (IX) or (X), the former prepon-



(VII) (VIII) (IX) (X) (XI)

derating]. The original mixture of dioximes with acetyl chloride in pyridine [7] gave a mixture of diacetyl derivatives which was readily separated into its components by treatment with cold acetic anhydride.

The diacetyl derivative insoluble in acetic anhydride, on hydrolysis with sodium hydroxide in dioxan, yielded a dioxime, m. p. 250°. Beckmann rearrangement of this with polyphosphoric acid gave a dichlorodianthranilide, which yielded dianthranilide (I) on catalytic hydrogenolysis and was shown to be 4 : 10-dichlorodianthranilide (VIII), by hydrolysis to 3-chloroanthranilic acid [8] (CO_2H = 1). On the basis of a Beckmann *trans*-rearrangement we assign the *trans-trans*-configuration (V) to this dioxime.

Similar hydrolysis of the diacetyl derivative soluble in acetic anhydride yielded another dioxime, m. p. 267°. Beckmann rearrangement of this yielded a dichloro-oxo-*iso*indolobenziminazole (IX) or (X); this structure is confirmed by the close similarity of the light

* We use the terms *syn* and *anti* to describe the mutual stereochemical relations of the oxime groups, and *cis* and *trans* to describe the configurations of these groups with respect to the nearer chlorine atom.

[6] Freund and Achenbach, *Ber.*, 1910, **43**, 3251.
[7] Cf. Einhorn and Hollandt, *Annalen*, 1898, **301**, 95.
[8] Baker, Schaub, Joseph, McEvoy, and Williams, *J. Org. Chem.*, 1952, **17**, 143.

absorption to that of the chlorine-free compound [9,10] and also by the similarity of the light absorption of the derived 2-(chloro-methoxycarbonylphenyl)chlorobenziminazole to that of the chlorine-free analogue, 2-*o*-methoxycarbonylphenylbenziminazole [9] (III; R = Me); we have no evidence to enable us to distinguish between structures (IX) and (X). The formation of an *iso*indolobenziminazole from the dioxime of m. p. 267° shows this to be the *cis-trans*-compound (VI), without any assumption concerning the stereochemical course of the Beckmann rearrangement, since either *cis*- or *trans*-rearrangement would yield initially the chlorophthaloyl-chloro-*o*-phenylenediamine (XI), which could yield either (IX) or (X).

No trace of the third, *cis-cis*-dioxime (IV) postulated by Freund and Achenbach [6] could be found in the crude mixture of 1 : 5-dichloroanthraquinone dioximes; neither could its expected rearrangement product, 1 : 7-dichloroanthraquinone, be found in the Beckmann rearrangement product from this mixture. The absence of this stereoisomeride is not surprising, since models show considerable overlapping of the chlorine atoms and the hydroxyimino-group.

Contrary to expectation, and to the statement of Freund and Achenbach,[6] both 1 : 5-dichloroanthraquinone dioximes give the bis*iso*oxazole (VII) when heated with dilute alkali. Although qualitative observations of the rate of formation of (VII) supported the configurations assigned to the two diacetyl derivatives it seemed desirable to confirm these by direct measurement of the rates of cyclisation of the two oximes. In one series of experiments this was done by weighing the *iso*oxazole formed in 2N-sodium hydroxide at 100°; in a second, the liberation of chloride ion in 0·5N-potassium hydroxide at 100° was measured; the results, expressed as first-order velocity constants, were as follows:

	k_1 (hr.$^{-1}$)	
Oxime	Bis*iso*oxazole formation in 2N-NaOH	Cl^- liberated in 0·5N-KOH
trans-trans (V)	0·184	0·136
cis-trans (VI)	0·173	0·152

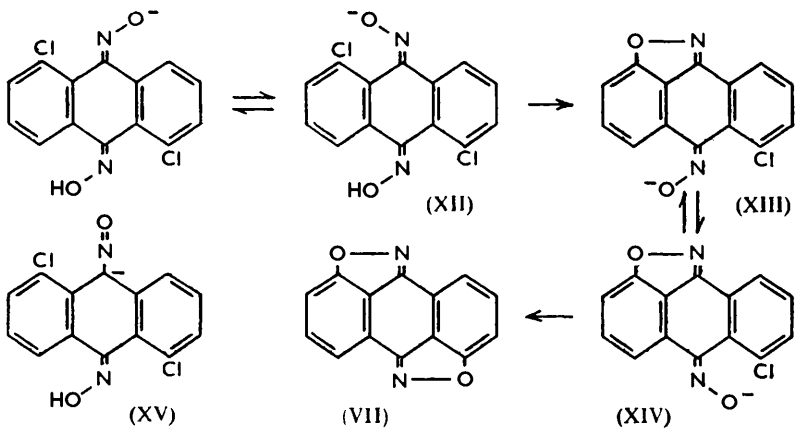
The small difference in the rate of formation of the bis*iso*oxazole from the two oximes was very surprising and an experiment was therefore carried out in which the two pure oximes were each heated at 100° with 0·5N-potassium hydroxide for three hours; the composition of the recovered oxime was ascertained by acetylation, followed by separation of the diacetyl derivatives. The results were:

		Recovered oxime	
		Composition (%)	
Starting material	Yield (%)	(V)	(VI)
trans-trans (V)	69	35	65
cis-trans (VI)	56	23	77

Clearly, bis*iso*oxazole formation is preceded, or accompanied, by stereochemical interconversion of the two oximes with production of an equilibrium mixture. It is probable that only one hydroxyimino-group is ionised under the reaction conditions and the relative insensitivity of the reaction rate to hydroxyl-ion concentration supports the view that the cyclisation involves the oximate anion, rather that the un-ionised hydroxyimino-group. The probable reaction sequence is as annexed, in which the slowest, rate-determining stage must be the first cyclisation, (XII) ⟶ (XIII); this is necessitated by the overall first-order kinetics of the reaction and the absence of the mono*iso*oxazole [as (XIII) or (XIV)] from the products of the interrupted hydrolyses. The second cyclisation might well be expected to be faster than the first, since the closure of the first *iso*oxazole ring renders the whole tetracyclic system rigidly planar; the inverted anion (XIV) is thus fixed in a position peculiarly favourable to further cyclisation to the bis*iso*oxazole (VII). It seems probable that the stereochemical inversions proceed by way of the nitroso-carbanions, *e.g.*, (XV).

[9] Bistrzycki and Lecco, *Helv. Chim. Acta*, 1921, **4**, 425.
[10] Porai-Koshitz and Antoshulskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1943, **13**, 339.

The stereochemical inversion of oximes under the influence of alkali was observed by early workers,[11] but its significance for the classical work of Meisenheimer [12] on the cyclisation of the oximes of *o*-substituted aromatic ketones has not been generally appreciated. In one of Meisenheimer's papers [13] stereochemical inversion under the influence



of alkali was observed to accompany *iso*oxazole ring formation; in this case, the rates of the two reactions were sufficiently different to justify Meisenheimer in neglecting the stereochemical inversion when interpreting his results. In our case, however, it is clearly not possible to ignore the stereochemical inversion and it therefore appears that it is not generally safe to assign oxime configurations on the basis of cyclisations carried out in alkali; ketoxime configurations are thus more safely based on the Beckmann rearrangement, the *trans*-nature of which is now overwhelmingly supported by other evidence.[12]

Experimental

Figures for light absorption are $\lambda_{max.}$ in mμ, followed by $\varepsilon_{max.}$ in parentheses.

Beckmann Rearrangement of Anthraquinone Dioxime.—Anthraquinone dioxime [3] (2 g.) was stirred into polyphosphoric acid [14] (60 g.) at 100° and the mixture heated, with stirring, in an oil-bath at 140° for 80 min.; dissolution was complete in 60 min. The product was poured into water (300 ml.); recrystallisation of the precipitated solid from water yielded dianthranilide (I) (1·7 g., 85%), m. p. 334° (Found: C, 70·45; H, 4·5; N, 11·7. Calc. for $C_{14}H_{10}O_2N_2$: C, 70·6; H, 4·2; N, 11·75%); the m. p. was not depressed on admixture with a specimen of dianthranilide, m. p. 330°, prepared by Schroeter and Eisleb's method.[2]

1 : 5-*Dichloroanthraquinone Dioximes.*—1 : 5-Dichloroanthraquinone (12 g.) and hydroxylamine hydrochloride (72 g.) were refluxed in pyridine (400 ml.) for 36 hr. The cooled solution was stirred into an excess of 2N-sulphuric acid and ice, and the precipitated solid digested with cold 2N-sodium hydroxide (150 ml.). After filtration from unchanged quinone, the filtrate was acidified and the precipitate (15 g.) dried at 50° and exhaustively extracted with boiling chlorobenzene. The insoluble mixture of dioximes (5·25 g., 40%), washed with light petroleum (b. p. 60—80°) and dried at 50°, had m. p. 225° (decomp.) (Found: N, 9·00%).

Such a mixture of dioximes (12 g.) was refluxed for 7 hr. with 2N-sodium hydroxide. The insoluble bis*iso*oxazole (VII) (5·1 g., 56%), recrystallised from acetic acid, had m. p. 330—335° (decomp.) (Found: N, 12·1. Calc. for $C_{14}H_6O_2N_2$: N, 12·0%). Acidification of the filtrate gave a mixture of dioximes (4·0 g., 33%), m. p. 262° (decomp.).

Another sample of the original mixture of dioximes (6·5 g.), in anhydrous pyridine (50 ml.),

[11] For refs. see Meisenheimer and Theilacker in K. Freudenberg, "Stereochemie," Leipzig, 1933, p. 1030; cf. Montgomery and Dougherty, *J. Org. Chem.*, 1952, **17**, 823.
[12] For references see Blatt, *Chem. Rev.*, 1933, **12**, 220.
[13] Meisenheimer, Zimmermann, and Kummer, *Annalen*, 1926, **446**, 205.
[14] Bell, *Ind. Eng. Chem.*, 1948, **40**, 1464.

was treated with acetyl chloride (3·5 g.). After 24 hr. at room temperature, the mixture was poured into ice and 2N-sulphuric acid. The precipitated solid was washed with 2N-sulphuric acid and water and dried in a vacuum-desiccator. This mixture of diacetyl derivatives (8·3 g.) was stirred at room temperature for 3½ hr. with redistilled acetic anhydride (50 ml.). The insoluble material (5·1 g., 62%), m. p. 210—215° (decomp.), was recrystallised from dioxan, affording 1 : 5-*dichloroanthraquinone* trans-trans-*diacetyldioxime* as leaflets, m. p. 236° (Found : C, 55·5; H, 3·0; N, 7·2. $C_{18}H_{12}O_4N_2Cl_2$ requires C, 55·25; H, 3·1; N, 7·2%). The acetic anhydride filtrate was stirred with ice and water until all the anhydride was hydrolysed; the solid (2·5 g., 30%), m. p. 175—185° (decomp.), was recrystallised from benzene–hexane, affording the *cis-trans*-diacetyldioxime as a *benzene complex*, prisms, m. p. 207° (Found : C, 58·9; H, 3·4; N, 6·5; loss of wt. at 100°, 10·4. $C_{18}H_{12}O_4N_2Cl_2,\frac{1}{2}C_6H_6$ requires C, 58·6; H, 3·5; N, 6·5; C_6H_6, 9·1%), which lost benzene at 50°/1 mm. to give the benzene-free compound, m. p. 207° (Found : C, 55·6; H, 3·1; N, 7·4%).

The *trans-trans*-diacetyl compound (650 mg.) was gently warmed at 50° with N-sodium hydroxide (6·7 ml.) and dioxan (1 ml.). As soon as solution was complete, the mixture was cooled in ice and acidified with 2N-hydrochloric acid; the precipitated 1 : 5-*dichloroanthraquinone* trans-trans-*dioxime* (V) (500 mg., 98%) had m. p. 250° (decomp.) (Found : N, 9·45. $C_{14}H_8O_2N_2Cl_2$ requires N, 9·1%). Similar hydrolysis of the *cis-trans*-diacetyl compound (650 mg.) required 3 hr. at 60° and gave 1 : 5-*dichloroanthraquinone* cis-trans-*dioxime* (VI), (470 mg., 92%), m. p. 267° (decomp.) (Found : N, 9·0%).

Beckmann Rearrangement of 1 : 5-*Dichloroanthraquinone Dioximes*.—(a) trans-trans-*Dioxime*. The *trans-trans*-dioxime (400 mg.) was heated at 90° with polyphosphoric acid (12 g.) for 2 hr. The clear pale yellow solution was cooled and poured into ice-water (50 ml.), and the precipitated solid recrystallised from aqueous 2-ethoxyethanol, affording 4 : 10-*dichlorodianthranilide* (VIII) (290 mg., 72%), as plates, m. p. 307° (Found : C, 55·0; H, 2·7; N, 8·8. $C_{14}H_8O_2N_2Cl_2$ requires C, 54·8; H, 2·6; N, 9·1%).

This product (200 mg.) was hydrogenated in ethanol (40 ml.), containing potassium hydroxide (1 g.), over 2% palladised calcium carbonate (1 g.). When hydrogen uptake ceased the mixture was filtered, neutralised (10N-hydrochloric acid), and evaporated under reduced pressure. Recrystallisation of the residue from water gave dianthranilide (145 mg., 93%), m. p. and mixed m. p. 336°.

Another sample (100 mg.) was refluxed for 24 hr. with 20% aqueous potassium hydroxide (5 ml.). Acidification and recrystallisation from water gave 3-chloroanthranilic acid (90 mg., 81%), needles, m. p. 194°, not depressed on admixture with a specimen, m. p. 194°, prepared by the method of Baker *et al.*[8] who give m. p. 188°.

(b) cis-trans-*Dioxime*. The *cis-trans*-dioxime (700 mg.) was similarly rearranged with polyphosphoric acid (20 g.). Recrystallisation of the product from 2-ethoxyethanol gave 1 : 6(or 4 : 9)-*dichloro*-11-*oxo*iso*indolo*[2 : 1-*a*]*benziminazole* (Ring Index No. 2271) (IX or X) (380 mg., 58%) as yellow needles, m. p. 282° (Found : C, 58·8; H, 2·0; N, 9·8; Cl, 24·8. $C_{14}H_6ON_2Cl_2$ requires C, 58·2; H, 2·1; N, 9·7; Cl, 24·5%); light absorption in ether : 238 (28,000), 274 (35,800), 310 (5,400), 313 (7,800), 355 (7,800). An authentic specimen of 11-oxo-*iso*indolo[2 : 1-*a*]benziminazole[9,10] showed the following light absorption in ether : 235 (22,600), 271 (35,400), 290 (8,400), 300 (10,000), 335 (4,900).

The dichloro-oxo*iso*indolobenziminazole (500 mg.) was suspended in methanol (5 ml.) and treated with 2N-sodium hydroxide (1 drop). After 10 min. at room temperature, a homogeneous colourless solution was obtained, from which water precipitated 4(or 7)-*chloro*-2-[3(or 6)-*chloro*-2-*methoxycarbonylphenyl*]*benziminazole* (510 mg., 92%), which crystallised from aqueous methanol in plates, m. p. 191—192° (Found : N, 8·6. $C_{15}H_{10}O_2N_2Cl_2$ requires N, 8·7%); light absorption in ether : 242·5 (13,800), 305 (19,400); when heated above its m. p. the compound resolidifies to give the parent compound (IX or X), m. p. 282°. Authentic 2-*o*-methoxycarbonylphenylbenziminazole[9] (III; R = Me) showed the following light absorption in ether : 237·5 (11,600), 303 (13,500).

Similar treatment of the dichloro-compound with 2-ethoxyethanol and alkali gave 4(or 7)-*chloro*-2-[3(or 6)-*chloro*-2-2′-*ethoxyethoxycarbonylphenyl*]*benziminazole* (73% yield), which crystallised from aqueous 2-ethoxyethanol in plates, m. p. 175° (Found : C, 57·7; H, 4·3; N, 7·3. $C_{18}H_{16}O_3N_2Cl_2$ requires C, 57·0; H, 4·2; N, 7·4%).

(c) *Mixed dioximes*. Rearrangement of the original mixture of stereoisomeric dioximes (4 g.) with polyphosphoric acid (120 g.) at 150° gave a product (3·4 g.) which was recrystallised

from 2-ethoxyethanol. Recrystallisation of the first crop from ethanol and again from 2-ethoxyethanol gave the dichloro-oxo*iso*indolobenziminazole, (IX or X) (0·6 g., 15%), m. p. 284°. Addition of water to the original 2-ethoxyethanol mother-liquors and recrystallisation of the precipitate from ethanol–ether gave 4 : 10-dichlorodianthranilide (VIII) (2·1 g., 52%), m. p. 292°.

Similar treatment of the mixed dioximes remaining after refluxing the original mixture with alkali (p. 1903) likewise gave the benziminazole derivative (18%) and 4 : 10-dichlorodiathranilide (40%).

Action of Alkali on the 1 : 5-*Dichloroanthraquinone Dioximes.*—(a) *Qualitative experiments.* (i) The *trans-trans*-diacetyldioxime (100 mg.) was refluxed for 22 hr. with 2N-sodium hydroxide (2 ml.) and water (5 ml.). Dissolution was complete when the temperature reached 80° and the bis*iso*oxazole began to separate after 30 min. The insoluble product (60 mg., 100%), recrystallised from 2-ethoxyethanol, gave the bis*iso*oxazole (VII) as golden-yellow needles, m. p. 328° (decomp.) (Found : N, 12·1. Calc. for $C_{14}H_6O_2N_2$: N, 12·0%) (Freund and Achenbach [6] give m. p. 304°).

(ii) The *cis-trans*-diacetyldioxime (300 mg.) was similarly treated with 2N-sodium hydroxide (4 ml.) and water (10 ml.). Dissolution occurred at a lower temperature and bis*iso*oxazole began to separate almost at once. The insoluble product (180 mg., 100%) crystallised from 2-ethoxyethanol in golden-yellow needles, m. p. and mixed m. p. 327—328° (decomp.).

(b) *Kinetic experiments.* (i) The stereoisomeric dioximes (1 g.) were refluxed, with mechanical stirring, with 2N-sodium hydroxide. At intervals, the reaction mixture was cooled in ice, the precipitated bis*iso*oxazole filtered off and washed with a little water, and the filtrate returned to the reaction vessel for continued heating; the precipitates were further washed with water, dried, and weighed. In spite of the obvious experimental inadequacies the log plots were satisfactorily linear for 5 hr. (*ca.* 60% reaction) and led to the following first-order velocity constants : *trans-trans*-dioxime, 0·184 hr.$^{-1}$; *cis-trans*-dioxime, 0·173 hr.$^{-1}$.

(ii) The dioximes (153·5 mg.) were dissolved in N-potassium hydroxide (5 ml.), and the solutions made up to 10 ml. with water. Portions (1 ml.) were sealed in separate tubes and heated at 100° in a steam-bath. At intervals, tubes were withdrawn, cooled in ice, and opened; chloride ion was then determined by Volhard's method after acidification with nitric acid. The log plots were again satisfactorily linear for 5 hr. and led to the following first-order velocity constants : *trans-trans*-dioxime, 0·136 hr.$^{-1}$; *cis-trans*-dioxime, 0·152 hr.$^{-1}$.

(c) *Interrupted hydrolyses.* (i) The *trans-trans*-dioxime (1·52 g.) was heated for 3 hr. with 0·5N-potassium hydroxide (99 ml.). The insoluble bis*iso*oxazole (0·225 g., 19·4%) had m. p. 319° (decomp.), raised to 327—328° (decomp.) by recrystallisation from 2-ethoxyethanol. The aqueous filtrate was acidified and the precipitated solid (1·21 g., 80%) filtered off, washed, and dried in a vacuum-desiccator. This mixture of dioximes was acetylated, in the usual manner, with acetyl chloride (0·63 g.) in pyridine (10 ml.). The crude product (1·51 g.) was kept in acetic anhydride (12 ml.), with occasional shaking, for 24 hr. at room temperature. The insoluble *trans-trans*-diacetyldioxime (0·469 g., 24·3%) had m. p. and mixed m. p. 232—233° (decomp.) after recrystallisation from acetic anhydride; the soluble *cis-trans*-diacetyldioxime (0·891 g., 46·1%), precipitated by water in the usual manner, had m. p. and mixed m. p. 204—206° after recrystallisation from benzene–hexane.

(ii) The *cis-trans*-dioxime (1·54 g.), treated in the same way, yielded : (i) bis*iso*oxazole (0·366 g., 31·0%), m. p. 324—326° (decomp.) after recrystallisation from 2-ethoxyethanol; (ii) *trans-trans*-diacetyldioxime (0·324 g., 12·6%), m. p. and mixed m. p. 234—235° (decomp.) after recrystallisation from aqueous dioxan; (iii) *cis-trans*-diacetyldioxime (0·857 g., 43·7%), m. p. and mixed m. p. 197—201° after recrystallisation from benzene–hexane.

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