Synthesis of Oximes from (Arene)Cr(CO)$_3$ Complexes by Nitrosation at the Benzylic Position

Denis Sénéchal,[a] Marie-Claude Sénéchal-Tocquer,[a] Daniel Gentric,[a] Jean-Yves Le Bihan,[a] Bertrand Caro,[a] Michel Gruselle,[b] and Gérard Jaouen[b]

[a] *Laboratoire de la Chimie des Organométalliques, U.A. 415 Université de Rennes, I.U.T. Lannion, Route de Perros-Guirec, 22300 Lannion, France*

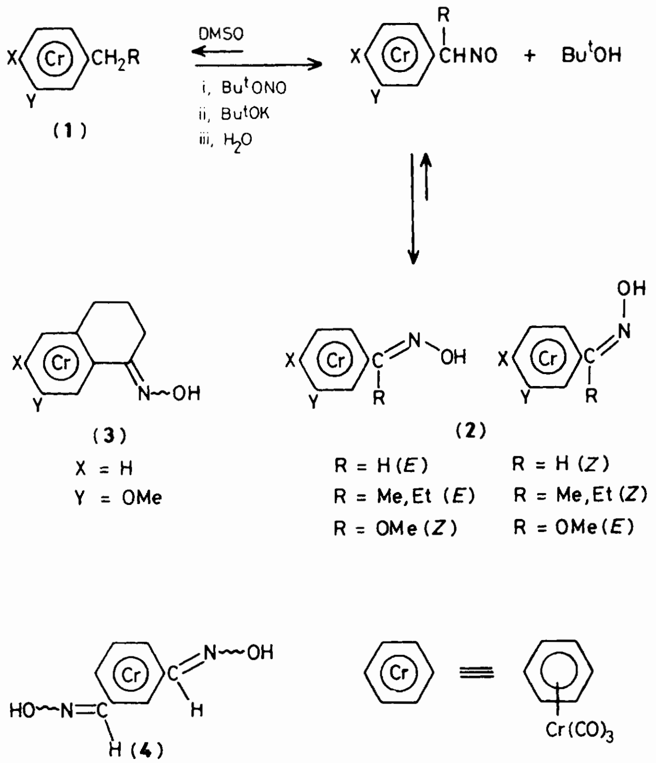
[b] *Ecole Nationale Supérieure de Chimie de Paris, U.A. 403, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*

In basic media, aromatic hydrocarbons complexed by Cr(CO)$_3$ units are readily nitrosated at the benzylic position by Bu^{t}ONO, giving rise to (*Z*)- and (*E*)-oximes in moderate to excellent yields.

As a consequence of the electron-withdrawing effect of the Cr(CO)$_3$ moiety,[1] temporary complexation of an arene substrate increases its susceptibility to proton abstraction from a carbon chain. This increased tendency towards anion formation allows electrophilic attack by substrates that would be unreactive towards the uncomplexed arene.[2] This can overcome synthetic limitations which prevent access to functionalized benzylic species.

Nitrosation of carbanions in basic media is a useful reaction for the preparation of oximes.[3] So far this approach has been limited to aromatic hydrocarbons with benzylic hydrogens activated by *ortho* or *para* nitro groups.[4] We now report that the activation by Cr(CO)$_3$ units, which are easy to attach and remove, provides a novel route to oximes. The use of the enhanced kinetic acidity of Cr(CO)$_3$-benzylic hydrogens has previously been limited to C–C bond formation[5] with few exceptions.[6]

Bu^{t}OK (2 equiv.) was added to a dimethyl sulphoxide



Scheme 1

Table 1.

R	Oximes (2) X	Y	Total yield/%	(*E*)/(*Z*) Ratio/%	M.p./°C
H	H	H	65	(*E*) 26 (*Z*) 39	127 127[b]
H	H	H	80[a]	(*E*) 64 (*Z*) 16	— —
H	H	OMe	67	(*E*) 20 (*Z*) 47	112 97
H	Bu^t	H	37	(*E*) 28 (*Z*) 9	146[b] 124
H	Me	H	45	(*E*) 22.5 (*Z*) 22.5	118 140
Me	H	H	49	(*E*) 34.5 (*Z*) 14.5	137 117[b]
Et	H	H	47	(*E*) 34.5 (*Z*) 12.5	117 120[b]
OMe	H	H	85	(*Z*) 46.5 (*E*) 38.5	135 86
	(**3**)		60	Mixture of (*Z*)- and (*E*)-isomers	
	(**4**)		38	Mixture of isomers	

[a] Reaction temperature 20 °C instead of 0 °C. [b] Decomposition.

(DMSO) solution of complexed aromatic hydrocarbons (**1**) (1 equiv.) and t-butyl nitrite (5 equiv.) at 0 °C giving rise, after hydrolysis, to a mixture of isomeric oximes (**2**) and (**3**) with yields between 37—80% (Table 1) (Scheme 1). The oximes were separated by t.l.c. (silica gel; solvent diethyl ether–light petroleum) and characterized by ^{1}H n.m.r.,[7] i.r., and mass spectroscopy and elemental analysis.

From Table 1, it can be seen that substitution by alkyl groups of either the *para* position on the arene ring or the benzylic site decreases the reaction yield. In order to shed light on the regioselectivity of this functionalisation, the behaviour of *ortho, meta*, and *para* complexed xylenes has been examined in the presence of a large excess of base (4 equiv.) and t-butyl nitrite (10 equiv.). While for the *ortho* derivative no oxime formation (but several unidentified products) was detected, the *para* compound gave an (*E*)–(*Z*) mixture of mono-oximes. A mixture of isomeric dioximes (**4**) (38%) together with monoximes (18%), is obtained from the *meta* substituted substrate. The result from the *o*-xylene complex is certainly a consequence of the proximity of the two methyl groups; the difference in reactivity observed between the *meta* and *para* xylene complexes could be a result of the electronic effect of the potassium oximate group. It has been reported that complexation of the Cr(CO)$_3$ moiety does not affect the electronic properties of the substituent compared to the free ligand.[2,8]

Formation of a new carbanion from the *para* methyl oximate anion seems unlikely because of delocalisation of the negative charge on the arene species. Such a delocalisation cannot occur in the *meta* complex, therefore dioximes are formed.

It appears that the oxime isomer ratio depends on (i) the reaction temperature, (ii) the substitution at the benzylic position, and (iii) the presence of substituents on the arene ring. Finally, it is worth noting that methyl ether benzyl tricarbonyl chromium led to (*Z*)- and (*E*)-methyl hydroximates (Table 1) in excellent yield (85%).

This result, free from Wittig transposition,[9] provides a direct pathway to this type of compounds.

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