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OLEFIN SYNTHESIS VIA FRAGMENTATION OF HINDERED ESTER HALIDES

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Hindered methyl esters possessing allylic or benzylic bromine substituents undergo smooth dealkylative decarboxylation to afford olefinic derivatives.

Heterolytic fragmentations play a significant role in synthetic methodology.[1] A subclass of such reactions, halide-initiated dealkylative decarboxylations, provides a convenient source of enolates[2] and ylides[3,4]. While attempting to extend to ammonium salts our recently disclosed[4] decarboxylative fragmentation, we discovered an unexpected reaction. NBS bromination of ester 1a gives halide 1b. Attempted displacement of the bromide with pyrrolidine (1.5M) in CCl_4 leads only to slow formation of amide 1c. Surprisingly, treatment of 1b with neat pyrrolidine at reflux, rather than producing amine 1d, affords olefin 3a in good yield (59%).

Conversion of 1b to 3a in pyrrolidine requires heating overnight at reflux. Upon examining other solvents, we find that HMPA at 140-145° is even more satisfactory. Added halide anion is not required. After thermolysis to disappearance of starting material, a standard work-up is performed[5].

In the Table we report[6] selected examples of allylic and benzylic halides which undergo this transformation. Particularly noteworthy is our conversion of a malonate to a synthetically useful[7] diene ester (entry 6). Our fragmentation is somewhat reminiscent of the well-known[8] β-bromopropionic acid decarboxylations. We initially postulated a cyclic 6-membered transition state involving synchronous attack upon the methyl group by departing bromide. However, the facile reaction of terminal allylic halides suggests a more complex mechanism.

Synthesis of suitable precursors constitutes the main limitation of our new methodology. For hindered benzylic systems bromination is sluggish and appreciable quantities of byproducts result. Comparable allylic substrates undergo NBS bromination only at their terminal carbon with concomitant formation of a trans-disubstituted double bond.

Further studies exploring mechanistic, stereochemical, and synthetic aspects of this fragmentation are in progress.

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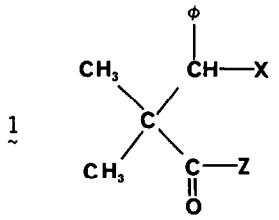
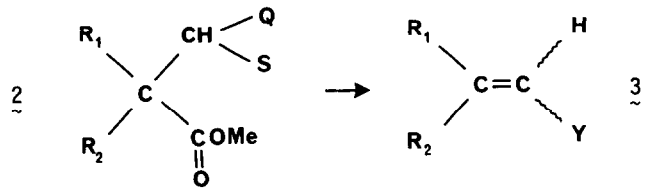


1

1a X=H; Z=OCH_3
1b X=Br; Z=OCH_3
1c X=Br; Z=NC_4H_8
1d X=NC_4H_8; Z=OCH_3

TABLE



2 3

HMPA - 143°C

(1.) 2a ≡1b:	R_1=R_2=CH_3; Q=Br; S=Ø	3a	R_1=R_2=CH_3; Y=Ø (95%)
(2.) 2b	R_1,R_2=$(CH_2)_5$; Q=Br; S=Ø	3b	R_1,R_2=$(CH_2)_5$; Y=Ø (80%)
(3.) 2c	R_1=R_2=S=Ø; Q=Br	3c	R_1=R_2=Y=Ø (71%)
(4.) 2d	R_1=CH_3; R_2=$COOCH_3$; Q=Br; S=Ø	3d	R_1=CH_3; R_2=$COOCH_3$; Y=Ø (70%)
(5.) 2e	R_1=Ø; R_2=$COOCH_3$; Q=Br; S=Ø	3e	R_1=Ø; R_2=$COOCH_3$; Y=Ø (70%)
(6.) 2f	R_1=CH_3; R_2=$COOCH_3$; Q,S=(=$CHCH_2Br$)	3f	R_1=CH_3; R_2=$COOCH_3$; Y=CH=CH_2 (68%)

References and Notes:

1. K. B. Becker, C. A. Grob in "The Chemistry of Double-Bonded Functional Groups," Part 2, Supplement A, S. Patai, Ed., Interscience, New York, 1977, pp. 653-723.
2. S. Takei, Y. Kawano, Tet. Lett., 4389 (1975); M. Asaoka, K. Miyake, H. Takei, Chem. Lett., 1149 (1975); R. G. Eilerman, B. J. Willis, J. Chem. Soc., Chem. Commun., 30 (1981).
3. H. J. Bestmann, H. Hartung, I. Pils, Angew. Chem. Intern. Ed., 4, 957 (1965).
4. J. L. Belletire, D. R. Walley, M. J. Bast, Syn. Commun., 12, 469 (1982).
5. The thermolysis is performed under an argon atmosphere at a concentration of approx. 1 ml HMPA/mmole substrate. Work-up involves dilution with ethyl ether and repeated extraction with water. A final Kugelrohr-type purification of the residue follows distillation of the ether through a Vigreaux column. The water washes have a neutral pH. For the conversion of 1b to 3a, 1,3-dimethyl-2-imidazolidinone is a successful alternative solvent to HMPA.
6. All compounds gave satisfactory analytical data.
7. D. B. Tulshian, B. Fraser-Reid, J. Amer. Chem. Soc., 103, 474 (1981).
8. W. R. Vaughan, W. F. Cartwright, B. Henzi, J. Amer. Chem. Soc., 94, 4978 (1972).

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