Triazoles. Part IV. Ultra-violet Absorption Spectra of Some 1 : 2 : 4-Triazoles.*

By M. R. Atkinson, E. A. Parkes, and J. B. Polya.

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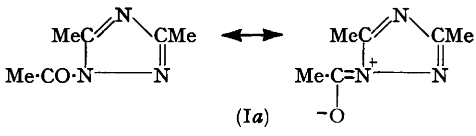
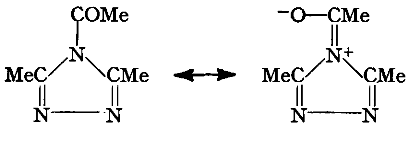
1 : 2 : 4-Triazole and its alkyl derivatives do not have absorption bands above 215 mμ but acetyl-3 : 5-dimethyl-1 : 2 : 4-triazole has a *K*-band at 222 mμ. Substitution in 1 : 2 : 4-triazole of phenyl results in increasing bathochromic shifts in the order 4-Ph < 1-Ph < 3-Ph. The introduction of methyl groups into phenyltriazoles causes hypsochromic and hypochromic shifts when the substitution is vicinal, and bathochromic and hyperchromic shifts otherwise. The same trend of shifts is observed for di- and tri-phenyltriazoles except that the effects of isolated phenyl chromophores partially compensate for the hypsochromic and hypochromic shifts due to vicinal substitution. The similarity of the spectra of 3-hydroxy-1-phenyl-1 : 2 : 4-triazole and 2-methyl-3-oxo-1-phenyl-1 : 2 : 4-triazoline suggests the triazolone structure for the former.

The Einhorn–Brunner reaction between phenylhydrazine and *N*-acetylcinnamamide affords 3-methyl-1-phenyl-5-styryl-1 : 2 : 4-triazole, the structure of which follows from its degradation to 3-methyl-1-phenyl-1 : 2 : 4-triazole.

Ultra-violet absorption spectra have been determined for a number of triazoles which have been prepared in earlier work (Parts I, II, and III, *J.*, 1952, 3418; 1954, 141, 3319) by new syntheses or by the methods of other authors. The Table lists the triazoles examined in the order of their occurrence in the Discussion, together with spectrographic data, m. p.s or b. p.s, and references to the preparative methods adopted by us. The measurements were carried out in spectrographic ethanol, except for acetyl-3 : 5-dimethyl-1 : 2 : 4-triazole (I) which was examined in hexane solution owing to its sensitivity to alcoholysis. The spectra of triazoles in aqueous and alcoholic solution are practically identical, as illustrated by the case of 3-phenyl-1 : 2 : 4-triazole (II). Acidic triazoles have been examined also as anions in the presence of 100—1000 molar excess of alcoholic potassium hydroxide. The cations of triazoles (in the presence of a similar molar excess of alcoholic hydrogen chloride) and the neutral substances have identical spectra; again the case of


(I*a*)


(I*b*)

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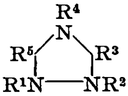
* Part III, *J.*, 1954, 3319.

(II) may serve as an illustration. All the triazoles examined obey Beer's law in concentrations not exceeding 2×10^{-4}M.

1 : 2 : 4-Triazole and its alkyl derivatives like 3 : 5-dimethyl-, 1-ethyl-3 : 5-dimethyl-, 4-ethyl-3 : 5-dimethyl-, and 1 : 3 : 5-trimethyl-1 : 2 : 4-triazoles have no absorption bands above 215 mμ. Attempts to shift possible maxima just below 215 mμ into the range of

1 : 2 : 4-*Triazoles*



No.	R^1	R^2	R^3	R^4	R^5	M. p.*	Neutral		Anion	
							$\lambda_{max.}$ (mμ)	$\varepsilon \times 10^{-3}$	$\lambda_{max.}$ (mμ)	$\varepsilon \times 10^{-3}$
I	Ac	—	Me	—	Me	90·5°	222	6·9	—	—
II	(H)	—	Ph	(H)	H	119	241·5	14·1	257	13·5
III	Ph	—	H	—	H	47	239	10·9	—	—
IV	—	—	H	Ph	H	120	224·5	10·9	—	—
V	Ph	—	Me	—	H	89·5	244	15·4	—	—
VI	Ph	—	H	—	Me	—	224·5	7·6	—	—
VII	Ph	—	Me	—	Me	47·5	230	9·0	—	—
VIII	Ph	—	Et	—	Me	—	230	9·4	—	—
IX	Ph	—	Me	—	Et	—	230	10·6	—	—
X	Me	—	Ph	—	H	23	243	15·1	—	—
XI	Me	—	H	—	Ph	59	235	11·9	—	—
XII	—	—	Ph	Me	H	117	270	0·55	—	—
XIII	—	—	Me	Ph	H	67	272; 267	0·4	—	—
XIV	—	—	Me	Ph	Me	236	259	0·3	—	—
XV	Me	—	Ph	—	Me	117	245	15·3	—	—
XVI	Me	—	Me	—	Ph	72	239	12·7	—	—
XVII	Ph	—	Me	—	Ph	81	252	10·5	—	—
XVIII	Ph	—	Ph	—	Me	93	253	22·1	—	—
XIX	Ph	—	Ph	—	H	83	265	23·4	—	—
XX	Ph	—	H	—	Ph	90·5	248	13·6	—	—
XXI	—	—	Ph	Ph	H	142·5	235·5	14·7	—	—
XXII	—	—	Me	Me	Ph	137	235·5	11·5	—	—
XXIII	—	—	Ph	Ph	Me	163	232	14·7	—	—
XXIV	(H)	—	Ph	(H)	Ph	191	255	22·7	276	21·9
							234	21·8		
XXV	—	—	Ph	Ph	Ph	298—300	256·5	8·0	—	—
XXVI	(H)	—	Me	(H)	Ph	166	244	15·6	261	15·1
XXVII	Me	—	Ph	—	Ph	85	247	19·4	—	—
XXVIII	—	—	Ph	Me	Ph	242	251	24·4	—	—
XXIX	Ph	—	Ph	—	Ph	120	244	29·2	—	—
XXX	Ph	—	Me	—	PhCH:CH	74	300	52·3	—	—
XXXI	Ph	—	OH	—	H	274	282	9·1	284	11·5
XXXII	Ph	Me	:O	—	—	296—297 †	280	7·4	—	—
XXXIII	Ph	—	OH	—	Ph	288—290	294	5·7	302	6·7
							226	15·6	230	15·5
XXXIV	Ph	—	Me	—	OH	167	249	16·8	261	14·6
XXXV	H	H	OH	H	Ph	321—322	264	10·9	273	6·7
									223·5	13·8
XXXVI	Me	—	Ph	—	OH	219	269·5	12·8	267	8·7
									223·5	13·8

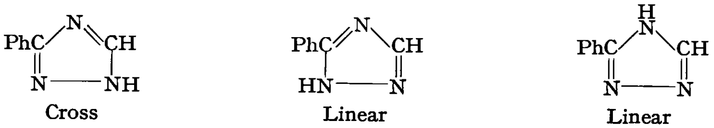
* B. p.: (VI) 264°/752, (VIII) 278°/755, (IX) 281—282°/760 mm. † With decomp.

(H) denotes acidic hydrogen. (I) in hexane, acetyl possibly at R^4. (III), neutral in water; $\lambda_{max.}$ 239·5 mμ, ε 14,100; cation $\lambda_{max.}$ 241·5 mμ, ε 14,400. Possibly fine structure in spectra of (XII), (XIII), and (XIV).

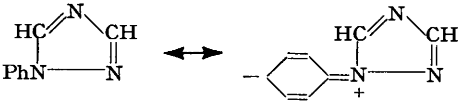
Preparations: (III), (VIII), (IX), (XVII), (XVIII), (XX), see Part I; (I), (XXVII), (XXVIII), see Part II; (II), (X), (XI), (XV), (XVI), (XXIV), (XXVI), (XXXIV), (XXXVI), see Part III; (XXX), (XXXII), see p. 4264; (IV), Pellizzari and Massa, *Atti R. Accad. Lincei*, 1901, **10**, [I], 363; (V) Bamberger and Frei, *Ber.*, 1902, **35**, 746; (VI), Bamberger and de Gruyter, *Ber.*, 1893, **26**, 2385; Bamberger, *Ber.*, 1911, **44**, 3564; (VII), Komzak and Polya, *J. Appl. Chem.*, 1952, **2**, 666; (XII), Young and Oates, *J.*, 1901, **79**, 659; (VI), (XIII), Pellizzari, *Gazzetta*, 1911, **41**, [II], 20; (XIV), (XXV), Pellizzari and Alciatore, *Atti R. Accad. Lincei*, 1901, **10**, [I], 444; (XIX), Atkinson and Polya, *J. Amer. Chem. Soc.*, 1953, **75**, 1471; (XXI), Marckwald and Bott, *Ber.*, 1896, **29**, 2914; (XXII), (XXIII), Scheuing and Walach, G.P. 541,700; *Chem. Abs.*, 1932, **26**, 2469; (XXIII), Heller, Köhler, Gottfried, Arnold, and Herrmann, *J. pr. Chem.*, 1928, **120**, 49; (XXIX), Engelhardt, *ibid.*, 1896, **54**, 153; (XXXI), Widmann, *Ber.*, 1893, **26**, 2612; (XXXIII), Young, *J.*, 1895, **67**, 1063; (XXXV), Young and Witham, *J.*, 1900, **77**, 224.

the instrument by anion- or cation-formation failed. The *K*-band of 1- or 4-acetyl-3 : 5-dimethyl-1 : 2 : 4-triazole (I) may be due to extended conjugation through the partial ionic character of structures such as (I*a* or *b*). It will be seen below that substituents on $N_{(1)}$ have stronger bathochromic effects than those on $N_{(4)}$. This suggests (I*a*) as the more likely structure, in agreement with other considerations (Part II).

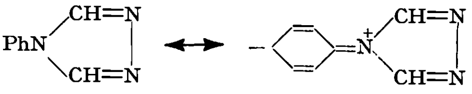
The intense single bands of the isomeric phenyltriazoles (II, III, and IV) may be regarded as *K*-bands due to the conjugation of benzene and traizole chromophores and compared with that of diphenyl (Gillam and Hey, *J.*, 1939, 1170). The higher intensity and $\lambda_{max.}$ of 3-phenyltriazole (II) is readily explained by its more extended conjugation in the ground state, while conjugation of the phenyl and triazolyl moieties in 1-phenyl-1 : 2 : 4-triazole (III) and 4-phenyl-1 : 2 : 4-triazole (IV) is possible in the ionic forms only. The difference between the spectra of (III) and (IV) could be derived from the theory of linear and cross conjugation which has been used in the discussion of some related problems in the tetrazole series (Elpern and Nachod, *J. Amer. Chem. Soc.*, 1950, **72**, 3379). More appropriate might be the empirical comparison of (III) and (IV) with phenylhydrazine and aniline respectively, the high-intensity bands of which are in the same relation (Grammaticakis, *Bull. Soc. chim.*, 1951, **18**, 965).



(II)



(III)



(IV)

The substitution of 1-phenyl-1 : 2 : 4-triazole by alkyl groups results in small bathochromic-hyperchromic or hypsochromic-hypochromic shifts, as shown by 3- (V) and 5-methyl-1-phenyl-1 : 2 : 4-triazole (VI) (Fig. 1). The practically identical spectra of 3 : 5-dimethyl- (VII), 3-ethyl-5-methyl- (VIII), and 5-ethyl-3-methyl-1-phenyl-1 : 2 : 4-triazole (IX) show that the effects of ethyl and methyl groups are practically the same, and on comparison with those of (III) that the hypsochromic-hypochromic effects due to 5-substitution outweigh the bathochromic-hyperchromic effects due to 3-substitution. The same effects are noted when the spectra of (II), 1-methyl-3-phenyl- (X), 1-methyl-5-phenyl- (XI), and 4-methyl-3-phenyl-1 : 2 : 4-triazole (XII) are compared. In the last case vicinal substitution results in the complete deconjugation of the phenyl and the triazolyl chromophore on the evidence of a single blurred band, the location, intensity, and possible fine structure of which permit its identification as a *B*-band. In a similar way total deconjugation is observed in derivatives of (IV) such as 3-methyl-4-phenyl- (XIII) (Fig. 2) and 3 : 5-dimethyl-4-phenyl-1 : 2 : 4-triazole (XIV).

Similar deconjugating (uncoupling) effects by vicinal substituents have been observed by other authors, notably for substituted benzotriazoles (Krollpfeiffer, Pötz, and Rosenberg, *Ber.*, 1938, **71**, 596; Ramart-Lucas, Hoch, and Grumez, *Bull. Soc. chim.*, 1949, **16**, 447) and methylphenyl-1 : 2 : 3-triazoles (Ramart-Lucas *et al.*, *loc. cit.*). In the former case the effect of vicinal substitution is restricted to a slight hypochromic effect but in the latter there are also significant hypsochromic effects. In comparison with (II), 1 : 5-dimethyl-3-phenyl-1 : 2 : 4-triazole (XV) shows a slight bathochromic-hyperchromic effect and 1 : 3-dimethyl-5-phenyl-1 : 2 : 4-triazole (XVI) a slight hypsochromic and considerable hypochromic effect. This suggests that the effect of two vicinal methyl groups is less than that of vicinal methyl and phenyl groups, although another interpretation might be that the deformation due to the steric interference of two vicinal methyl groups has less effect on the coupling of phenyl and triazolyl chromophores than the deflection of the phenyl group by a vicinal methyl group. However, it is tempting to consider the first explanation in the light of the discussion of cases where steric interference leads to a reduction of the extinction coefficient without a significant shift of the band maximum to shorter wave-length, which have been interpreted as " restriction of the transition to vibrational states allowing of a high degree of uniplanarity in the excited state " (Braude, Sondheimer, and Forbes, *Nature*, 1954, **173**, 117). In order to test this theory the dipole moments of triazoles will have to be determined. Possibly the best pair of substances in the present series from this point of view would be 3-methyl-1 : 5-diphenyl- (XVII) and 5-methyl-1 : 3-diphenyl-1 : 2 : 4-triazole (XVIII) which absorb at almost the same wave-length though the extinction coefficient of the former (10,500) is much lower than that of the latter (22,100).

The absorption spectra of diphenyl- and triphenyl-triazoles are in agreement with the observations on those of methylphenyl- and dimethylphenyl-triazoles but present some additional features. Thus phenyl groups that are uncoupled from the triazolyl group act as isolated chromophores and contribute to the intensity of the bands. Thus hypochromic effects are partially masked, and small bathochromic effects may be observed in comparison with the parent monophenyltriazoles. These overlapping effects are illustrated by 1 : 3- (XIX) and 1 : 5-diphenyl-1 : 2 : 4-triazole (XX) (Fig. 1). The vicinal deconjugating effect is not observed with 3 : 4-diphenyl-1 : 2 : 4-triazole (XXI) to the expected extent (Fig. 2). The same applies to 3 : 4-dimethyl-5-phenyl- (XXII) and 3-methyl-4 : 5-diphenyl-1 : 2 : 4-triazole (XXIII). No explanation can be given at present but it appears that vicinal substitution has less effect on *C*-phenyl than on *N*-phenyl. 3 : 5-Diphenyl- (XXIV) and 3 : 4 : 5-triphenyl-1 : 2 : 4-triazole (XXV) (Fig. 2) absorb at the same wave-length but the extinction coefficient of the latter is very low; this may be another example of the effect discussed by Braude, Sondheimer, and Forbes.

FIG. 1. *Light absorption of* 1-*phenyl*-1 : 2 : 4-*triazole and derivatives.*

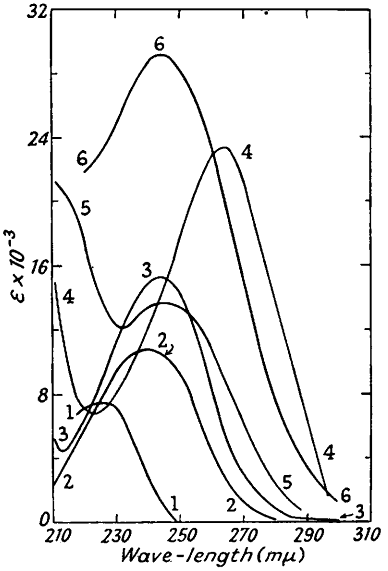


FIG. 2. *Light absorption of* 4-*phenyl*-1 : 2 : 4-*triazole and derivatives.*

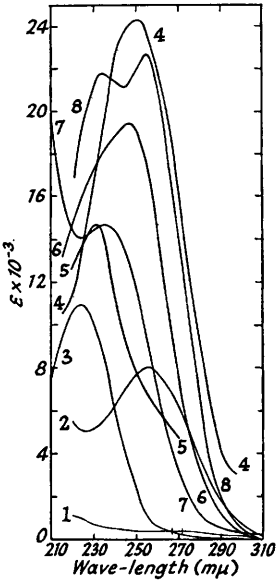


FIG. 1. 1, 5-Methyl-1-phenyl-. 2, 1-Phenyl-. 3, 3-Methyl-1-phenyl-. 4, 1 : 3-Diphenyl-. 5, 1 : 5-Diphenyl-. 6, 1 : 3 : 5-Triphenyl-.

FIG. 2. 1, 3-Methyl-4-phenyl-1 : 2 : 4-triazole, location of shallow bands indicated by transverse line. 2, 3 : 4 : 5-Triphenyl-. 3, 4-Phenyl-. 4, 4-Methyl-3 : 5-diphenyl-. 5, 3-Methyl-4 : 5-diphenyl-. 6, 1-Methyl-3 : 5-diphenyl-. 7, 3 : 4-Diphenyl-. 8, 3 : 5-Diphenyl-.

The spectra of 3-phenyl- (II) and 3-methyl-5-phenyl-1 : 2 : 4-triazole (XXVI) are similar apart from the slight bathochromic-hyperchromic effect of the non-vicinal methyl group in the latter compound. The spectra of each of these triazoles closely resemble only one of their respective *N*-methyl derivatives: the spectra of (II) and 1-methyl-3-phenyl-1 : 2 : 4-triazole (X), and those of (XXVI) and 1 : 5-dimethyl-3-phenyl-1 : 2 : 4-triazole (XV), respectively, are practically identical (Fig. 3). As the steric and electronic effects of *N*-methyl groups cannot be assessed accurately, these data do not permit a definite assignment of the mobile hydrogen in the acidic triazoles (II) and (XXVI), although assignment to the hydrazinic nitrogen distant from the phenyl group appears more probable than the two other possibilities, at least in the case of (II). This would favour the cross-conjugated structure rather than the linear conjugated forms.

The spectrum of 3 : 5-diphenyl-1 : 2 : 4-triazole (XXIV) (Fig. 2) has two maxima of approximately equal intensity, which suggests the presence of the tautomeric 1*H*-1 : 2 : 4- and 4*H*-1 : 2 : 4-triazole structures in equilibrium. The *N*-methyl derivative corresponding to the former, 1-methyl-3 : 5-diphenyl-1 : 2 : 4-triazole (XXVII), has a single maximum, which might be considered to have arisen by a hypsochromic shift of the band of (XXIV) at the longer wave-length since in this case the two phenyl groups cannot conjugate through the triazole ring. On the other hand, the single band of 4-methyl-3 : 5-diphenyl-1 : 2 : 4-triazole (XXVIII) might be thought to have undergone a bathochromic shift from the band of (XXIV) at the shorter wave-length, as in this case the structure which permits the conjugation of the two phenyl groups through the triazole ring is stabilised. For the reason stated before, this does not prove, but makes probable, that the 234-mμ band of (XXIV) corresponds to the 4*H*-1 : 2 : 4-, and the 255 mμ band to the 1*H*-1 : 2 : 4-structure. The spectrum of 1 : 3 : 5-triphenyl-1 : 2 : 4-triazole (XXIX) is determined by the following effects : lack of conjugation through the ring between 3- and 5-phenyl groups; deconjugation through the steric interaction of 1- and 3-phenyl groups; summation of the intensities due to isolated phenyl groups. The overall effect is a hypsochromic-hyperchromic shift in comparison with the 1-substituted diphenyltriazoles (Fig. 1). A similar effect is observed on comparing the spectra of *m*- and *p*-terphenyl (Gillam and Hey, *loc. cit.*).

FIG. 3. *Light absorption of* 3-*phenyl*-1 : 2 : 4-*triazole and derivatives.*

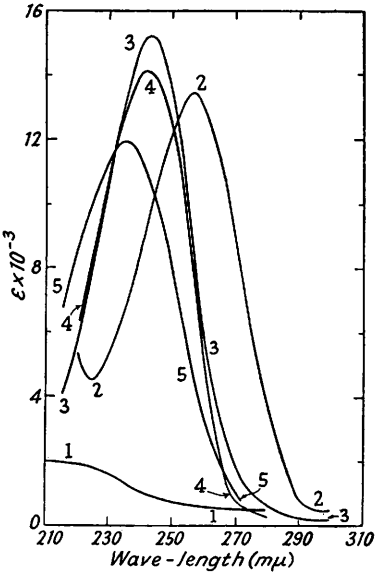


FIG. 4. *Light absorption of* 3-*hydroxy*-1-*phenyl*-1 : 2 : 4-*triazole and derivatives.*

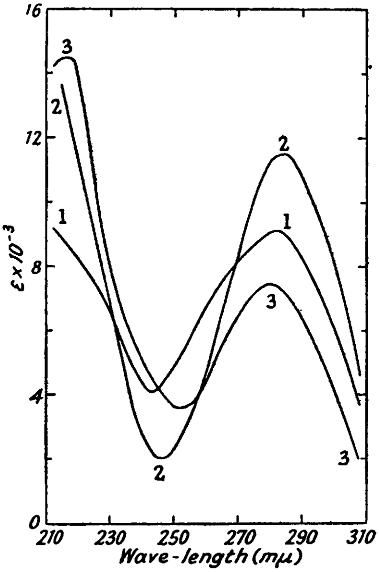
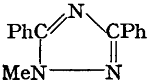
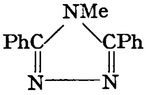


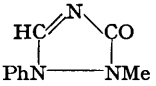
FIG. 3. 1, 4-Methyl-3-phenyl-. 2, Anion of 3-phenyl-. 3, 1-Methyl-3-phenyl-. 4, 3-Phenyl-. 5, 1-Methyl-5-phenyl-.

FIG. 4. 1, 3-Hydroxy-1-phenyl-1 : 2 : 4-triazole. 2, Anion of 3-hydroxy-1-phenyl-1 : 2 : 4-triazole. 3, 2-Methyl-3-oxo-1-phenyl-1 : 2 : 4-triazoline.

Some caution is necessary in predicting deconjugating effects from vicinal substitution alone. Thus 3-methyl-1-phenyl-5-styryl-1 : 2 : 4-triazole (XXX) absorbs at a considerably longer wave-length than any of the methyldiphenyltriazoles and has the characteristic high intensity of absorption displayed by many styryl compounds. The steric deconjugating effect is lessened by the distance of the bulky phenyl ring from the triazole nucleus and the effect of an increased order of conjugation predominates.


(XXVII)

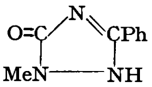

(XXVIII)

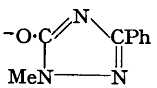

(XXXII)

The interpretation of the spectra of hydroxytriazoles is complicated by the possibility of tautomerism with triazolones. 3-Hydroxy-1-phenyl-1 : 2 : 4-triazole (XXXI) is converted by methyl sulphate into a methyl derivative which contains no methoxyl group and must be formulated as 2-methyl-3-oxo-1-phenyl-1 : 2 : 4-triazoline (XXXII). The maxima of the bands of (XXXII) and (XXXI) and the anion of the latter occur at practically the same wave-length (Fig. 4); this suggests a triazolone structure for (XXX). The introduction of phenyl into (XXXI) would be expected to lead to steric deconjugation but the spectrum of 3-hydroxy-1 : 5-diphenyl-1 : 2 : 4-triazole (XXXIII) undergoes a bathochromic-hypochromic shift in comparison with (XXXI). This might be explained by assuming a triazolone structure for (XXXIII) in which the 5-phenyl group may conjugate with the carbonyl-oxygen atom. The appearance of a second, high-intensity band at 226 mμ may account for the effect of the isolated 1-phenyl group. The spectrum of 5-hydroxy-3-methyl-1-phenyl-1 : 2 : 4-triazole (XXXIV) in comparison with that of 3-methyl-1-phenyl-1 : 2 : 4-triazole (V) displays a small bathochromic-hyperchromic shift, which cannot be explained on the principles applicable to the other triazoles in the present series.

On comparison of the spectra of 3-hydroxy-5-phenyl-1 : 2 : 4-triazole (XXV) with those of the related 3 : 5-substituted methylphenyl- and diphenyl-triazoles (XXV, XXIV) bathochromic-hypochromic shifts are observed. These, in conjunction with the case of (XXXIV), may be regarded as evidence for the auxochromic effect of oxygen in hydroxytriazoles or triazolones. 5-Hydroxy-1-methyl-3-phenyl-1 : 2 : 4-triazole (XXXVI) in comparison with (XXXV) displays a bathochromic-hyperchromic shift. In this case the absence of the steric deconjugating effect might be explained by considering that methylation stabilizes the structure (XXXVI*a*) which affords the best conjugated structure.

(XXXVI*a*)

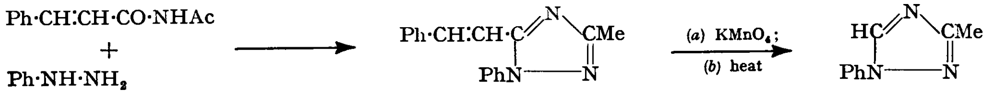




(XXXVI*b*)

The anions of the acidic triazoles absorb at longer wave-lengths than the neutral substances except in the case of (XXXVI), the anion (XXXVI*b*) of which would accommodate the negative charge on the oxygen rather than on the less electronegative nitrogen and thus lead to a less effectively conjugated form.

3-Methyl-1-phenyl-5-styryl-1 : 2 : 4-triazole (XXX) has been prepared by an Einhorn–Brunner reaction between *N*-acetylcinnamamide (Rodionov and Kiseleva, *J. Gen. Chem., U.S.S.R.*, 1948, **18**, 1912; Thompson, *J. Amer. Chem. Soc.*, 1951, **73**, 5841) and phenylhydrazine hydrochloride. The first of these reactants has been obtained by the direct



(XXX) (V)

acylation of cinnamamide with acetic anhydride in the presence of a catalytic amount of acetyl chloride. Oxidation and subsequent decarboxylation to 3-methyl-1-phenyl-1 : 2 : 4-triazole (V) (Andreocci, *Atti R. Accad. Lincei*, 1890, **4**, [II], 212) proves the structure of

(XXX) and provides another example in support of the rule previously suggested for the orientation of substituents in products of unsymmetrical Einhorn–Brunner reactions.

Triazoles are often contaminated by varying amounts of anilides which are difficult to remove by crystallization or sublimation In such cases the product is refluxed with dilute mineral acid for 4—12 hours. After filtering and cooling, diazotization followed by boiling and addition of alkali permits the extraction of pure triazoles with organic solvents.

EXPERIMENTAL

M. p.s are corrected.

Ultra-violet absorption spectra were measured between 210 and 350 mμ with a Unicam spectrophotometer; 10-mm. quartz cells were used. The concentrations ranged from 5×10^{-5} to 5×10^{-4}M in most cases, and 10^{-3} to 2×10^{-2}M in the case of alkyltriazoles.

For the characteristics and preparation of the known compounds see the Table.

N-*Acetylcinnamamide*.—Cinnamamide (2·6 g.), acetic anhydride (2·0 g.), and acetyl chloride (0·1 c.c.) were boiled under reflux for 0·5 hr. Volatile materials were removed by distillation up to 60°/25 mm. Recrystallization of the residual oil from chloroform gave *N*-acetylcinnamamide (1·4 g., 44%), colourless rhombic plates, m. p. 127° (Rodionov and Kiseleva give 122—124°, Thompson 131—132°) (Found: C, 69·9; H, 5·8; N, 7·6. Calc. for $C_{11}H_{11}O_2N$: C, 69·8; H, 5·9; N, 7·4%).

3-*Methyl*-1-*phenyl*-5-*styryl*-1 : 2 : 4-*triazole*.—*N*-Acetylcinnamamide (13·9 g.) and phenylhydrazine hydrochloride (10·6 g.) were heated at 140—150° for 4 hr. The product was neutralized with aqueous sodium carbonate (10%) and extracted with chloroform (3 × 150 c.c.). The extract was dried (Na_2SO_4) and evaporated. The residue was boiled with potassium hydroxide (15 g.) in 90% ethanol (100 c.c.) for 12 hr. The solution was evaporated to 150 c.c. after addition of water (150 c.c.). The resultant aqueous solution was extracted with ether, and the ether extract washed with aqueous sodium carbonate, dried, and evaporated. The residue was treated with Fehling's solution (100 c.c.) at 100°. Further ether-extraction (200 c.c.) and evaporation of the ether left a crude material (9·8 g.), m. p. 68—72°. Attempted distillation at 2 mm. caused partial decomposition. The remainder of the material was treated with picric acid in ethanol. On recrystallization of the precipitate from 80% ethanol 3-*methyl*-1-*phenyl*-5-*styryl*-1 : 2 : 4-*triazole picrate* was obtained as monoclinic crystals, m. p. 172° (Found: C, 56·9; H, 3·8. $C_{23}H_{18}O_7N_6$ requires C, 56·3; H, 3·7%). The picrate was decomposed by filtration of its chloroform solution through a column of alumina. Evaporation of the eluate left 3-*methyl*-1-*phenyl*-5-*styryl*-1 : 2 : 4-*triazole*, m. p. 72—74°, which sublimed at 145°/0·1 mm. as colourless prisms, m. p. 74° (Found: C, 78·5; H, 5·7; N, 16·4. $C_{17}H_{15}N_3$ requires C, 78·1; H, 5·8; N, 16·1%). The picrate has an unstable lower-melting form of m. p. 154°.

Other Triazoles.—The above picrate (1 g.) was crushed with 4N-sulphuric acid (10 c.c.), and the whole was filtered and extracted with ether (50 c.c.). The acid solution was treated with water (50 c.c.) and potassium permanganate (5 g.). After 10 minutes' stirring at room temperature the mixture was treated with ethanol (50 c.c.), and the residue removed by filtration and washed with ethanol (10 c.c.). The combined washings and filtrate were concentrated to 30 c.c. and again filtered. The acid solution was neutralized with aqueous sodium hydroxide and evaporated to dryness. The residue was heated 200° for 0·5 hr. cooled, and extracted with ether (50 c.c.). Evaporation of the ether left a colourless oil (20 mg.) which partially crystallized. With methanolic picric acid a precipitate of fine yellow needles was obtained. Recrystallized from methanol these had m. p. 169—170° and mixed m. p. with picrate of 3-methyl-1-phenyl-1 : 2 : 4-triazole 169·5° (lit., m. p. 171°).

3-Hydroxy-1-phenyl-1 : 2 : 4-triazole (10 g.) and sodium hydroxide (2·5 g.) were dissolved in the minimum amount of water and shaken with methyl sulphate (5·9 c.c.) for 0·5 hr. The product gradually crystallized; it was collected, washed with water, and dried, giving material (5·8 g.) of m. p. 286—290°. Recrystallization from pentanol gave 2-*methyl*-3-*oxo*-1-*phenyl*-1 : 2 : 4-*triazoline*, m. p. 296—297° (decomp.) (Found: C, 61·7; H, 5·3; N, 24·0; MeO, nil. $C_9H_9ON_3$ requires C, 61·7; H, 5·2; N, 24·0%).

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