A New Radical Decarboxylation Reaction for the Conversion of Carboxylic Acids into Hydrocarbons

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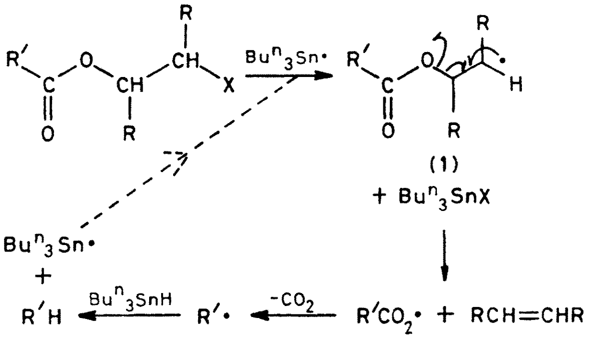
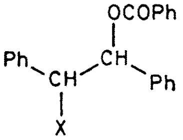
Summary The esters of *trans*-9-hydroxy-10-phenylthio- or -10-chloro-9,10-dihydrophenanthrene are smoothly reduced under neutral conditions by tri-n-butylstannane to furnish, by radical elimination, phenanthrene and the nor-hydrocarbon formed from decomposition of the corresponding acyloxy radical

THE decarboxylation of unactivated carboxylic acids to the corresponding nor-hydrocarbons is a useful synthetic reaction[1,2] The thermolysis of per-esters is often used, but requires a relatively high temperature and does not give good yields[2,3] Alternative procedures involving decarbonylation are known but require two steps[4] A process consisting of a modified Hunsdiecker reaction followed by reduction of the derived halide with tri-n-butylstannane has also been described[5]

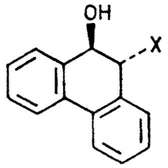


SCHEME

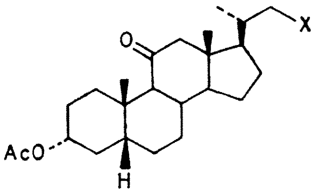
We envisaged that efficient generation of carboxyl radicals could be achieved by an olefin-forming radical fragmentation reaction[6] (Scheme) In the steroidal series, however, it has been shown[7] that tri-n-butylstannane reduction of vicinal chlorohydrin esters leads only to dehalogenation and not to fragmentation of the intermediate radical (**1**) We considered that the formation of a conjugated olefinic system would provide the additional driving force necessary for the fragmentation Decarboxylation followed by hydrogen atom transfer from tri-n-butylstannane would complete the chain reaction



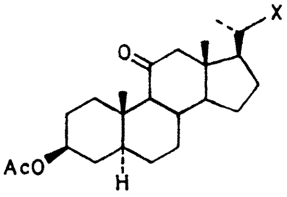
(2) X = Cl
(3) X = H



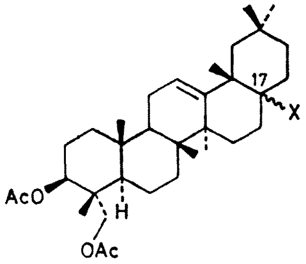
(4) X = SPh
(5) X = Cl



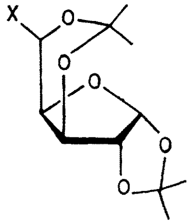
(6) X = CH_2CO_2H
(7) X = Me



(8) X = CO_2H
(9) X = H



(10) X = β − CO_2H
(11) X = H



(12) X = CO_2H
(13) X = H

TABLE[a]

Acid	Method of synthesis[b]		Temp[f]	Yield/%
Stearic acid	(i)	Heptadecane	(A)	90
(**6**)	(i)	(**7**)	(A)	72
(**8**)	(i)	(**9**)[c]	(A)	68
Adamantane-1-carboxylic acid	(ii)	Adamantane	(A)	62
(**10**)	(ii)	(**11**)	(A)	59
3-Dimethylaminobenzoic acid	(i)	*NN*-Dimethylaniline[d]	(B)	65
4-Acetoxybenzoic acid	(i)	Acetoxybenzene[e]	(B)	21
Coumarin-3-carboxylic acid	(iii)	Coumarin	(A)	0
			(B)	16
			(C)	53

[a] Satisfactory analyses and spectral data were obtained for all new compounds [b] (i) Dicyclohexylcarbodi imide, 4 dimethylaminopyridine (C Gilon, Y Klausner, and A Hassner *Tetrahedron Lett* , 1979, 3811) (ii) Ester formation *via* acid chloride (iii) 2-Chloro-*N*-methylpyridinium iodide, 4-dimethylaminopyridine (T Mukaiyama, *Angew Chem Int Ed Engl* , 1979, **18** 707) [c] D H R Barton, M V George, and M. Tomoeda *J Chem Soc* , 1962, 1967 [d] Isolated as the picrate [e] Isolated as 2 4,6-tribromophenol [f] (A) Reflux in benzene (B) Reflux in toluene (C) Reflux in xylene

Initially, we studied the reduction of the chloro-benzoate (**2**).[8] However, treatment with tri-n-butylstannane in refluxing toluene solution led exclusively to the benzoate (**3**) by replacement of halogen. Stilbene was not formed.

It was therefore apparent that the formation of a fully aromatic system was desirable. Ring opening of phenanthrene epoxide[9] with thiophenoxide anion led smoothly to the crystalline alcohol (**4**). Although optimum conditions have yet to be established, esterification with the appropriate carboxylic acid can be realised by a variety of methods. Subsequent dropwise addition of tri-n-butylstannane (3 equiv.) to a refluxing solution of the ester in benzene or toluene with added azobisisobutyronitrile as radical initiator led to the formation of the desired hydrocarbon.

Examination of the Table reveals that preparatively useful yields of hydrocarbons can be obtained under mild conditions from primary, secondary, and tertiary carboxylic acids. The steroidal examples (**6**), (**8**), and (**10**) illustrate the functional group compatibility of this new reaction. The higher reaction temperatures required for the decarboxylation of aromatic and $\alpha\beta$-unsaturated ester derivatives are in accordance with previous data.[10]

We have extended this work to the reduction of esters of *trans*-9-hydroxy-10-chloro-9,10-dihydrophenanthrene[11] (**5**). Here the work-up procedure is easier. The ester from the acid (**8**) gave the decarboxylated product (**9**) (72%); whilst the ester from the acid (**6**) gave product (**7**).

In the carbohydrate series we have converted the glucuronic acid derivative[12] (**12**) into the decarboxylated product (**13**) (53%) without difficulty using the phenylthio-ester method.

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