3,4-Diaryl-2-hydroxy-1,2,5-triazabicyclo[3,2,1]oct-3-enes from the Peracid Oxidation of 3,4-Diaryl-6,7-dihydro-1-methyl-1*H*-1,2,5-triazepines

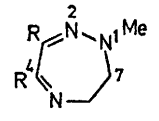
By DONALD L. TREPANIER and SAMUEL WANG
(*Dow Chemical U.S.A., Human Health Research and Development Laboratories, Zionsville, Indiana* 46077)
and CHARLES E. MOPPETT*†
(*Dow Chemical U.S.A., Eastern Research Laboratory, Wayland, Massachusetts* 01778)

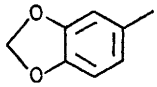
Summary The reaction of benzil with 1-(2-aminoethyl)-1-methylhydrazine led to 6,7-dihydro-1-methyl-3,4-diphenyl-1*H*-1,2,5-triazepine, which on treatment with *m*-chloroperbenzoic acid gave 2-hydroxy-3,4-diphenyl-1,2,5-triazabicyclo[3,2,1]oct-3-ene; this in turn yielded 1-acetyl-2,3-dihydro-5,6-diphenyl-1*H*-imidazo[1,2-*a*]imidazole on reaction with acetic anhydride.

WE have found that 3,4-diaryl-6,7-dihydro-1-methyl-1*H*-1,2,5-triazepines are readily available from the reaction of benzils with 1-(2-aminoethyl)-1-methylhydrazine (I).[1] For example, treatment of benzil with (I) in the presence of benzene and toluene-*p*-sulphonic acid with azeotropic removal of water led to (II), (82%); an orange, crystalline solid, m.p. 118° (from Pr^iOH); ν (Nujol) 1610, 1575, 1490, 965, 770, and 690 cm^{-1}; δ ($CDCl_3$) 2·87 (3H, s, NMe), 3·35—3·87 (4H, m, NCH_2CH_2N), and 6·8—7·5 (10H, m, C_6H_5); M^+ 263, $C_{17}H_{17}N_3$; λ_{max} (EtOH) 230 (ε 15,570), 253 (12,760), 290sh (6890), and 360 nm (3570); λ_{max} (EtOH–1N-HCl) 263 and 405 nm.

$NH_2CH_2CH_2NMeNH_2$

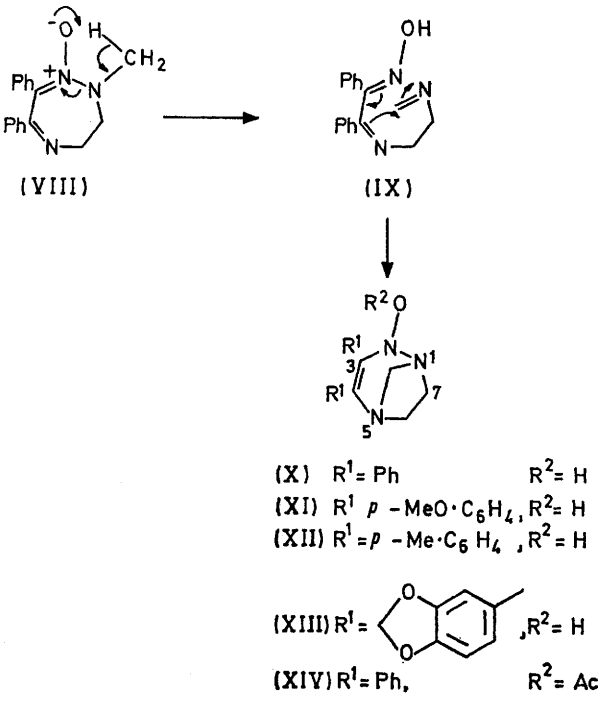
(I)



(II) R = Ph
(III) R = *p*-MeO·C_6H_4
(IV) R = *p*-Me·C_6H_4
(V) R = 
(VI) R = *m*-MeO·C_6H_4
(VII) 4,5-dihydro

† Present address: Medical Research Laboratories, Pfizer Inc., Groton, Connecticut 06340.

The generality of this reaction was demonstrated by the preparation of (III)—(VI) from (I) and the appropriately substituted benzil.‡



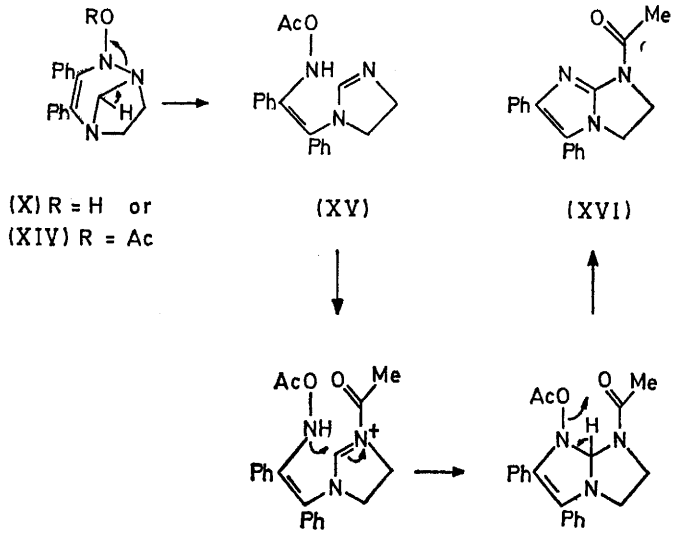
SCHEME 1.

Reduction of (II) with sodium borohydride gave 4,5,6,7-tetrahydro-1-methyl-3,4-diphenyl-1*H*-1,2,5-triazepine (VII), m.p. 113—114°;§ which was also derived from the reaction of (I) with α-bromo-α-phenylacetophenone.

Treatment of (II) with *m*-chloroperbenzoic acid led to a white crystalline solid, m.p. 184—185° (from EtOH), which we formulate as 2-hydroxy-3,4-diphenyl-1,2,5-triazabicyclo-[3,2,1]oct-3-ene (X); ν (Nujol) 3250, 1640, 895, and 700 cm^{-1}; δ ($CDCl_3$) 2·62—3·97 (5H, m, NCH_2CH_2N and NOH), ¶ AB quartet, δ_A 5·23, δ_B 4·67 (J_{AB} 18 Hz, NCH_2N), and 6·78—7·56 (10H, m, C_6H_5); M^+ 279, $C_{17}H_{17}N_3O$; λ_{max} (EtOH) 242 (ε 10,470); λ_{max} (EtOH–1N-HCl) 256 nm; positive test for hydroxylamine with triphenyltetrazolium chloride.[2,3]

We believe that a reasonable mechanism (Scheme 1) for the formation of (X) involves, initial electrophilic attack by the peracid to generate (VIII) which is constrained to undergo a [2,3] sigmatropic shift[4,5] leading to (IX) which may then, by a conventional Diels–Alder reaction give (X).

The other triazepines (III)—(V) were transformed in similar fashion to the 3,4-diaryl-2-hydroxy-1,2,5-triazabicyclo[3,2,1]oct-3-enes (XI)—(XIII).



SCHEME 2

Acetylation of (X) with Ac_2O–C_5H_5N at 40° gave the acetyl derivative (XIV), m.p. 122—124°.§ The mass spectrum of (XIV) displays a M + 42 peak[6] which probably arises through a thermal reaction involving the acetylation of the neutral molecule by keten prior to ionization. We believe that this observation has some bearing on the acetylation experiment leading to (XVI). Base-catalysed hydrolysis (EtOH–KOH) of (XIV) regenerated (X).

Treatment of either (X) or (XIV) with acetic anhydride at 100°, however, led to (XVI), m.p. 199—201° (from ethanol). It is apparent from inspection of molecular models that the proton of the methylene bridge *endo* to the ethylene backbone of (X) or (XIV) is *trans* coplanar to the N(1)–(2) bond; an ideal geometry for a 1,2-elimination reaction generating in this case (XV) which, by addition and elimination according to the synopsis of Scheme 2 leads to (XVI).

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‡ The rate of reaction of those benzils with *para* oxygen substituents is slower than that for benzil, 3,3′-dimethoxybenzil, and 4,4′-dimethylbenzil. We attribute this to the electron-donating properties (+ mesomeric effect) of the *para* oxygen substituents which results in a decreased electrophilicity for these benzils.

§ Structure assignment in agreement with spectral data.

¶ One of the protons of this multiplet is readily exchanged with deuterium oxide.

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