

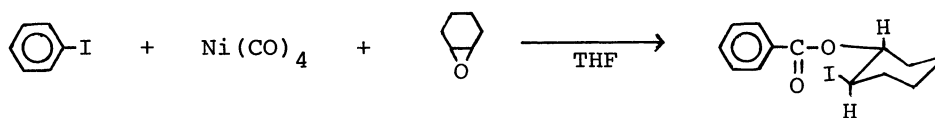
THE REACTION OF ORGANOHALIDES WITH NICKEL CARBONYL IN THE
PRESENCE OF OLEFIN OXIDES

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Reaction of aroyl- or alkenoylnickel carbonyl halide complexes, derived from the reaction of organohalides with nickel carbonyl, with olefin oxides afforded halohydrin esters.

Recently it has been shown that the complex derived from the reaction of organohalides with nickel carbonyl $[\text{Ni}(\text{CO})_4]$ is electrophilic in nature. The complex, which is most likely aroylnickel carbonyl halide, reacts with enamines to give α -aroyl ketones in good yield.¹⁾ In this paper, we wish to report a new example of electrophilic reaction of the aroylnickel carbonyl halide complex; the reaction of the complex with olefin oxides to give halohydrin esters.


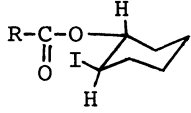
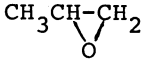
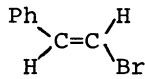

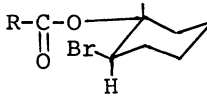
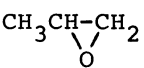
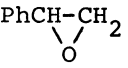
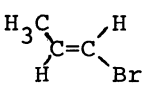

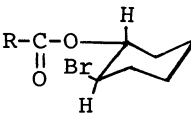
The reaction of iodobenzene with $\text{Ni}(\text{CO})_4$ in tetrahydrofuran (THF) has been known to give benzil.²⁾ When this reaction was carried out in the presence of cyclohexene oxide, the product obtained was trans-2-iodocyclohexyl benzoate. The reaction was carried out as follows. A mixture of iodobenzene (0.03 mol), $\text{Ni}(\text{CO})_4$ (0.03 mol) and cyclohexene oxide (0.02 mol) in THF (50 ml) was stirred at 55-60°C for 15 hr under nitrogen. The mixture was then hydrolyzed with 2N-HCl and extracted with ether followed by distillation to give β -iodocyclohexyl benzoate (65%). The reaction using some organohalides and olefin oxides gave similar results as shown in the Table.



Obviously, aroylnickel carbonyl iodide is initially formed as an intermediate from the reaction of iodobenzene with $\text{Ni}(\text{CO})_4$ and the complex thus formed undergoes electrophilic attack on oxygen atom of cyclohexene oxide.

It is interesting that the halogen atom of the starting material was introduced into the product in the present reaction, whereas in the hitherto known acylation of olefins,³⁾ alkynes,⁴⁾ and imines⁵⁾ using acyl-(or aroyl-)nickel carbonyl halides, the acylated products did not bear the halogen atom of the starting organohalides.

Table Halohydrin esters obtained from the reaction of organohalides with $\text{Ni}(\text{CO})_4$ in the presence of olefin oxides

Halide R-X	Olefin oxide	Solv.	Yield* ¹ %	Bp [°C/mmHg]	ν_{CO} [cm^{-1}]	Product* ² (Yield of isomer)
Ph-I		THF	65	135-137/0.2	1730	
	$\text{CH}_3\text{CH}=\text{CH}_2$ 	THF	66	101-105/0.3	1735	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{I}$ (58.4)
						$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}_2\text{CH}(\text{I})\text{CH}_3$ (7.6)
		DMF	78	174-180/0.2	1720	
	$\text{CH}_3\text{CH}=\text{CH}_2$ 	DMF	69	133-136/0.4	1725	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$ (51.7)
						$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ (17.3)
	$\text{PhCH}=\text{CH}_2$ 	DMF	50	170-175/0.3	1730	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}(\text{Ph})\text{CH}_2\text{Br}$ (37.5)
						$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}_2\text{CH}(\text{Ph})\text{Br}$ (12.5)
		DMF	50	68-75/0.8	1730	

*1 Based on olefin oxide used.

*2 The products were isolated by using column chromatography or preparative GLC, and confirmed by the spectroscopic analyses. The products from propylene oxide and styrene oxide were analyzed as the mixture of the isomers.

References

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(Received November 5, 1977)