Tetrahedron Letters No. 19, pp 1545 - 1548, 1975. Pergamon Press. Printed in Great Britain.

A NEW SYNTHESIS OF OLEFINS FROM β-HYDROXY CARBOXYLIC ACIDS

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(Received in Japan 17 February 1975; received in UK for publication 1 April 1975)

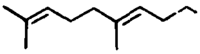
Ever since the discovery of Wittig reaction in 1953,[1] a great deal of efforts have been devoted by synthetic chemists to explore even more general and efficient route for carbonyl-olefination,[2] and two of the modern and successful methods are those of Barton[3] and Coates.[4] Recently, a number of effective procedures for converting carbonyl compounds to β-hydroxy carboxylic acids have become available.[5] We report herein a new approach for the dehydrative-decarboxylation of β-hydroxy carboxylic acids to olefins, which is operationally simple, highly selective, and efficient.

Treatment of N,N-dimethylformamide dimethyl acetal (DMF acetal)[6] with a wide variety of β-hydroxy carboxylic acids in chloroform furnished the corresponding olefins in synthetically useful yields. Best results were obtained in general by using excess DMF acetal (~6 equiv) over β-hydroxy carboxylic acid in dry chloroform at 25° for 1 hr. The resulting solution was heated at reflux for 5-10 hr, concentrated in vacuo, and the residue subjected to simple column chromatography (silica gel, hexane) to yield the pure olefin.

The synthetic process is precedented only by the recently well developed method of Adam[5c] and Krapcho:[7] the formation of β-lactone with benzenesulfonyl chloride-pyridine followed by pyrolysis at 140-160°. The present one-flask olefin synthesis, however, appeared to be much more convenient than the previous route in view of higher yield of the products and the operational simplicity. We need neither isolate any unstable intermediate nor control strictly the reaction and work-up conditions. Furthermore, with our new procedure in hand, mono-, di-, tri-, and tetrasubstituted ethylenic derivatives can all be synthesized under very mild conditions. Some of our results are given in Table I.

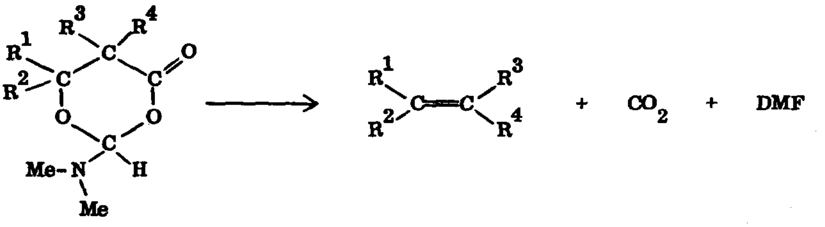
Table I. Olefins Synthesized from β-Hydroxy Carboxylic Acids.[a]

$R^1R^2C(OH)-C(COOH)R^3R^4 \xrightarrow{\text{DMF acetal}} R^1R^2C{=}CR^3R^4$

R^1, R^2		R^3, R^4		% Yields[d]
$-(CH_2)_{11}-$[e]		H	H	91
$-(CH_2)_{11}-$		Me	H	92
$-(CH_2)_{11}-$		Me	Me	90
$-(CH_2)_4-$		Ph	H	84
$\underline{n}-C_9H_{19}$	H[e]	H	H	55
$\underline{n}-C_8H_{17}$	H	Me	Me	63
$\underline{n}-C_9H_{19}$	H	Me	H	90[f]
Ph	Ph[e]	H	H	88
Ph	H[g]	$\underline{n}-C_5H_{11}$	H	90
	Me	Me	Me	70

[a] Most of these reactions were carried out on a 1 mmol scale. [b] Unless otherwise stated, the β-hydroxy carboxylic acids were prepared from the corresponding carbonyl compounds and the carboxylic acid dianions as described in ref. 7. [c] All products have been isolated by column chromatography (silica gel, hexane) and adequately characterized by analytical and spectral data. [d] Yields were not optimized except cyclododecylidene cases. [e] Prepared by the reaction of the lithium enolate of ethyl acetate (M. W. Rathke, J. Amer. Chem. Soc., **92**, 3222 (1970)) followed by hydrolysis. [f] Determined by glpc assay. [g] Prepared by (1) treatment of n-hexyl phenyl ketone with lithium diisopropylamide in dry THF at 0° followed by (2) reaction with carbon dioxide in the presence of sodium borohydride.

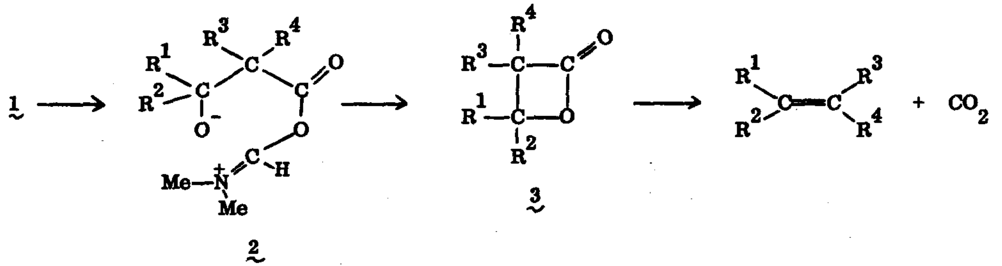
With regard to the mechanism of formation of olefins from β-hydroxy carboxylic acids, it is attractive to suppose the elimination occurs via intermediate of type **1** capable of thermally allowed [2 + 2 + 2] fragmentation to yield the olefins, carbon dioxide, and dimethylformamide (eq. 1).[8,9] Reasonable



(1)

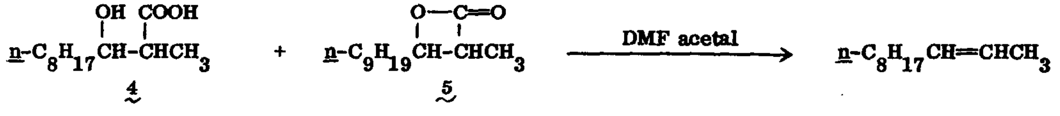
1

alternative mechanisms can be devised, however, which deserve serious consideration: the mixed acetal 1 on being heated transforms into the imidate 2, and then β-lactone 3 which finally undergoes a fragmentation to produce the desired olefin (eq. 2).

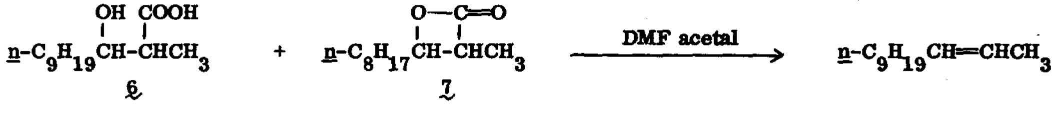


(2)

The supposition that elimination occurs via the concerted fragmentation mechanism and against the β-lactone pathway is consistent with the demonstration of the much greater ease of such elimination from the intermediate 1 than from the corresponding β-lactone. Thus, a mixture of the β-hydroxy carboxylic acid 4, the β-lactone 5,[10] and excess DMF acetal in dry chloroform was heated at reflux. After 3 hr, the produced olefins were separated by chromatography and analyzed by glpc. 2-Undecene was produced in 54% yield, while none of 2-dodecene was present (<1%). On the other hand, the β-hydroxy carboxylic aicd 6, and the β-lactone 7[10] were treated similarly to afford only 2-dodecene (57%) after 3 hr. Even after 18 hr, 2-undecene was produced <5%, while the yield of 2-dodecene was raised up to 90%.



$$\underset{4}{n\text{-}C_8H_{17}CH(OH)\text{-}CH(COOH)CH_3} + \underset{5}{n\text{-}C_9H_{19}CH\text{-}CHCH_3\ (O\text{—}C{=}O)} \xrightarrow{\text{DMF acetal}} n\text{-}C_8H_{17}CH{=}CHCH_3$$



$$\underset{6}{n\text{-}C_9H_{19}CH(OH)\text{-}CH(COOH)CH_3} + \underset{7}{n\text{-}C_8H_{17}CH\text{-}CHCH_3\ (O\text{—}C{=}O)} \xrightarrow{\text{DMF acetal}} n\text{-}C_9H_{19}CH{=}CHCH_3$$

The designation of the CO_2 and DMF extrusion from **1** as a [2 + 2 + 2] cycloreversion implies concertedness for this reaction. The above results indicate, but do not conclusively prove, these properties.

REFERENCES

1. G. Wittig and G. Geissler, *Ann. Chem. Liebigs*, **580**, 44 (1953).
2. J. Reucroft and P. G. Sammes, *Quart. Rev. (London)*, **25**, 135 (1971).
3. D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Perkin I*, 305 (1972).
4. (a) R. L. Sowerby and R. M. Coates, *J. Amer. Chem. Soc.*, **94**, 4758 (1972); (b) I. Kuwajima and M. Uchida, *Tetrahedron Lett.*, 649 (1972); I. Kuwajima, S. Sato, and Y. Kurata, *ibid.*, 737 (1972).
5. (a) G. Moersch and A. R. Burkett, *J. Org. Chem.*, **36**, 1149 (1971); (b) P. E. Pfeffer, E. Kinsel, and L. S. Silbert, *ibid.*, **37**, 1256 (1972); (c) W. Adam, J. Baeza, and J. C. Liu, *J. Amer. Chem. Soc.*, **94**, 2000 (1972).
6. Purchased from Aldrich Chemical Company, Inc.
7. M. U. S. Sultanbawa, *Tetrahedron Lett.*, 4569 (1968); A. P. Krapcho and E. G. E. Jahngen, Jr., *J. Org. Chem.*, **39**, 1322 (1974); A. P. Krapcho and E. G. E. Jahngen, Jr., *ibid.*, **39**, 1650 (1974); See also ref. 5c.
8. In support of this hypothetical intermediate **1** we cite the facile exchange reaction in formamide acetal with *vic*-diols: H. Newman, *Chimia*, **23**, 267 (1969). See also, F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Lett.*, 5223 (1970).
9. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.
10. Prepared from the corresponding β-hydroxy carboxylic acid by the procedure of Krapcho (ref. 7) in 30-40% yields.