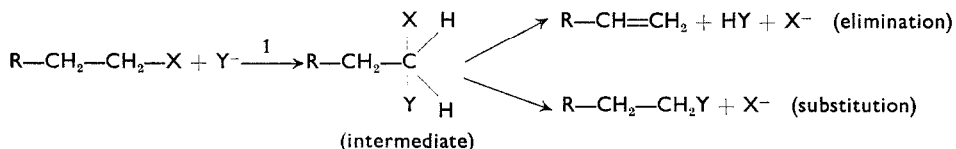


NOTES

An example of merged bimolecular substitution and elimination

(Received 5 August 1957)

WINSTEIN, DARWISH and HOLNESS¹ have recently postulated the existence of a new mechanism of simultaneous S_N2 and E_2 reactions which they call "merged bimolecular substitution and elimination". The mechanism may be schematized as follows:



Presumably formation of the intermediate (step 1) is rate-determining.

In an investigation which we are undertaking with different ends in mind, we have found evidence in support of the merged mechanism. When 4,4-dimethylcyclohexyl tosylate (I) was treated with sodium thiophenolate in 87% ethanol and the reaction followed acidimetrically, an overall second-order rate constant ($k_s + k_e$) of 19.04 (all rate constants given in l. mole⁻¹ sec⁻¹ × 10⁵) was found. Iodimetric titration during reaction indicated that the entire* rate was due to substitution, i.e. $k_s = 19.04$ and $k_e = 0$. This result should be contrasted with one for the parent compound cyclohexyl tosylate (II) where the reaction with thiophenolate proceeded at an overall specific rate $k_s + k_e$ of 18.35, of which however only part was substitution ($k_s = 10.09$) and part was elimination ($k_e = 8.26$).² The agreement of the overall rate constants ($k_s + k_e$) was at first sight reasonable, since I and II exist at about the same equilibrium mixture of equatorial and axial conformations (with respect to the tosylate grouping) (Fig. 1) and the feebly electron-donating methyl groups should have no appreciable polar affect at the remote 4-position of the ring.^{3,4†} The difference in the individual rate constants k_s and k_e is, however, at first sight surprising. One can perhaps understand why elimination in I is slower than in II, since in I the axial hydrogens at C₂ are shielded from attack by base by the axial

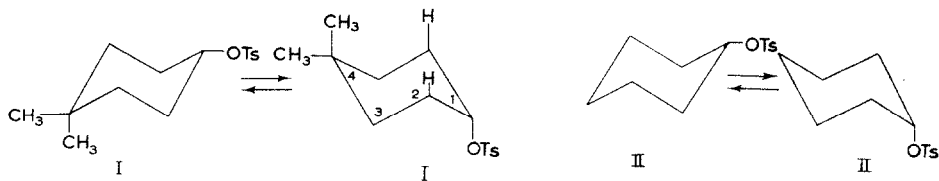


FIG. 1.

methyl at C₄. Indeed, we have found that the rate of bimolecular elimination for I with sodium ethoxide in absolute ethanol (0.349) is less than that for II (0.570) and the difference is magnified for the more bulky⁵ base potassium *t*-butoxide in *t*-butanol (0.310 vs. 0.823). As thiophenolate may well

* The accuracy of the method is such that if more than 5-10 per cent of the total reaction had been elimination, it would have been detected.

† Cyclohexanol and 4,4-dimethylcyclohexanol are acetylated at the same rate with acetic anhydride in pyridine.

¹ S. Winstein, D. Darwish and N. J. Holness *J. Amer. Chem. Soc.* **78**, 2915 (1956).

² E. L. Eliel and R. S. Ro *Chem. & Ind. (Rev.)* 251 (1956); *J. Amer. Chem. Soc.* **79**, 5995 (1957).

³ J. F. J. Dippy, S. R. C. Hughes and J. W. Laxton *J. Chem. Soc.* 4102 (1954).

⁴ E. L. Eliel and C. A. Lukach *J. Amer. Chem. Soc.* **79**, 5986 (1957).

⁵ H. C. Brown and I. Moritani *J. Amer. Chem. Soc.* **75**, 4112 (1953); H. C. Brown, I. Moritani and Y. Okamoto *Ibid.* **78**, 2193 (1956).

have an even larger steric requirement than *t*-butoxide, the very slow elimination rate of I with this base is explained. It is not clear, however on the basis of the classical⁶ S_N2-E_2 dichotomy why the decrease in elimination rate for I should lead to a corresponding increase in substitution rate so as to keep the overall rate approximately the same as for cyclohexyl tosylate. On the basis of the merged mechanism¹ the interpretation is clear: The rate determining step 1 (equation above) proceeds at the same rate for I and II, but whereas the intermediate from II is converted partly to elimination and partly to substitution product, the intermediate from I gives substitution product exclusively (or nearly so) since elimination is sterically prevented. It is implied in this view that the product determining step in the merged mechanism involves attack by external base in so far as formation of the elimination product is concerned.

The merged mechanism implies that the rate-determining and product-determining steps are discrete. There are many instances in which this is not the case,⁶ hence the merged mechanism cannot be general. It has been implied,¹ (and the present results seem to support this) that the merged mechanism is likely to be observed with strong nucleophiles of feebly basic properties, such as bromide and thiophenolate. The operation of the merged mechanism may be responsible for the remarkably high elimination rates observed in the reaction of cyclohexyl tosylate,² *cis*-4-*t*-butylcyclohexyl tosylate³ and *t*-butyl chloride⁷ with sodium thiophenolate.

The present results are in good agreement with those obtained in the reaction of $(CH_3)_2CDCHOTsCH_3$ with bromide ion by Winstein *et al.*⁸

EXPERIMENTAL*

4,4-Dimethylcyclohexyl tosylate prepared from the parent alcohol⁴ by the method of Tipson,⁹ was a liquid purified by low-temperature crystallization.

Anal. Found: C, 63.93; H, 8.33; S, 11.36. $C_{15}H_{22}O_3S$ requires C, 63.80; H, 7.85; S, 11.35 per cent.

Kinetic measurements were performed as described elsewhere.²

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⁶ C. K. Ingold *Structure and Mechanism in Organic Chemistry* Chaps. VII and VIII. Cornell University Press, Ithaca, N. Y. (1953).

⁷ P. B. D. de la Mare and C. A. Vernon *J. Chem. Soc.* 41 (1956).

⁸ S. Winstein, D. Darwish and J. Takahashi Private communication.

⁹ R. S. Tipson *J. Org. Chem.* 9, 235 (1944).

Resonance energies of two unusually stable hydrocarbon free radicals

(Received 24 August 1957)

THE radical α, γ -bis(diphenylene)- β -phenylallyl (I) was first prepared by Koelsch in 1932.¹ Its stability is such that it reacts only slowly with molecular oxygen,^{1,2} but electron spin resonance (ESR) measurements² have completely confirmed its radical nature.² In benzene solution I shows 1.1 radicals per mole by comparison of the integrated intensity of its ESR spectrum with that of diphenylpicrylhydrazyl.² The pentaphenylcyclopentadienyl radical (IV) is also reported³ to be much more stable than the triphenylmethyl radical toward reaction with molecular oxygen and toward dimerization, although it does not appear to be quite as stable as I.⁴ The present note reports that the great stability of I and IV toward reaction with molecular oxygen and toward dimerization is completely accountable on the basis of their resonance energies, as calculated by the simple L.C.A.O.M.O. method.⁵

¹ C. F. Koelsch *J. Amer. Chem. Soc.* 79, 4439 (1957).

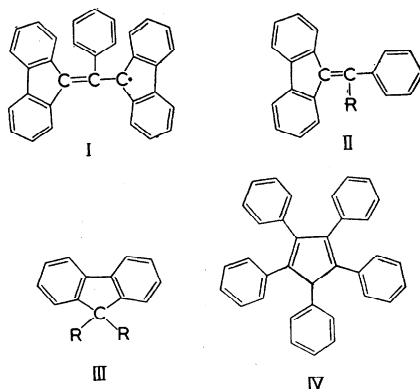
² J. E. Wertz and J. L. Vivo Acrivos Unpublished results.

³ K. Ziegler and B. Schnell *Liebigs Ann.* 445, 266 (1925).

⁴ J. Wertz Unpublished results.

⁵ A. J. Streitwieser *J. Amer. Chem. Soc.* 74, 5288 (1952). This paper contains very similar calculations and further references.

Notes



The increase in resonance energy (Δ D.E.) on forming I by dissociation of a group from the position marked with a dot is given by the π -electron delocalization energy of I less that of II and that of III. Δ D.E. for I calculated in this way is 2.84β and Δ D.E. calculated for IV in a similar manner is 3.23β .^{*} For comparison the much less stable triphenylmethyl radical has Δ D.E. = 1.80β .⁶ Thus I and IV have predicted resonance energies greater than that of the triphenylmethyl radical by about one β (the carbon-carbon resonance integral) or more. An appropriate value for β is thought to be about 20 kcal/mole.⁶

The fact that IV is calculated to have the higher resonance energy while I actually appears to be somewhat more stable may be due to steric inhibition to coplanarity in IV.

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* Numerical calculations were performed on the Remington Rand "Univac" by the Numerical Analysis Laboratory of the University of Minnesota.

⁶ C. A. Coulson *Valence* p. 240. Clarendon Press Oxford (1953).

Relation between the "regular" and Kekulé structures for benzene

(Received 3 September 1957)

In *Chemistry and Industry* p. 1520 (1955), it was shown that Pauling's bond energies can be used to arrive at the conclusion that the distribution of energy about each carbon atom in benzene is symmetrical. This cannot, of course, be so in the Kekulé structure. However, it is remarkable that the resultant of two forces of magnitude 58.6 and 100 (corresponding to the Pauling bond energies of single and double carbon-carbon bonds respectively) acting at 120° (the angle between the carbon-carbon bonds in both the regular and Kekulé rings) has a magnitude of 87.2 i.e. very near to the 87.3 kcal assigned as the energy of the C-H bond. For equilibrium to be attained at each carbon, the C-H bond direction would have to form an angle of approximately 144° with that of the C=C bond of the ring.

It is possible, therefore, to picture the change of Kekulé to regular structure as involving shortening and lengthening of the single and double bonds respectively, accompanied by a change in the direction of the C-H bonds.

Another remarkable feature to be detected by the present approach is that the pair of values 58.6 and 100 are very near the possible limits permitted by the equation

$$P^2 + Q^2 - PQ = 87.2^2$$

If $P = 100$ and $Q = 58.6$, the equation is valid. For all values of P between 100 and 87.2 (when it becomes equal to Q) a corresponding value of Q can be calculated, but when P reaches or exceeds 100.6 no corresponding value for Q is possible. This suggests that distortion of the regular to the

Kekulé structure is the limit of possible distortion. It can hardly be assumed that the Pauling bond energy values have such a degree of accuracy that this conclusion is out of the question.

Thurlton, Norwich, Norfolk

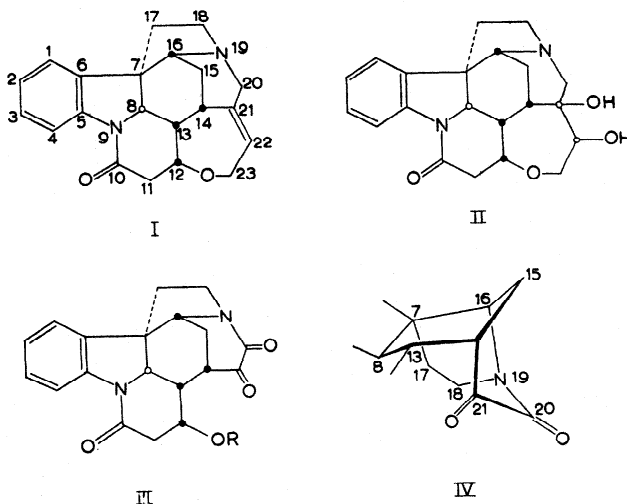
J. C. EARL

Stereochemical control of some reactions of strychnine

(Received 16 September 1957)

IN the elucidation of the structure of strychnine, Robinson's interpretation of an extended series of reactions carried out by Leuchs was of crucial importance.^{1,2} The mechanisms of these reactions have remained obscure, but may now be explained by taking account of the stereochemistry of strychnine and its products. The relative configurations at the asymmetric centres of strychnine have been shown from chemical³ and X-ray diffraction⁴ evidence to be as indicated in (I). Hydrogen atoms above the plane of the molecule (β) have been represented by closed circles; below (α), by open circles. Bonds coming above the plane of the molecule have been represented by solid lines; below, by broken lines. Recently, it has been shown⁵ that the absolute configuration of strychnine is the reverse of that indicated in (I).

A model of (I) shows the underside of the double bond to be turned in towards the centre of the molecule, and hence protected from attack.³ This may explain why chlorine⁶ and bromine,⁷ which generally add *trans*,⁸ leave it unaffected, and attack the aromatic ring. The only addition reactions of the double bond thus far noted, hydroxylation by permanganate⁹ and hydrogenation¹⁰ both involve



¹ R. Robinson *Proc. Roy. Soc. A* **130**, 431 (1931).

² R. Robinson *Progress in Organic Chemistry* (Edited by J. W. Cook) Vol. 1, p. 1. Butterworths, London (1952).

³ H. L. Holmes *The Alkaloids* (Edited by R. H. F. Manske and H. L. Holmes) Vol. II, p. 536. Academic Press, New York (1952).

⁴ J. H. Robertson and C. A. Beevers *Acta Cryst.* **4**, 270 (1957); C. Bokhoven, J. C. Schoone and J. M. Bijvoet *Ibid.* **4**, 275 (1957).

⁵ A. F. Peerdeman *Ibid.* **9**, 824 (1956).

⁶ H. Leuchs and K. Steinborn *Ber. Dtsch. Chem. Ges.* **71**, 1577 (1938).

⁷ H. Leuchs and P. Boll *Ibid.* **43**, 2362 (1910).

⁸ C. K. Ingold *Structure and Mechanism in Organic Chemistry* p. 658. Bell and Sons, London (1953).

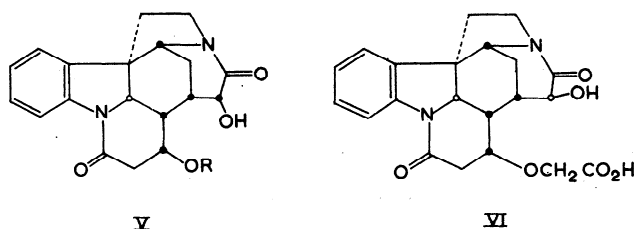
⁹ M. Kotake and T. Mitsuwa *Bull. Chem. Soc. Japan* **11**, 231 (1936); V. Prelog and A. Katheriner *Helv. Chim. Acta* **31**, 505 (1948).

¹⁰ A. Skita and H. H. Franck *Ber. Dtsch. Chem. Ges.* **44**, 2862 (1911); A. E. Oxford, W. H. Perkin and R. Robinson *J. Chem. Soc.* 2389 (1927).

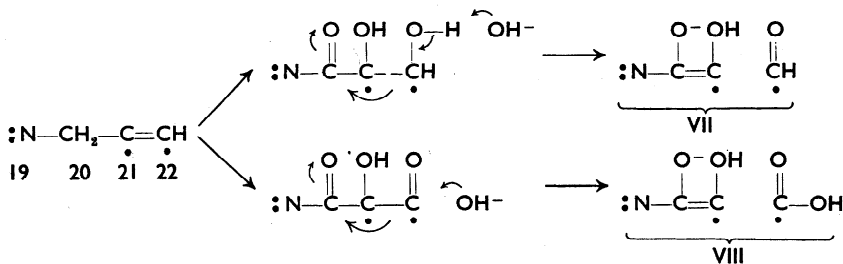
cis addition.¹¹ Hence it seems certain that dihydroxystrychnine from the former reaction has the configuration shown in (II).³

More prolonged oxidation with potassium permanganate affords strychninonic acid (III; R = CH₂CO₂H).¹² The newly formed δ -lactam ring is relatively unstable to hydrolysis,¹³ because the atoms C₁₆, C₁₈ and C₂₁ cannot all be in the same plane as the amide linkage¹⁴ (see perspective partial formula (IV)).

Reduction of the carbonyl group (C₂₁ = O) of strychninonic acid by either catalytic hydrogenation¹⁵ or sodium amalgam¹⁶ probably involves addition to the more accessible top-side of the molecule, so that strychninonic acid has the formula (V; R = CH₂CO₂H). The epimeric dihydrostrychninonic acid, formed in small yield with strychninonic acid in the permanganate oxidation,¹³ is accordingly formulated as (VI).



Holmes³ adduced as further evidence for the configuration at C₂₁ in dihydrostrychninonic acid the similar configuration in dihydroxystrychnine (II), which may be an intermediate. However, the configuration of any intermediate is probably irrelevant, since the formation of dihydrostrychninonic acid involves a hydrolysis of C₂₁-C₂₂ at some stage [C₂₁ gains both a hydroxyl group and a hydrogen atom, and so the change from strychnine is not an oxidation alone]. The only plausible mechanisms¹ for this hydrolysis are those shown leading to the enolic form of dihydrostrychninonic acid (VIII) or of an aldehydic precursor (VII). Either mechanism involves the formation of the enolate ion IX, in



which the asymmetry at C₂₁ is lost. The protonation of this enolate ion will, for stereoelectronic reasons,¹⁷ lead to the formation of a quasi-axial C₂₁-hydrogen bond, giving the configuration shown in (VI) (partial perspective formula (X)).

Models of strychninonic acid (V; R = CH₂CO₂H) and hydroxydihydrostrychninolone-A (V; R = H), set up with the Courtaulds' atomic models,¹⁸ show the α -oriented C₂₁ hydroxyl group to be pressing against the C₁₂ oxygen atom. In dihydrostrychninonic acid (VI) there is only minor steric compression of the C₁₂ oxygen atom from the α -oriented C₂₁ hydrogen atom; while in strychninonic acid (III; R = CH₂CO₂H) and hydroxydihydrostrychninolone-A (III; R = H) there is no interference

¹¹ L. Crombie *Quart. Rev. Chem. Soc., Lond.* **6**, 101 (1952).

¹² H. Leuchs *Ber. Dtsch. Chem. Ges.* **41**, 1711 (1908).

¹³ H. Leuchs and P. Reich *Ibid.* **43**, 2417 (1910); H. Leuchs and L. E. Weber *Ibid.* **42**, 3703 (1909).

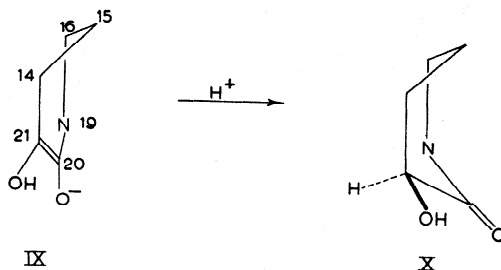
¹⁴ L. Pauling, R. B. Corey, and H. R. Branson *Proc. Nat. Acad. Sci., Wash.* **37**, 205 (1951).

¹⁵ V. Prelog and S. Szpilfogel *Helv. Chim. Acta* **28**, 1669 (1945).

¹⁶ H. Leuchs and W. Schneider *Ber. Dtsch. Chem. Ges.* **42**, 2494 (1909).

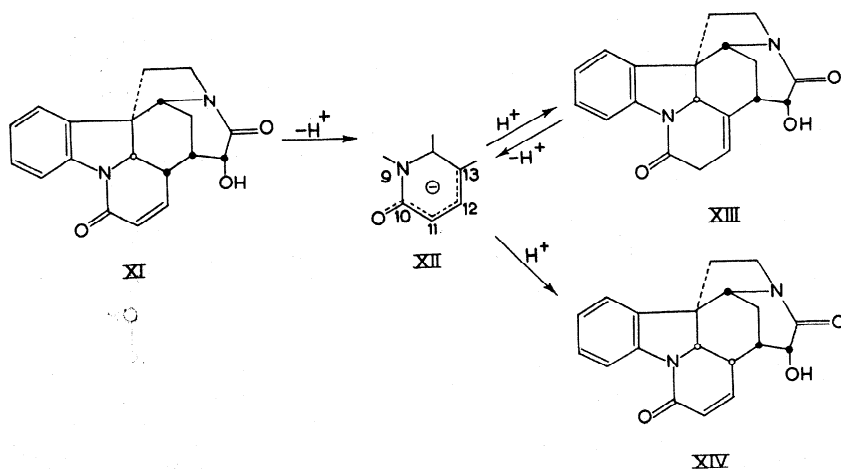
¹⁷ E. J. Corey and R. A. Sneath *J. Amer. Chem. Soc.* **78**, 6269 (1956).

¹⁸ G. S. Hartley and C. Robinson *Trans. Faraday Soc.* **48**, 847 (1952).



between the C_{12} oxygen atom and the C_{21} carbonyl oxygen. The different degrees of steric compression may explain the varying ease of elimination of the C_{12} oxygen function in forming an $\alpha\beta$ -unsaturated lactam¹⁹ [(V; R = $\text{CH}_2\text{CO}_2\text{H}$)¹⁶ > (V; R = H)²⁰ > (VI)²¹ > (III; R = $\text{CH}_2\text{CO}_2\text{H}$), (III; R = H)²⁰]. The especially easy elimination from strychninolic acid (V; R = $\text{CH}_2\text{CO}_2\text{H}$) to give strychninolone-A (XI) is probably facilitated by the inductive effect of the carbonyl group.

It has been suggested previously²² that strychninolic acid eliminates glycollic acid more readily than does dihydrostrychninonic acid because only in the former is hydrogen bonding between the C_{21} hydroxyl group and the outgoing C_{12} oxygen atom possible. Such an explanation does not explain why the same order of reactivities is found in the acid-catalysed elimination,²⁰ which must involve protonation of the C_{12} oxygen, and in which consequently hydrogen-bonding by the hydroxyl group cannot be significant.



When treated with bases, strychninolone-A (XI) isomerises to strychninolone-B (XIII);²¹ more drastic treatment results in further isomerisation to strychninolone-C (XIV),^{21,23} which differs from strychninolone-A only in configuration at C_{13} .²⁴ On models it can be seen that in strychninolone-C the chain of atoms N-C₁₂ has become more nearly coplanar with the benzene ring than it is in strychninolone-A. The increased resonance consequent on greater planarity would explain the greater thermodynamic stability of strychninolone-C, the lessened reactivity of its Δ^{11} double bond (e.g. to the addition of hydrazine²⁰), and the bathochromic shift in absorption (strychninolone-A, $\lambda_{\text{max}} = 282 \text{ m}\mu$; strychninolone-C, $\lambda_{\text{max}} = 297 \text{ m}\mu$).³

¹⁹ Cf. J. Kenner *Chem. & Ind. (Rev.)* 727 (1955).

²⁰ J. T. Edwards and R. Robinson *Tetrahedron* 1, 28 (1957).

²¹ H. Leuchs and G. Schwaebel *Ber. Dtsch. Chem. Ges.* 47, 1552 (1914).

²² R. B. Woodward Quoted in reference 3.

²³ H. Leuchs and W. Bendixsohn *Ber. Dtsch. Chem. Ges.* 52, 1443 (1919).

²⁴ V. Prelog, S. Szpilfogel and J. Battagay *Helv. Chim. Acta* 30, 366 (1947).

The formation of strychninolone-B before the more thermodynamically stable strychninolone-C is an example of kinetic control, the addition of a proton to the common intermediate anion(X) taking place more rapidly at the centre of the mesomeric system.²⁵

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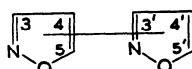
* Present address: Chemistry Dept., McGill University, Montreal, Canada.

²⁵ G. A. R. Kon and E. A. Speight *J. Chem. Soc.* 2727 (1926); C. K. Ingold, E. de Salas and C. L. Wilson *Ibid.* 1328 (1936); A. J. Birch *Ibid.* 1551 (1950); R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore *J. Amer. Chem. Soc.* 74, 4223 (1952).

Synthesis of 5:5'-bi-isoxazole

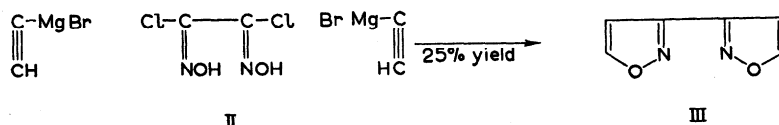
(Received 8 November 1957)

ALTHOUGH a number of substituted bi-isoxazole derivatives have been reported in the literature, none of the six fundamental members (I) which are theoretically possible was known until 1957. Only



I

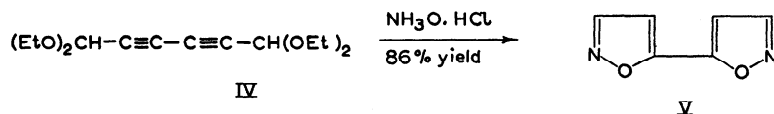
quite recently¹ we succeeded in synthesising 3:3'-bi-isoxazole (III), which is formed when ethynylmagnesium bromide acts on dichloroglyoxime (II), according to scheme:



II

III

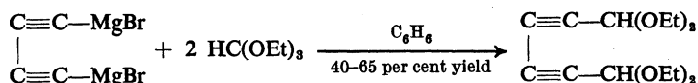
In the performance of experiments aimed to the preparation of the other possible isomers, we have now synthesised 5:5'-biisoxazole (V), which is obtained in excellent yield on treatment of hexadiindial tetraethylacetal (IV) with hydroxylamine hydrochloride:



IV

V

Grard² has reported the preparation of (IV) by oxidation of propargylic aldehyde acetal. Since the preparation of the latter is difficult and the yield of (IV) poor, a new synthesis of (IV) has been achieved by condensation of diacetylene magnesium bromide³ with ethyl orthoformate:



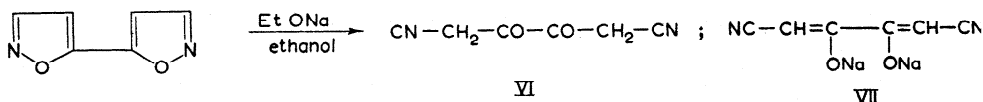
5:5'-Bi-isoxazole (V) is a crystalline solid m.p. 116–117.5° (the 3:3'-isomer melts at 73–73.5°) of faint pleasant odour. It is volatile in steam, and soluble in most organic solvents. Its chemical

¹ A. Quilco, G. Gaudiano and A. Ricca *Gazz. Chim. Ital.* 87, 638 (1957).

² G. Grard *C. R. Acad. Sci., Paris* 189, 925 (1929).

³ F. Bohlman *Chem. Ber.* 84, 553 (1951).

behaviour corresponds to that of simple *isoxazoles* with a free 3-position: accordingly, it is readily isomerized by alkaline alkoxides solutions giving the sodium salt (VII) of 3:4-diketoadipic nitrile (VI).



Whereas the sodium salt, which probably possesses structure (VII), is very stable in alkaline solutions, the free diketonitrile (VI) appears to be extremely labile. Aqueous solutions of (VII) turn rapidly to orange-red and then to brown when treated at ordinary temperature with dilute acids, owing to the formation of condensation products.

The study of the chemical and spectrochemical behaviour of the two symmetrical bi-*isoxazoles* is in progress, and will be reported later.

EXPERIMENTAL

Hexadiindial tetraethylacetal (IV). Diacetylene (4.5 g) dissolved in anhydrous ether (15 ml) was slowly introduced, under continual stirring, into a cooled solution of ethylmagnesium bromide prepared from 6 g of magnesium. After the addition of the diacetylene, the reaction mixture was stirred for at least 1 hr at room temperature, when most of the solvent was distilled. Towards the end, the temperature of the bath was allowed to rise to 60°, and maintained for 5–10 min. Ethyl orthoformate (48 g) dissolved in 50 ml of dry benzene was then introduced over a period of 10 min under continual cooling and stirring. The reaction was completed by refluxing at 70–80° for 1½ hr. The brown semi-solid reaction mixture was poured into a solution of 20–30 g of ammonium acetate in 500 ml of ice-water. The benzene layer was separated and the aqueous layer extracted with ether. The combined organic extracts, dried over K₂CO₃, gave, after removal of the solvent and the unchanged orthoformate by distillation at ordinary pressure, 10–15 g of a liquid b.p. 142°/2 mm, with n_D^{25} 1.4686. Yield 40–65 per cent (Found: C, 66.09; H, 8.69. Calc. for C₁₄H₂₂O₄: C, 66.1; H, 8.7 per cent). According to Grard, hexadiindial tetraethylacetal has b.p. 140–141°/3 mm and n_D^{25} 1.4638.

5:5'-Bi-isoxazole (V). To a solution of 3.4 g of (IV) in 34 ml of ethanol, 4.3 g of NH₃O.HCl dissolved in 7 ml of water were added. After ½ hr refluxing on the water-bath most of the alcohol was removed *in vacuo* at ordinary temperature and the residue distilled in steam. The aqueous distillate (600–700 ml), which contains the bi-*isoxazole* partly dissolved and partly in solid crystalline form, was saturated with ammonium sulphate and then extracted with ether. The extract, dried over Na₂SO₄, gave after removal of the solvent 1.6 g of nearly pure 5:5'-bi-*isoxazole*. Yield 86 per cent. Recrystallised from ethanol it forms beautiful needles m.p. 116–117.5° (Found: N, 20.6. Calc. for C₆H₄O₂N₂: N, 20.5 per cent).

5:5'-Bi-*isoxazole* has a characteristic not unpleasant odour, similar to that of the 3:3'-isomer. It is readily soluble in warm alcohol, benzene and chloroform, and can be recrystallised from boiling water in which it is slightly soluble at ordinary temperature.

Isomerisation to 3:4-diketoadipic nitrile (VI). 5:5'-Bi-*isoxazole* (0.5 g), dissolved in 8 ml of warm anhydrous ethanol, was introduced into the cooled Na-ethoxide solution prepared from 0.5 g of Na in 15 ml of ethanol. A gelatinous precipitate of diketoadipic nitrile sodium salt (VII) separated immediately with evolution of heat and on keeping, and more rapidly on gentle heating, became crystalline. The filtered solid was washed with absolute alcohol and dried *in vacuo* over P₂O₅. Yield 0.65 g (theoretical for the anhydrous disodium salt 0.66 g).

The salt was purified by dissolving in 3–4 ml of water and subsequent precipitation with 80 ml of anhydrous ethanol. It forms crops of small needles, readily soluble in water; the solution giving an intense dark red enolic reaction with FeCl₃. The analysis indicates that the salt contains two molecules of water (Found: N, 13.0; Na, 22.1. Calc. for C₆H₂O₂N₂Na₂·2H₂O: N, 12.9; Na, 21.9 per cent). One molecule is easily eliminated by heating at 110° *in vacuo* over P₂O₅ (loss of weight: found 8.9, calc. for Na₂-salt, 2H₂O → Na₂-salt, H₂O 8.3 per cent). The analysis of the partially dehydrated salt: (Found: N, 14.4; Na, 23.2. Calc. for C₆H₂O₂N₂Na₂, H₂O: N, 14.1; Na, 23.2 per cent).