Reaction of Iodobenzene with Nickel Carbonyl in the Presence of Enamines

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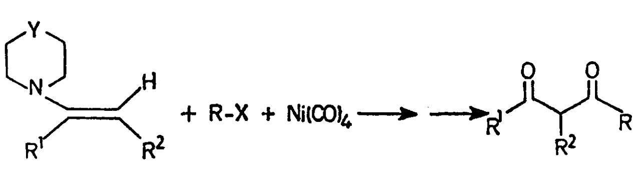
Summary The reaction of iodobenzene with nickel carbonyl in the presence of enamines gave β-diketones in high yields.

IT has already been reported that the acyl-nickel complexes prepared from nickel carbonyl and organic halides react with olefins or acetylenes to give addition products.[1] In these acylations, only olefins having electron-withdrawing substituents such as acrylonitrile, were used because it was assumed that olefins having better co-ordinating ability would give better results. Reactions of olefins substituted by electron-donating groups have not been studied so far. However, acylation of an olefin having electron-donating groups could take place if the acyl groups of the complexes were sufficiently electrophilic† or if the acyl halide was formed by reductive elimination from the complex. It is not necessary in such cases for olefins to be co-ordinated to the metal. We have studied enamines, as representative electron-rich olefins, and have found that β-diketones were obtained in high yields in the reaction of iodobenzene with nickel carbonyl in their presence.



(I) (II)

A mixture of the enamine (0·03 mol), iodobenzene (0·01 mol), and nickel carbonyl (0·01 mol) in benzene (25 ml) was refluxed for 6 h. The mixture was then hydrolysed with 2N-HCl and extracted with ether to give the β-diketone. Similar results were obtained with dimethylformamide or tetrahydrofuran (see Table).

TABLE. Reaction of iodobenzene with nickel carbonyl in the presence of enamines

Enamine (I)	RX	Solvent	Yield of (II)/%
$R^1,R^2=[CH_2]_4$, Y=O ..	PhI	Benzene	87
"	"	DMF	75
"	"	THF	87
"	PhBr	DMF	40
$R^1,R^2=[CH_2]_3$, Y=O ..	PhI	Benzene	73
"	"	DMF	86
R^1=Ph, R^2=H, Y=O ..	"	Benzene	91
$R^1=Pr^n$, R^2=Et, Y=O ..	"	DMF	56
$R^1,R_2=[CH_2]_4$, $Y=CH_2$ ..	"	DMF	52

Without the enamine, the reaction of iodobenzene with nickel carbonyl gave various products including benzophenone, benzil, and benzoyl iodide in both dimethylformamide and benzene. Bauld has reported that the reaction of iodobenzene with nickel carbonyl in hexane or tetrahydrofuran gave benzil,[2] but these compounds were not obtained in the presence of enamines.

The marked difference between the reactions with and without enamines suggests that enamines may be an effective scavenger of an intermediate benzoyl nickel complex.

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† The electrophilic nature of the complex can be judged from its reaction with ethanol to give an ester (ref. 2).

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[2] N. L. Bauld, *Tetrahedron Letters*, 1963, 1841.