Triazines and Related Products. Part XI.[1] Dimroth Rearrangements of 3-Substituted 3,4-Dihydro-4-imino-1,2,3-benzotriazines in Acetic Acid

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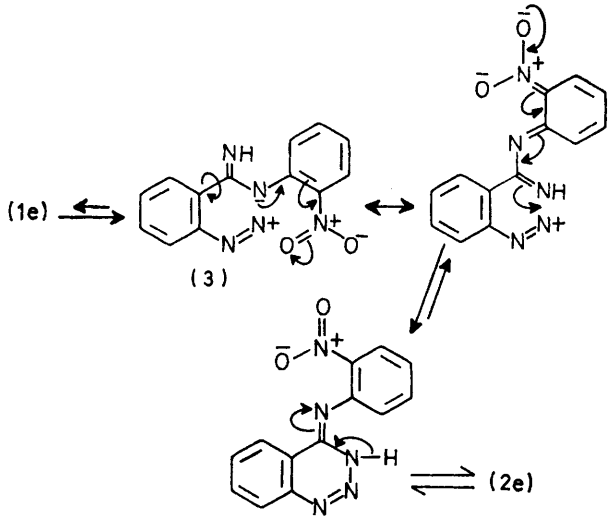
3-Substituted 3,4-dihydro-4-imino-1,2,3-benzotriazines (1) rearrange to the isomeric substituted 4-amino-1,2,3-benzotriazines (2) in acetic acid regardless of the nature of the 3-substituent. 3-Substituted 4-arylimino-3,4-dihydro-1,2,3-benzotriazines (4) are stable in acetic acid.

THE rate of Dimroth rearrangements of 1-substituted 1,2-dihydro-2-iminopyridines is markedly influenced by the nature of the rearranging group.[2] Similarly, the propensity to rearrangement of certain 4-iminobenzotriazines (1) in 95% ethanol or 2N-hydrochloric acid depends on electronic and steric effects of the 3-substituent.[3] We have now prepared additional members of the series (1) and report that all the 4-iminobenzotriazines (including the compounds resistant to the foregoing conditions) rearrange smoothly to the isomeric series (2) in boiling acetic acid.

A $-I$ or $-M$ substituent in the 3-aryl nucleus of the 4-iminotriazines (1) accelerates the rearrangement regardless of its position, although the effect is particularly marked when the substituent occupies an *ortho*- or *para*-position. For example, the imine (1e) formed by

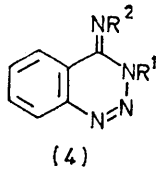
a; R = Ph
b; R = *o*-ClC_6H_4
c; R = *m*-$CN{\cdot}C_6H_4$
d; R = *m*-$NO_2{\cdot}C_6H_4$
e; R = *o*-$NO_2{\cdot}C_6H_4$
f; R = *p*-$NO_2{\cdot}C_6H_4$
g; R = *p*-$CN{\cdot}C_6H_4$
h; R = *o*-MeC_6H_4
i; R = *p*-MeC_6H_4
j; R = *p*-EtC_6H_4
k; R = $PhCH_2$
l; R = $Ph[CH_2]_2$
m; R = *p*-$[N{:}C(NH_2){\cdot}N{:}C(NH_2){\cdot}N{:}C-]C_6H_4$



cyclisation of 1-*o*-cyanophenyl-3-*o*-nitrophenyltriazene is so unstable it cannot be isolated; it rearranges spontaneously to the isomer, 4-*o*-nitroanilino-1,2,3-benzotriazine (2e).[3] We now attribute this reactivity to the electronic influence of the *o*-nitro-substituent, which, by delocalising the negative charge developed on the amidine nitrogen atom formed following heterolytic fission of the N(2)–N(3) bond disturbs the equilibrium (1e) ⇌ (3) in favour of the acyclic species. Bond rotation followed by recyclisation at the more nucleophilic (unsubstituted) amidine nitrogen atom leads to the rearranged product (2e). Similar rate-enhancing effects operate in the *p*-nitro- and *p*-cyano-phenyltriazines (1f and g).

In contrast, $+I$ substituents on the phenyl group (1h—j) destabilise the acyclic zwitterion and these iminotriazines are incompletely rearranged in both ethanol and 2N-hydrochloric acid. 4-Iminotriazines with 3-aralkyl substituents (1k and l) are completely stable in 2N-hydrochloric acid [they can in fact be prepared in this medium by retro-Dimroth rearrangement of the isomers (2k and l)].[3]

Boiling acetic acid promotes reversible ring-opening of the 4-iminobenzotriazines (1a—m)—the zwitterionic intermediates can be trapped as azonaphthol derivatives and rearrangement proceeds rapidly and in high yield (>85%) to the thermodynamically favoured 4-amino-series (2a—m). Acetic acid is the only reagent we have found to rearrange the 3-benzyltriazine (1k). Apart from its stability in 2N-hydrochloric acid,[3] this triazine is stable in ethanol, ethanol containing toluene-*p*-sulphonic acid, ethanolic ammonia, piperidine, pyridine, collidine, and boiling *o*-dichlorobenzene. The 3-substituted 4-aryliminobenzotriazines (4a—g), which also undergo ring-fission and form azonaphthol derivatives when heated in acetic acid containing 2-naphthol, were recovered unchanged from boiling acetic acid alone.



	R^1	R^2
a;	$PhCH_2$	Ph
b;	Me	Ph
c;	Et	Ph
d;	Pr^i	Ph
e;	Me	*o*-ClC_6H_4
f;	Me	*o*-$NO_2{\cdot}C_6H_4$
g;	Ph	Ph

EXPERIMENTAL

1-o-Cyanophenyl-3-p-tolyltriazene.— Anthranilonitrile (11·8 g) in 10N-hydrochloric acid (50 ml) was cooled to 0° and diazotised with sodium nitrite (7·1 g) in water (20 ml). The diazonium solution was neutralised with an excess of sodium acetate trihydrate, and stirred for 2 h at 0° with finely powdered *p*-toluidine (10·7 g). The red solid was kept overnight at 4°, collected, washed with water, and crystallised from toluene–light petroleum to give brown *needles* or *prisms* (9·5 g), m.p. 95—96°, $\nu_{max.}$ (KBr) 3320

[1] Part X, M. F. G. Stevens, *J.C.S. Perkin I*, 1972, 1221.
[2] D. J. Brown in ' Mechanisms of Molecular Migrations,' ed. Thyagarajan, vol. 1, Wiley, New York, 1968, p. 209.
[3] H. N. E. Stevens and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1970, 765.

(NH) and 2223 cm^{-1} (C≡N), τ ($CDCl_3$) 7·65 (CH_3) (Found: C, 71·2; H, 5·3; N, 23·8. $C_{14}H_{12}N_4$ requires C, 71·1; H, 5·2; N, 23·7%).

1-o-*Cyanophenyl*-3-p-*ethylphenyltriazene*.—This *triazene*, prepared (85%) by coupling diazotised anthranilonitrile with *p*-ethylaniline (1 mol. equiv.) crystallised from benzene–light petroleum as red needles, m.p. 72—73°, $\nu_{max.}$ (KBr) 3200 (NH) and 2232 cm^{-1} (C≡N) (Found: C, 72·2; H, 5·7; N, 22·3. $C_{15}H_{14}N_4$ requires C, 72·0; H, 5·6; N, 22·4%).

3,4-*Dihydro*-4-*imino*-3-p-*tolyl*-1,2,3-*benzotriazine*.—A solution of 1-*o*-cyanophenyl-3-*p*-tolyltriazene (20 g) in 70% aqueous ethanol (250 ml) was boiled (45 min). Dilution with ice–water (200 ml) precipitated a red oil which rapidly solidified. This solid (18 g, 90%) crystallised from aqueous ethanol to afford buff needles of the *tolylbenzotriazine*, m.p. 103—104° (Found: C, 71·0; H, 5·3; N, 23·6. $C_{14}H_{12}N_4$ requires C, 71·1; H, 5·2; N, 23·7%); $\lambda_{max.}$ (EtOH) 261, 268, 309, and 318 nm (log ε 3·99, 3·97, 3·76, and 3·77).

3-p-*Ethylphenyl*-3,4-*dihydro*-4-*imino*-1,2,3-*benzotriazine*.—Cyclisation of 1-*o*-cyanophenyl-3-*p*-ethylphenyltriazene in 70% aqueous ethanol afforded the *triazine* (95%) as brown prisms, m.p. 112—113° (from aqueous methanol) (Found: C, 72·1; H, 5·5; N, 22·2. $C_{15}H_{14}N_4$ requires C, 72·0; H, 5·6; N, 22·4%), $\lambda_{max.}$ (EtOH) 261, 268, 310, and 319 nm (log ε 3·99, 3·96, 3·80, and 3·82).

Other 4-imino-1,2,3-benzotriazines were prepared by published methods.[3]

4-p-*Toluidino*-1,2,3-*benzotriazine*.— 3,4-Dihydro-4-imino-3-*p*-tolyl-1,2,3-benzotriazine (5·0 g) was boiled in acetic acid (25 ml) for 20 min. The *product* (4·8 g, 96%) precipitated from the cooled solution, and crystallised from ethanol as cream *needles*, m.p. 207—208° (efferv.) (Found: C, 71·0; H, 5·3; N, 23·9. $C_{14}H_{12}N_4$ requires C, 71·1; H, 5·2; N, 23·7%).

4-p-*Ethylanilino*-1,2,3-*benzotriazine*, prepared (85%) by cyclisation of 3-*p*-ethylphenyl-3,4-dihydro-4-imino-1,2,3-benzotriazine in acetic acid, crystallised from ethanol as buff prisms, m.p. 176—177° (efferv.) (Found: C, 72·2; H, 5·5; N, 22·1. $C_{15}H_{14}N_4$ requires C, 72·0; H, 5·6; N, 22·4%).

[4] S. M. Mackenzie and M. F. G. Stevens, *J.C.S. Perkin I*, 1972, 295.

Similarly prepared from the appropriate 3-substituted 4-imino-1,2,3-benzotriazines were the following 4-substituted 1,2,3-benzotriazines (% yield and m.p. in parentheses): anilino [3] (95, 200—201°); *o*-chloroanilino [3] (93, 168—169°); *m*-cyanoanilino [3] (93, 242—243°); *m*-nitroanilino [3] (95, 244—245°); *o*-toluidino [3] (90, 163—164°); benzylamino [3] (95, 207—209°); phenethylamino [3] (90, 202—204°); *p*-(4,6-diamino-*s*-triazin-2-yl)anilino [4] (95, 259—260°).

N-*Benzyl*-N′-*phenyl*-2-*nitrobenzamidine*.— *N*-Benzyl-2-nitrobenzamide [5] (25·2 g) in anhydrous benzene (300 ml) was boiled with phosphorus pentachloride (31·2 g) for 2 h. To the cooled mixture was added aniline (9·3 g) and boiling was continued for 2 h. Solvent was removed, and the oily residue was dissolved in ethanol and poured onto ice–concentrated aqueous ammonia. The pale yellow *nitrobenzamidine* (85%) crystallised from ethanol; m.p. 96—97° (Found: C, 72·1; H, 5·2; N, 12·7. $C_{20}H_{17}N_3O_2$ requires C, 72·5; H, 5·1; N, 12·7%).

Catalytic hydrogenation of the nitrobenzamidine over palladium–charcoal afforded 2-*amino*-N-*benzyl*-N′-*phenylbenzamidine* (85%), m.p. 78—79° (from aqueous ethanol) (Found: C, 79·4; H, 6·9; N, 13·6. $C_{20}H_{19}N_3$ requires C, 79·7; H, 6·3; N, 14·0%).

3-*Benzyl*-3,4-*dihydro*-4-*phenylimino*-1,2,3-*benzotriazine*.—Diazotisation of the aforementioned aminobenzamidine in 2N-sulphuric acid with sodium nitrite (1 mol. equiv.) followed by basification of the solution with aqueous ammonia gave the *triazine* (90%), m.p. 112—113° (yellow needles from ethanol) (Found: C, 76·7; H, 5·0; N, 17·7. $C_{20}H_{16}N_4$ requires C, 76·9; H, 5·2; N, 17·9%), $\lambda_{max.}$ (EtOH) 265, 273, and 317 nm (log ε 3·93, 3·94, and 3·54).

3-Benzyl-3,4-dihydro-4-phenylimino-1,2,3-benzotriazine (4a) and the other 3,4-disubstituted triazines (4b—g) [3] were all recovered unchanged from boiling acetic acid (1 h).

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[5] A. C. Mair and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1971, 2317.