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The Decarboxylative Dehydration of 4.5-Unsaturated 3-Hydroxycarboxylic Acids with Dimethylformamide Dimethylacetal - an Efficient Synthesis of Sensitive 1.3-Dienes.

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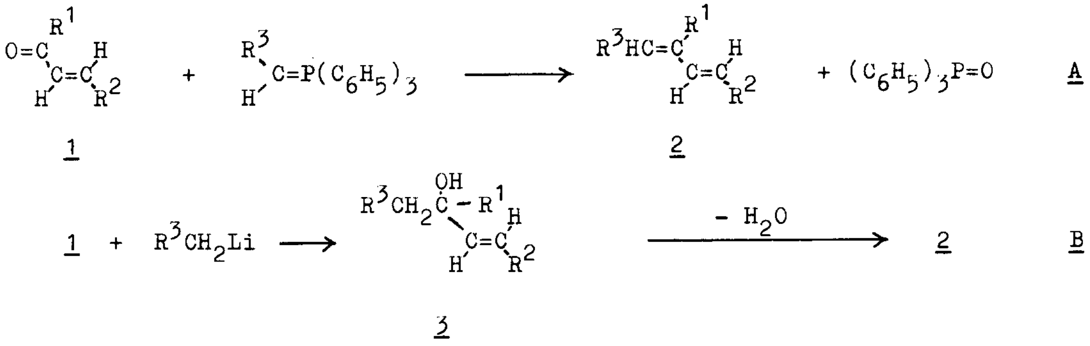
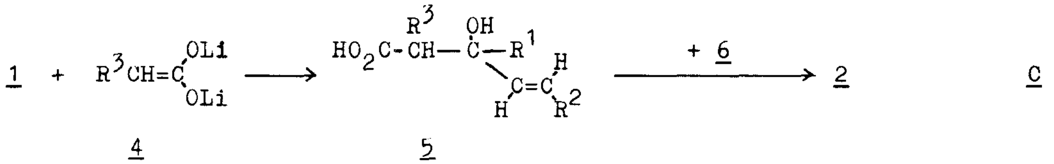
The olefination of $\alpha.\beta$-unsaturated ketones (1) is an important method for the preparation of 1.3-dienes[1]. Generally this reaction is performed in two ways, A and B, which are both deficient in certain respects. The WITTIG-condensation A, for instance, has to cope with the low reactivity of 1 towards phosphoranes and thus requires conditions too rigorous for the synthesis of sensitive dienes. So all efforts to prepare 1.3-diphenyl-1.3-butadiene (2a) from benzalacetophenone and methylene triphenylphosphorane resulted only in the formation of the 2a-dimers.[2] Similarly, reaction B implies prolonged heating of the carbinol intermediate 3 with dehydrating agents like $KHSO_4$, $POCl_3$ etc. which have an isomerizing, dimerizing or polymerizing effect on many dienes[3]. An additional drawback of B lies in the ambiguous regiochemistry of the dehydration step (3→2), if R^1 has at least one hydrogen α to the carbinol carbon.



We wish to report a new method (C) for a regiospecific olefination of 1 under very mild conditions, which allow even the synthesis of the unstable 1.3-diaryl-1.3-butadienes 2a-2c[4]. In a previous communication[5] we have shown that a variety of 4.5-unsaturated 3-hydroxycarboxylic acids 5 can easily be obtained from the addition of dilithium carboxylates (4) to 1. The decarboxylative dehydration[6] of 5 with dimethylformamide dimethylacetal (6) ($CHCl_3$, 22°, 1hr, workup by TLC (silicagel, ligroin-ether 4:1) or by distillation at 0.001 torr) furnishes 2 in good yields (Table 1).



The trans-styryl-unit of 1 is not affected by the reaction and reappears in 2 unchanged. The new dienes in Table 1 have been characterized by IR, ^{1}H-NMR and combustion analysis and, in the case of 2a, 2b and 2c, also by the formation of the dimers (2a-dimer: mp.135-137°[3], 2b-dimer: mp.141-142°, 2c-dimer: oil). From 2a the TCNE-(mp. 142-143°), maleic anhydride[7]-(mp.152-154°) and the 4-phenyl-1.2.4-triazoline-3.5-dione- (mp.167-168°) adducts have been prepared.

Table 1. Dienes 2 prepared according to equation C.

Diene	R^1	R^2	R^3	bp / 0.001 torr	% yield
2a	C_6H_5	C_6H_5	H	-	65[a]
2b	"	2-thienyl	H	-	86[a]
2c	"	2-furyl	H	-	62[a]
2d	CH_3	C_6H_5	H	70-80°	70
2e	C_2H_5	"	H	75-85°	80
2f	$CH(CH_3)_2$	"	H	80-90°	75
2g	$C(CH_3)_3$	"	H	90-100°	77
2h	H	"	H	35-45°	70
2i	H	"	CH_3	70-80°	75[b]
2j	C_6H_5	"	CH_3	100-110°	77[a,b]

a. In these cases C was run with mixtures of 5 and the corresponding 1.4-adduct[5] from 4 and 1. 6 converts the 1.4-adduct into the methyl ester which can be easily separated from 2 by TLC. The yields of 2a,b,c and j refer to the amount of 5 initially present in the mixture. b. Mixture of cis-trans-isomers.

References and Notes.

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