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ACYL DERIVATIVES OF HYDROXAMIC ACIDS AS A SOURCE OF CARBON RADICALS*

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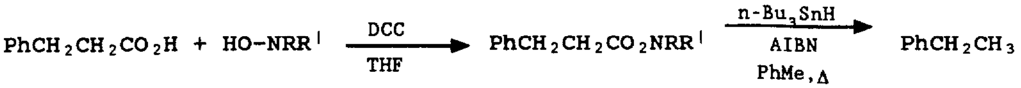
Summary. Acyl derivatives of a number of hydroxamic acids are smoothly reduced by tributyltin hydride with initiation by AIBN to give the corresponding nor-hydrocarbons in a new radical chain reaction.

In the last five years we have developed an extensive family of radical reactions based on acyl derivatives of several thiohydroxamic acids.[1] The most practical system is that using N-hydroxy-2-thiopyridone, an inexpensive, commercially available reagent.[2] The success of this chemistry is due to the disciplinary action of the thione function on carbon and other radicals and to the weakness of the nitrogen-oxygen bond. It was of interest to compare thiohydroxamic acid derivatives with ordinary hydroxamic acid derived compounds, since the latter retain the weak nitrogen-oxygen bond (Scheme 1).

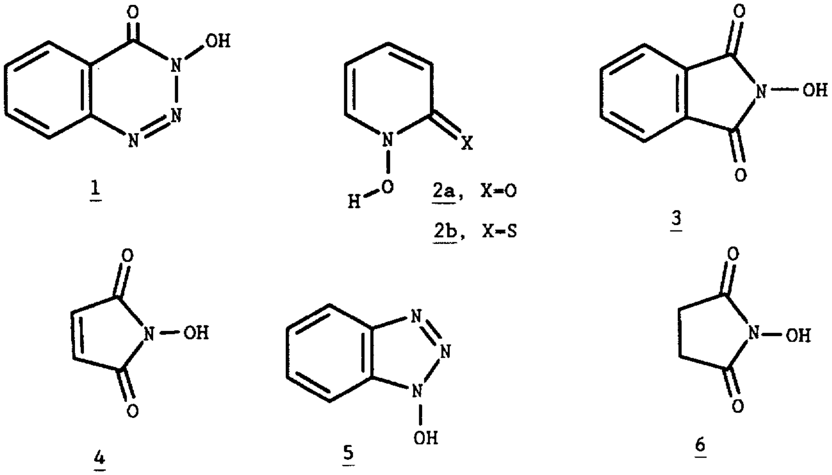
We summarize in Scheme 2 and Table 1 the radical chemistry that we have accomplished. The acyl derivatives of compounds 1 through 6 were readily prepared using cyclohexyl carbodiimide. For convenience, comparative experiments were carried out using dihydrocinnamic acid. The derivative (n mmol.) was reduced with a total of 3n mmol. of tributyltin hydride in toluene under reflux. The tin hydride and the initiator (0.1n mmol. of azo-isobutyronitrile (AIBN)) were added in toluene at the same time. The

This article is dedicated to the memory of an old friend, the late Professor Max Mousseron of Montpellier.



$$\mathrm{PhCH_2CH_2CO_2H + HO{-}NRR'} \xrightarrow[\mathrm{THF}]{\mathrm{DCC}} \mathrm{PhCH_2CH_2CO_2NRR'} \xrightarrow[\mathrm{AIBN}\atop \mathrm{PhMe,\Delta}]{n\text{-}\mathrm{Bu_3SnH}} \mathrm{PhCH_2CH_3}$$

Scheme 1



Scheme 2

Table 1.[a] DECARBOXYLATION OF VARIOUS DIHYDROCINNAMIC ACID DERIVATIVES

Entry	Starting Compound	Acyl Deriv. Yield (%)	MP of Acyl Deriv. (%)	PhEt(%)	Decarboxylation reaction time (hr.)
1	1	100	87-90	97	3.0
2	2a	100	76-79	73	2.5
3	3	88	79-80	62	1.5
4	4	30	97-99	49	1.25
5	5	93	88-91	0	3.0
6	6	48	108-110	2	1.5

a) The acyl derivatives were synthesized by using equimolar amounts of the corresponding carboxylic acid, N-hydroxy compound, and DCC in THF. The exceptions were: Entry 2 where methylene dichloride was used as solvent and Entry 3 where 4-dimethylaminopyridine was used in catalytic amount (10%). Compounds 1 through 6 were commercially available (from Aldrich).

yield of ethylbenzene was determined by g.l.c. with an appropriate internal standard.

Using N-hydroxybenzotriazin-4-one (Entry 1), an excellent yield of hydrocarbon was obtained. Without the initiator and the tributyltin hydride, there was no reaction and the acyl derivative was recovered unchanged. N-hydroxy-2-pyridone (Entry 2) behaved similarly. It was of interest that N-hydroxybenzotriazole 5 gave a derivative which showed no sign of fragmentation. Likewise N-hydroxysuccinimide 6 did not have a fragmenting derivative. The compounds 1 through 4, of which the derivatives all showed fragmentation, have in common the possible addition of the tin radical to the oxygen of a carbonyl group to give a stabilized radical. This can then fragment to give the acyloxy radical and thence the β-phenylethyl radical. In fact, the reduction for the derivative of 2a is analogous to that of the N-hydroxy-2-thiopyridone 2b derivative.[1]

We have examined the derivatives of 1 and 2a to see if their chemistry is of comparable efficiency to that of derivatives of 2b. In fact, the only reaction that works well for 1-based derivatives is the tin hydride reduction. Clearly, the thiocarbonyl group of 2b derivatives is very important for propagating chain reactions..

The dihydrocinnamyl derivative of 1 reported here was stable to tungsten light. Also, the tin hydride reduction was not affected by such light. This is another contrast, for the derivatives of 2b give radical chain chemistry merely on irradiation with tungsten light.

In a series of papers M. Hasebe[3] has shown that acyl derivatives of benzophenone oxime are photolyzed by a high pressure mercury lamp to give acyloxy radicals and then carbon radicals. These are non-chain photochemical reactions.

Similarly,[4] a high pressure mercury lamp is used in the photolysis and electron transfer cleavage of acyl derivatives of 3. This procedure gives carbon radicals, again in a non-chain reaction with a quantum yield of about 0.1.

Mention must also be made of the pioneering experiments[5] on the photolysis of aroyl derivatives of 2a in benzene to furnish diaryls by a non-chain radical reaction.

The conclusion to be drawn from this and related work[3-5] is that acyl derivatives of thiohydroxamic acids[1,2] are far superior to the corresponding hydroxamic acid derivatives in the scope of their radical chemistry.

Acknowledgement

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