

OXIDATION OF TRIPHENYLVERDAZYLs BY ACYL PEROXIDES.

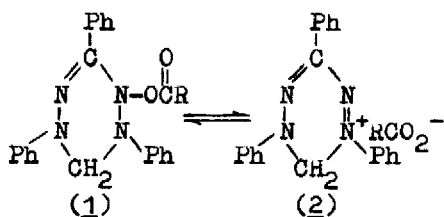
MECHANISM OF TRANSFORMATION OF THE TETRAZINE RING INTO N-FORMYLFORMAZAN

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Triphenylverdazyls readily react with diacyl peroxides.¹ It supposed that the main product of the reaction was the acyloxy-substitution product (1) which in polar solvents is in equilibrium with the verdazylum salt (2).¹



We have thoroughly studied the products of the reaction of triphenylverdazyls (3) with p-nitroperbenzoic acid and p-nitrobenzoyl peroxide in benzene, chlorobenzene and acetonitrile, and in no case have we detected compounds of type (1).² In all

cases the reaction first led to the formation of the verdazylum salt which then changed to N-formylformazan (2).³ One mole of the radical always consumed three moles of the peroxide.⁵ The reaction with peracid formed one mole of N-formylformazan,⁶ three moles of p-NO₂C₆H₄COOH⁷ and two moles of H₂O⁸, while the oxidation with peroxide led to the formation of one mole of N-formylformazan,⁶ four moles of p-NO₂C₆H₄COOH⁷ and one mole of p-nitrobenzoic anhydride.⁹ The results obtained are illustrated by Schemes 1 and 2.

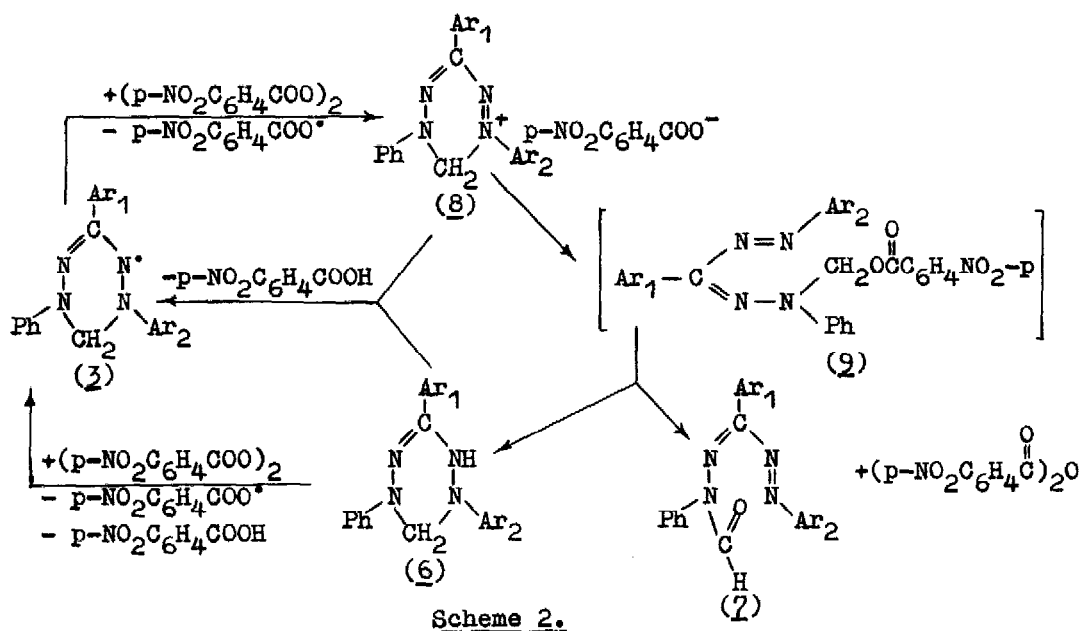
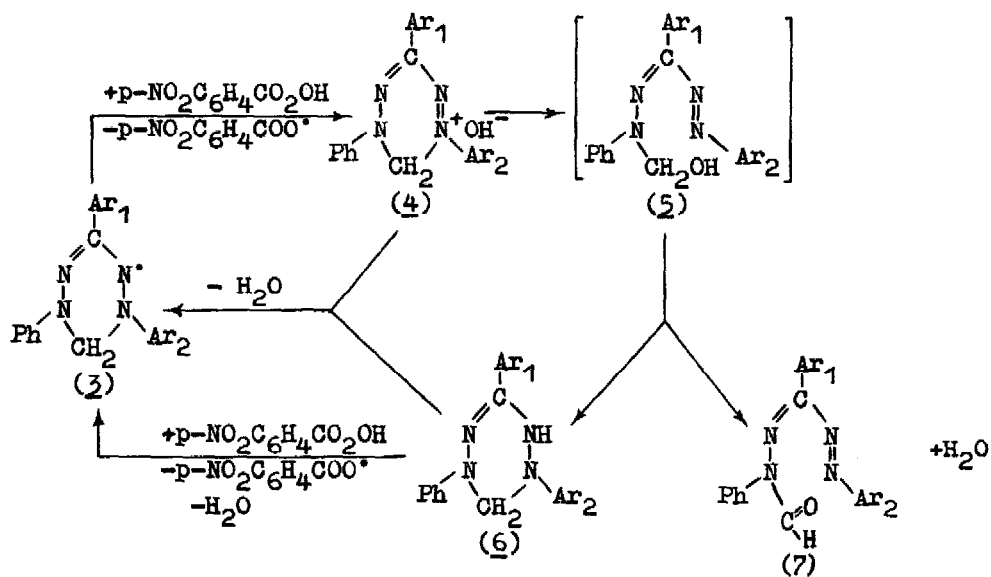
Here we deal with an example of a rapid-attenuation cyclic process in the course of which partial regeneration of the radical takes place. This can easily be observed if the radical and the peroxide are mixed in benzene in a ratio of 1 : 1.5. The green colour of the solution (for the radical λ_{\max} 720 nm) changes to blue-violet (for the salt λ_{\max} 540 nm) and then changes back to green. Addition of further peroxide leads to repetition of the cycle.

The Schemes explain the stoichiometric relations observed in these cases and agree well with our previous work¹⁰ in which the transformation of (4) into (6) and (7) is explained by the intermediary formation and disproportionation of the N-hydroxymethyl derivative (5).

The reaction of verdazyls with (p-NO₂C₆H₄COO)₂ proceeds faster than with p-NO₂C₆H₄CO₂OH. Verdazylum salt (8) formed in this case apparently rearranges into the formazan product (9) which then rapidly disproportionates to (6), (7) and p-nitrobenzoic anhydride^{9,11} (Scheme 2).

It has recently been shown that the oxidation of nitroxides by m-chloroperbenzoic acid also proceeds through the intermediary formation and decomposition of ammonium ion.¹³

The regeneration of the radical may proceed in two ways: through oxidation



(a) $\text{Ar}_1 = \text{Ar}_2 = \text{Ph}$; (b) $\text{Ar}_1 = \text{p-NO}_2\text{C}_6\text{H}_4$, $\text{Ar}_2 = \text{Ph}$; (c) $\text{Ar}_1 = \text{Ar}_2 = \text{p-CH}_3\text{OC}_6\text{H}_4$

of the intermediate leukoverdazyl by the peroxide or by reaction of the leukoverdazyl with the verdazylium salt. In the first case every cycle must result in the regeneration of one half of the radical entering the reaction, while in the second case two-thirds is regenerated.

The reactions of salts (4) or (8) with leukoverdazyls are the reverse of the disproportionation reactions of verdazyls in the presence of acid.¹⁴ These reactions proceed rapidly.¹⁵ It is known that in the presence of alkali the verdazylium salt reacts with leukoverdazyl, leading to the quantitative formation of the radical.¹⁶ We have shown that under our conditions the equilibrium $2(3) + p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H} \rightleftharpoons (8) + (6)$ is practically completely shifted to the left. Leukoverdazyls (6)¹⁷ under the action of an equimolecular amount of the peroxide, quickly turn into radicals (proved spectroscopically). Runs conducted in benzene showed that one mole of leukoverdazyl involves into the reaction four moles of peroxide ($p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{OH}$ or $p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{OCOC}_6\text{H}_4\text{NO}_2\text{-p}$). In both cases one mole of N-formylformazan (7) is formed, while the reaction with peracid leads to the formation of four moles of $p\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$ and that with peroxide - six moles.⁷ Compounds (7) are not oxidized by peroxide.

To clarify the contribution of the two modes of regeneration of the radical additional investigation is necessary.

In specially conducted runs it has been shown that the transformation of one mole of the radical into the verdazylium salt (and the transformation of one mole of leukoverdazyl into the radical) consumes one mole of the peroxide. Hence, these reactions must lead to the formation of the radical $p\text{-NO}_2\text{C}_6\text{H}_4\text{COO}^\bullet$ which forms p-nitrobenzoic acid by hydrogen abstraction from the solvent molecule.

The oxidation rate of radicals (3) by peracid into the verdazylium cation (4) is proportional to the first power of the concentration of each reagent (followed spectroscopically by the changes in the concentration of the radical and the salt). In the oxidation of (3c) in chlorobenzene at 15°C the reaction rate constant $k \sim 60 \text{ l/mol}\cdot\text{s}$.

The formation of verdazylium salts and aryloxy radical in the first stage of the reactions under study apparently proceeds as a result of nucleophilic attack of the verdazyl upon peroxide oxygen. The reaction proceeds rapidly and can easily be observed by the change of the green colour of the solution to blue-violet. In polar solvents (acetonitrile, propylenecarbonate) the salts are sufficiently stable and take several days to turn into N-formylformazan. In low-polar solvents (C_6H_6 , PhCl) the reaction is finished within 30-60 minutes. In both cases the end of the reaction is marked by the formation of orange-colored solutions of N-formylformazan (for (7a) $\lambda_{\text{max}} 360 \text{ nm}$).

The suggested mechanism of oxidation of verdazyls by acyl peroxides also explains the formation of N-formylformazan in the case of oxidation of verdazyls by the oxygen of the air in the presence of activated charcoal.⁴

We regard the transformation of verdazylium salts (4) and (8) into formazan

products (5) and (9) as another example of the reaction of Hofmann degradation of ammonium salts.

References and Footnotes

1. B.M. Yarmolyuk, O.M. Polumbrik and G.F. Dvorko, Neftekhimiya, 13, 719 (1973), 14, 775 (1974); Reakts. sposobn. organ. soedin., 10, 893,901 (1973).
2. The runs were conducted at room temperature with exclusion of oxygen at reagent concentrations $\sim 10^{-2}$ M.
3. 1,3,5-Triphenyl- and 1,5-diphenyl-3-p-nitrophenyl-N-formylformazan are described in ref.4.
4. R. Kuhn, F.A. Neugebauer and H. Trischmann, Monatsh., 98, 726 (1967).
5. The concentration of the peroxide at the end of the run could only be determined (sample with KI and $\text{CH}_3\text{CO}_2\text{H}$) if its initial concentration exceeded that of the radicals more than three times.
6. N-Formylformazans were obtained from the reaction solution as follows: most of benzene was removed in vacuum, $\text{p-NO}_2\text{C}_6\text{H}_4\text{COOH}$ was filtered off and (7) was precipitated from the filtrate by hexane. When the reaction was conducted in CH_3CN and PhCl the solvent was removed completely and (7) was extracted from the dry residue by benzene and precipitated from the benzene by hexane. The structure was confirmed by elemental analysis of (7c), spectroscopically and by comparison with an authentic sample of (7a, b). The yield of (6) was 50-85%.
7. p-Nitrobenzoic acid does not easily dissolve in benzene ($\sim 1.7 \times 10^{-3}$ M); in the course of the run most of the acid separates. When working in benzene, nitrobenzoic acid was obtained after removing most of the solvent and in PhCl and CH_3CN - after processing the dry residue with benzene.⁶ The acid was identified by comparison with an authentic sample. Its yield reached 90%.
8. Water was identified in the reaction with CaH_2 . The yield was 98%.
9. The anhydride of nitrobenzoic acid was obtained from the reaction solution in the form of the hydrazide from benzene after removing $\text{p-NO}_2\text{C}_6\text{H}_4\text{COOH}$.^{7,8} It was identified by comparison with an authentic sample.
10. E.A. Ponomareva, P.V. Tarasenko and G.F. Dvorko, Angew.Chem., 87, 453 (1975).
11. Transformation of diacyl peroxide into anhydride has previously been observed in the course of oxidation of sulphides to sulphoxides.¹²
12. W.A. Pryor and H.T. Buckley, J.Org.Chem., 37, 2885 (1972).
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14. F.A. Neugebauer, Angew.Chem., 85, 485 (1973).
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16. R. Kuhn, F.A. Neugebauer and H. Trischmann, Monatsh., 97, 1881 (1966).
17. Leukoverdazyls were obtained by the reaction $\text{PhNHNH}_2 + 2(3) \rightarrow 2(6) + \text{C}_6\text{H}_6 + \text{N}_2$. They were characterized by elemental analysis and spectroscopically.