

Table 1 Percent recovery of 2-aryl-2,3-dihydro-4H-1-benzopyran-4-one (1a-Xa) and 2'-hydroxychalkone (1b-Xb) at equilibrium attained from either direction over silica gel.

Comp. No ^a	R ¹	R ²	R ³	Percent recovery of		Total recovery (%)
				4H-1-benzopyran-4-one (a)	2'-hydroxychalkone (b)	
I	H	H	H	40	45	85
II	Br	H	H	75	18	93
III	Br	H	4-OMe	52	40	92
IV	COEt	H	4-OMe	55	38	93
V	COPh	H	H	60	29	89
VI	COPh	H	3-OMe	60	32	92
VII	COCH=CHPh	H	H	58	32	90
VIII	COCH=CHC ₆ H ₄ - OMe-p	H	4-OMe	55	40	95
IX	H	OMe	H	54	38	92
X	—	—	—	52	38	90

^a Compound numbers given in this column refer to those described in figure 1. For compounds XI and XII, R² is H and OMe respectively while R¹ is H for both.

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1. Tiroflat, J. and Corvaisier, A., *Compt. Rend.*, 1961, **252**, 3818.
2. Shimokoriyama, M., *J. Am. Chem. Soc.*, 1957, **79**, 4190 and references cited therein.
3. Rakosi-David, E. and Bogнар, R., *Acta Univ. Debrecen*, 1961, **7**, 141; *Chem. Abstr.*, 1963, **58**, 5617h.
4. Datta, C. P. and Roy, Lala, P. K., *Indian J. Chem.*, 1975, **13**, 425 and references cited therein.
5. Lowenbein, A., *Ber. dt. Chem. Ges.*, 1924, **57B**, 1515.
6. Chang, C. T., Chen, F. C., Chen, T. S., Hsu, K. K., Ueng, T. and Hung, M., *J. Chem. Soc.*, 1961, 3414.
7. Chen, F. C. and Chang, C. T., *J. Chem. Soc.*, 1958, 146.
8. Joshi, U. and Amin, G. C., *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1960, 267; *Chem. Abstr.*, 1960, **54**, 21067g.
9. Sangwan, N. K., Verma, B. S. and Dhindsa, K. S., *Chem. Ind. London*, 1984, No. 7, 271.
10. Sangwan, N. K., Dhindsa, K. S., Malik, O. P. and Malik, M. S., *Chim. Acta Turc.*, 1983, **11**, 65.
11. Sangwan, N. K., Dhindsa, K. S. and Malik, O. P., *Haryana Agric. Univ. J. Res.*, 1983, **13**, 380.
12. Sangwan, N. K. and Rastogi, S. N., *Indian J. Chem.*, 1980, **19B**, 500.
13. Koton, M. M., Andreeva, I. V., Turbina, A. I. and Sinyavskii, V. G., *Dokl. Akad. Nauk SSSR*, 1964, **159**, 602; *Chem. Abstr.*, 1965, **62**, 6570d.

RUTHENIUM(III) CATALYZED OXIDATION OF SECONDARY ALCOHOLS BY N-METHYLMORPHOLINE-N-OXIDE

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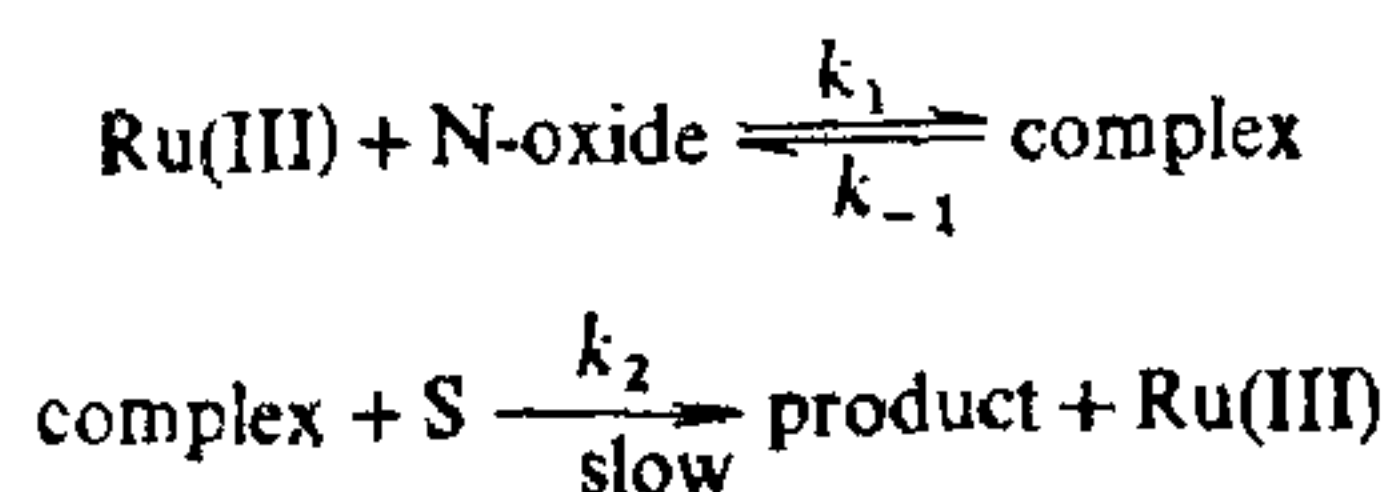
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OXIDATION of organic substrates by tertiary amine N-oxides like trimethylamine-N-oxide and N-methylmorpholine-N-oxide (N-oxide) in the presence of OsO₄ has been reported¹⁻³. Sharpless et al⁴ studied the Ru(III)-catalyzed oxidations by N-oxide of cholesterol, geraniol etc.

However, there are no reports of studies on the oxidation of secondary alcohols using N-oxide as oxidant. Pyridine-N-oxide and trimethylamine-N-oxide have been estimated using Ti(III) as a reductant⁵. We have carried out kinetic investigations on Ru(III)-catalyzed oxidation of cyclohexanol, 1-phenylethanol and 2-propanol by N-oxide in DMF as solvent, by determining titanometrically the concentration of N-oxide remaining at any instant. Aliquots of the reaction mixture were quenched by adding a known excess of Ti(III) solution. Conc. HCl and sodium citrate were added to prevent hydrolysis and to form a complex respectively. The excess of Ti(III) was back-titrated against standard Fe³⁺ using ammonium thiocyanate as indicator.

The oxidation reaction follows 1:1 stoichiometry

and the ketone formed has been qualitatively detected and quantitatively estimated according to the method due to Lappin⁶. The orders are one each in N-oxide and Ru(III). The order with respect to the substrate (S) is fractional at low concentrations (0.05 to 0.2 M) and zero at higher concentrations (0.5 M onwards). Spectral studies indicate that a 1:1 complex of Ru(III) and N-oxide is formed. EPR studies indicate that the oxidation state of Ru is not altered during the reaction. The mechanism given below



leading to the rate expression

$$\frac{d[\text{N-oxide}]}{dt} = \frac{k_1 k_2 [\text{Ru(III)}] [\text{N-oxide}] [\text{S}]}{k_{-1} + k_2 [\text{S}]} \quad (1)$$

accounts for the experimental results satisfactorily. Equation (1) can be rearranged as

$$\frac{1}{\text{Rate}} = \frac{(k_{-1}/k_2)}{k_1 [\text{Ru(III)}] [\text{N-oxide}] [\text{S}]} + \frac{1}{k_1 [\text{Ru(III)}] [\text{N-oxide}]} \quad (2)$$

Using the data from experiments at low concentrations of the substrate, (2) has been verified (table 1).

The agreement between the values of k_1 in table 1 supports the mechanism. At high concentrations of substrate, $[\text{S}] \gg k_{-1}/k_2$, a zero order in the substrate is observed. At low concentrations of substrate, k_{-1}/k_2 cannot be neglected in comparison with $[\text{S}]$ and a fractional order in the substrate is observed.

Though the ligand, PPh_3 , in the complex $\text{RuCl}_2(\text{PPh}_3)_3$, is oxidised to PPh_3O by the N-oxide, this complex is able to catalyse the oxidation reaction. In order to heterogenize this catalyst, experiments

were carried out with $\text{RuCl}_2(\text{PPh}_3)_3$ anchored to polystyrene divinylbenzene polymer with 2% cross linking. DMF could not be used since it leaches out the ruthenium species. When benzene is used as solvent no leaching takes place, but since N-oxide is not soluble phenyliodosoacetate (PIA) is used as oxidant. The anchored ruthenium on phosphinated polymer, prepared by the method of Allum *et al*⁷ contains about 1.13% of ruthenium as estimated by thiourea method⁸. Though the percentage of the product formed in the case of the anchored catalyst (12.5% conversion in 15 min) is about six times less than that of the homogeneous catalyst (80% conversion in 15 min), the anchored catalyst can be regenerated and the regenerated catalyst is found to be as effective as the original one. Only very low concentrations of PIA are used (< 0.001 M) in the case of anchored catalyst, since excess of PIA leads to leaching.

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- Schroder, M., *Chem. Rev.*, 1980, 80, 187.
- VanRheenan, V., Kelly, R. C. and Cha, D. Y., *Tetrahedron Lett.*, 1976, 29, 1973.
- Corey, E. J., Danheiser, R. L., Chandrasekaran, S. and Siret, P., *J. Am. Chem. Soc.*, 1978, 100, 803.
- Sharpless, K. B., Akashi, K. and Oshima, K., *Tetrahedron Lett.*, 1976, 29, 2503.
- Brooks, R. T. and Sternglanz, P. D., *Anal. Chem.*, 1959, 31, 561.
- Lappin, G. R. and Clark, L. C., *Anal. Chem.*, 1951, 23, 541.
- Allum, K. G. and Hancock, R. D., *Br. Patent*, 1972, 1277737.
- Ayres, G. H. and Young, F., *Anal. Chem.*, 1950, 22, 1277.

Table 1 Evaluation of rate constants from double reciprocal plots at low concentrations of substrate ($[\text{S}] < 0.2$ M)

Substrate	k_1 in $\text{M}^{-1} \text{min}^{-1}$		(k_{-1}/k_2)
	From pseudo first order plots	From double reciprocal plots	
Cyclohexanol	36.56 ± 0.81	35.72	0.044
1-Phenylethanol	39.11 ± 0.47	38.80	0.041
2-Propanol	34.29 ± 0.49	34.50	0.050

MID-HOLOCENE FOSSIL WOOD FROM BHIMA BASIN IN SOLAPUR DISTRICT, MAHARASHTRA.

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MORE than ten carbon-14 dates for Pre-Early Holocene and two for Mid-Holocene alluvial phases