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# Oxidation of 2,4-Diphenyl-1,5-benzodiazepine with Peracetic Acid

Masakatsu MATSUMOTO, Akira IIO and Teijiro YONEZAWA

*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto*

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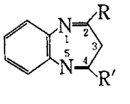
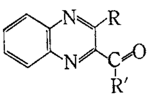
It has been reported that two 1,5-benzodiazepines, (I-a: R,R′$=CH_3$) and (I-b: R$=CH_3$, R′=Ph), undergo oxidative ring-contraction with peracetic acid or monopersulfuric acid.[1] In a recent publication,[2] we have also reported the photooxidation of the dimethyl- (I-a) and the diphenylbenzodiazepine (I-c: R,R′=Ph) in benzene; the diphenylbenzodiazepine (I-c) is oxidized photochemically at the 3-$CH_2$ group, as in the oxidation of the benzodiazepines (I-a) and (I-b). In the present paper, we will report the oxidation of the diphenylbenzodiazepine (I-c) with peracetic acid.

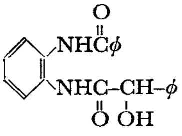


(I)



(II)

When the diphenylbenzodiazepine (I-c) was oxidized with peracetic acid, the corresponding ring-contraction product, 2-benzoyl-3-phenylquinoxaline (II-c), was not obtained; rather, Compound A, mp 154—156°C, was obtained as the main product, together with 2-phenylbenziminazole (IV), *N*-benzoyl-*o*-nitroaniline (V), and *N,N′*-dibenzoyl-*o*-phenylenediamine (VI). The NMR spectrum of Compound A in hexadeuteriodimethylsulfoxide showed two doublets (at $\tau=4.92$($J=4.0$ Hz, 1H) and $\tau=3.35$ ($J=4.0$ Hz, 1H)), three multiplets (centered at $\tau=2.75$ (5H), $\tau=2.40$ (5H), and $\tau=2.15$ (4H)), and two singlets (at $\tau=0.35$ (1H) and $\tau=-0.10$ (1H)). The doublet at $\tau=3.35$ and the two singlets disappeared upon the addition of of $D_2O$. The infrared spectrum appeared in KBr $\nu_{C=O}$ at 1645 cm$^{-1}$ and in $\nu_{N-H}$ and $\nu_{O-H}$ at 3370 $-$3220 cm$^{-1}$. The mass spectrum showed a parent peak at $m/e$ 346. On the basis of these results, Compound A was identified as an amine (III).



(III)

From the facts that, in the oxidation with peracetic acid, the diphenylbenzodiazepine (I-c) gave

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[1] J. A. Barltrop, C. G. Richards, D. M. Russell and G. Ryback, *J. Chem. Soc.*, **1959**, 1132.

[2] T. Yonezawa, M. Matsumoto and H. Kato, This Bulletin, **41**, 2543 (1968).

the amide (III), while the dimethyl- (I-a) and the methylphenylbenzodiazepine (I-b) gave acetylquinoxalines (II: $R'=CH_3$, a: $R=CH_3$, b: R=Ph), it is thought that, in the mechanism of the oxidative ring-contraction shown by Barltrop *et al.*,<sup></sup>1) there may be a subsequent, reversible reaction between the intermediates an alcohol (VII) and a quinoxaline (VIII), which plays important roles.*1

In the case of the diphenylbenzodiazepine (I-c), the alcohol (VII) formed at first might undergo ring-contraction to form the quinoxaline (VIII), which they might suffer further oxidation to give the amide (III), while in the case of the dimethyl- (I-a) and the methylphenylbenzodiazepine (I-b), the alcohol (VII) might form a 3,6-diaza-4,5-benzotropone (IX) by succesive oxidation and the 6-oxo intermediate (IX) is thought to be rearranged.

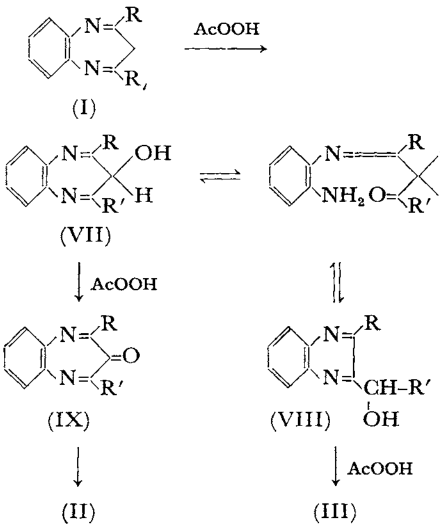
## Experimental

**2,4-Diphenyl-1,5-benzodiazepine (I-c).** This was prepared by the condensation of dibenzoylmethane with *o*-phenylenediamine catalysed by *p*-toluenesulfonic acid in xylene;1) colourless needles, mp 140.0°C, crystallized from methanol.

**Oxidation of I-c with Peracetic Acid.** A mixture of the diazepine (I-c) (0.5 g) and hydrogen peroxide (0.90 m*l* of a 30% aqueous solution) in 30% aqueous acetic acid (30 m*l*) with a slight amount of $H_2SO_4$ was set aside for two days. As the reaction proceeded, the violet reaction mixture turned dark brown. The reaction mixture was basified and filtered, and then the solid part was crystallized from hot water, giving pale brown crystals melting at 154—156°C, which were identified at the amide (III) described previously, in a yield of 44%.

Found: C, 72.91; H, 5.21; N, 8.20%. Calcd for $C_{21}H_{18}O_3N_2$: C, 72.82; H, 5.24; N, 8.09%.

The filtrate was extracted with methylene chloride, the extracts were condensed, and the residue was chromatographed in methylene chloride on silica gel. Then *N*-benzoyl-*o*-nitroaniline (V) mp 92°C from aqueous methanol, 2-phenylbenziminazole (IV) mp 313°C from methanol, and *N*,*N*′-dibenzoyl-*o*-phenylenediamine (VI) mp 324°C from ethanol*2 were obtained successively in yields of 8, 9, and 3% respectively. The three products, IV, V, and VI, were identified by comparing the IR spectra with those of authentic materials.



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*1 As the intermediates VII and VIII, some other forms can be considered.

*2 Many articles have given 300—303°C as the mp of compound VI.