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Palladium(O) Catalysed Conversion of α-Nitroepoxides into 1,2-Diketones
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A variety of α -nitroepoxides have been found to undergo conversion to the corresponding 1,2-diketones with $Pd(PPh_3)_4$. Two examples form α -nitroketones instead of 1,2-diketones.

Isomerisation of α,β -epoxy ketones and 1,3-diene epoxides by means of tetrakis (triphenylphosphine)palladium(0) $[Pd(PPh_3)_4]$ has been recently reported by Moyori et al.^{1,2)} to give 1,3-diketones and β,γ -unsaturated ketones (or dienols) respectively. Probable mechanisms to account for these conversions, as postulated by Noyori, suggest that Pd(0) acts as a nucleophile and prefers to attack the epoxy carbon which is α to a carbonyl group or to a double bond followed by a hydride transfer to palladium and then decomposition of these intermediates to form products. Noyori mechanisms for α,β -epoxy ketone to 1,3-diketone transformation are shown in Scheme 1 (Paths 'a' and 'b').



Scheme 1.

It is apparent that the preferential attack of Pd(0) at carbon-2 and subsequent isomerisation is taking place due to the presence of an electron withdrawing carbonyl group α to it, for ordinary epoxides (e.g. cyclohexene oxide) do not undergo³⁾ any isomerisation under similar conditions. We, therefore, became interested in finding out the behaviour of α -nitroepoxides towards Pd(0) and expected that these would yield α -nitroketones if the above mentioned mechanism is operative. Surprisingly, however, the reaction of α -nitroepoxides with Pd(0) alone or with Pd(0) and 1,2-bis(diphenylphosphino) ethane (dpe)⁴⁾ was extremely sluggish. A close examination of the Noyori mechanism (Scheme 1) indicates that if path 'b' were to operate in the present case also, an intermediate of type 'C' could directly form the products with the help of a mild base, like triethylamine, which could abstract the proton (marked^{*}) without involving the intermediates D and E. It was indeed found that addition of an equimolar amount of triethylamine brought the reaction to completion in short time. Results are summarised in Table 1.

Entry	a-Nitroepoxide	Product	Time/h	Yield/%
1	H ₅ C ₆ -CH	H ₅ C ₆ -C-CH ₃	10	49
2	H ₅ C ₆ -CH CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	H ₅ C ₆ -C-C-C ₆ H ₅	5	63
3	(4-CH ₃) H ₄ C ₆ -CH	(4-CH ₃)H ₄ C ₆ -C-C-CH ₃	30	48
4	$(4-CH_3)$ H ₄ C ₆ -CH C C C C ₆ H ₅	$(4-CH_3)H_4C_6-C-C-C_6H_5$	5	7 5
5	$H_5C_6-C \xrightarrow{2} CH(CH_2)_3CH_3$	$H_5C_6-CH-C(CH_2)_3CH_3$	7	55
6	H_3C-C $CH(CH_2)_3CH_3$	$H_3^{C-CH-C(CH_2)}$	12	56
7			7	50
8			6	40

Table 1. Conversion of α -nitroepoxides with Pd(PPh₂)

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The progress of reaction was periodically monitored both by thin layer chromatography and IR spectroscopy and found to proceed via the formation of α -nitroketones. However the amount of dione was always found to be higher than that of α -nitroketone and after a certain time (see Table 1) almost all the α -nitroketone had disappeared and the only product isolated was 1,2-diketone. Surprisingly, the α -nitroepoxides corresponding to entries 5 and 6 gave only α -nitroketones and no trace of 1,2-diketone was found to be present even after prolonged time.

The formation upto α -nitroketones could be visualised as indicated in Scheme 2. Their further conversion into 1.2-diketones may proceed via the Nef type reaction.⁵⁾ Work is in progress to elucidate the mechanism and extend the scope of this reaction.



Scheme 2.

In view of the fact that vinyl nitro compounds are easily available from the corresponding olefins⁶⁾ and their epoxidation to obtain α -nitroepoxides is also easy,⁷⁾ the present method offers a new synthetic method for the synthesis of 1,2-diketones from olefins.

A typical procedure for the conversion of 1,2-diphenyl-1-nitrooxirane into benzil is as follows: To a stirred solution of 1,2-diphenyl-1-nitrooxirane (100 mg, 0.41 mmol) in 3 ml of dry benzene were added $Ph(PPh_3)_4$ (23 mg, 0.02 mmol, 5 mol %) and triethylamine (0.06 ml, 0.41 mmol). The whole mixture was refluxed for 5 hrs under nitrogen atmosphere. It was cooled, neutralized with dil HCl⁸⁾ and then washed with water (2x5 ml) and brine (1x5 ml). After drying over anhydrous sodium sulfate, the solvent was removed under vacuum to get crude product whose purification by preparative thin layer chromatography gave pure benzil 55 mg (63% yield) which was characterised by spectral means.

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References

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- This (dpe) has been used as a ligand and found in many cases (Refs. 1 and 2) to increase the yield of products.
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 R.H. Fischer and H.M. Weitz, synthesis, <u>1976</u>, 53, α-Nitroepoxides corresponding to entries 7 and 8 were prepared by following this procedure.
- 8) In case of nitrocyclohexene and nitrocyclopentene oxides after neutralisation with dil HCl, the mixture was treated with saturated solution of NaCl and extracted with ethyl acetate and the products purified by distillation.

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