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## Reaction of 1,3-Dilithioacetylides with Carbonyl Electrophiles: Preparation of Allene-1,3-dicarboxylic Acids

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Summary 1,3-Dilithioalk-1-ynes react with carbon dioxide and give alk-2,3-dien-1,5-dioic acids; in contrast the acetylenes, alk-2-yn-1,5-diols are isolated on reaction with aldehydes and ketones.

1,3-DILITHIOALK-1-YNES<sup>1</sup> (1) can be used to prepare branched<sup>1,2</sup> and linear<sup>3</sup> acetylenes by regioselective alkylations with alkyl halides [Scheme,  $(1) \rightarrow (2) \rightarrow (3)$ ]. These



iii, CO<sub>2</sub>; iv, CH<sub>2</sub>O or  $[CH_2]_n C=O$  (n = 4, 5, or 6).

studies have now been extended by treating 1,3-dilithioacetylides with carbon dioxide, formaldehyde, and cyclic ketones.

Previous work on the carboxylation of 1,3-dilithiobut-1-yne led to the isolation of 2-methylglutaric acid from and 103.69 (s) p.p.m.]. That carboxylation had occurred at C-1 and C-3 to give the allene (4;  $R^1 = n - C_3 H_7$ ) was supported by the long range coupling of the proton at C-1 with methylene group at C-4<sup>5</sup> and confirmed by catalytic hydrogenation in the presence of palladium-charcoal to give the known 3-propylglutaric acid.<sup>6</sup> Two acetylenic monocarboxylic acids (5 and 6;  $R^1 = n-C_3H_7$ ) were also detected after the carboxylation reaction. Similar results were obtained from the carboxylation of dilithiopent-1-yne (1;  $R^1 = Et$ ) and dilithiohept-l-yne (1;  $R^1 = Bu^n$ ) (Table 1). When the order of addition was reversed and

R	Et	Pr <sup>n</sup>	Bun	n-C <sub>5</sub> H <sub>11</sub>
Isolated yield/%	33	37	$31 \cdot 5$	13.5b
M.p./°C	170—172	144—145	136 - 138	146—147

<sup>a</sup> Good analytical data were obtained for the reaction products but the yields were not optimised. b This reaction was carried out by passing carbon dioxide gas into the reaction mixture.

carbon dioxide gas was passed into hexane solutions of dilithio-oct-1-yne (1;  $R^1 = n-C_5H_{11}$ ) and also the lower homologues at ca. -40 °C only poor yields of allene dicarboxylic acids were obtained. The isolation of allene-1,3-dicarboxylic acids was unexpected since with other carbonyl electrophiles,1,2 e.g. formaldehyde, cyclopentanone, cyclohexanone, and cycloheptanone, the expected prop-2-ynylic and terminal acetylenic substitutions occurs and alk-2-yne-1,5-diols (7) are formed together with some of the monohydric alcohols (8 and 9) (Table 2). However, our results are in accord with previous attempts to prepare pent-2-yn-1,5-dioic acid ('glutinic acid')' or its dimethyl ester<sup>8</sup> which led to the isolation of penta-2,3-dien-1,5-dioic

TABLE 2. Alk-2-yn-1,5-diols, R<sup>1</sup>C(R<sup>2</sup>R<sup>3</sup>COH)H-C≡C-C(OH)R<sup>2</sup>R<sup>3</sup> (7), from reactions of formaldehyde and cyclic ketones with 1,3-dilithioalk-1-ynes (1).ª

 $R^2R^3$  (Yield/%)

	*					
R1	Н,Н	[CH <sub>2</sub> ] <sub>4</sub>	[CH <sub>2</sub> ] <sub>5</sub>	[CH <sub>2</sub> ] <sub>6</sub>		
Et	35 (b p 54-56 at 0.04 mmHg)	6 (m p 120-121)				
Pr <sup>n</sup>	46.5	(m.p. 126 - 121) 32 (m.p. 115 - 116)	23 (m p 00)			
Bun	(b.p. 42-45 at 0.1 mmig) 28 (b.p. 59 at 0.02 mmHg)	(m.p. 115—110)	(11.p. 90) 16 (mp. 96)	21 (m p. 95)		
	(0.p. 05 at 0 02 mmile)		(11. p. 00)	(		

<sup>a</sup> Good analytical data were obtained for the reaction products but the yields were not optimised. All b.p.s and m.p.s are in °C.

hydrogenation of the reaction product, but the unsaturated intermediate was not identified.4

Reaction of 1,3-dilithiohex-1-yne (1;  $R^1 = n-C_3H_7$ ) with a slurry of dry carbon dioxide led to the isolation of an allenic dicarboxylic acid (33%), m.p. 144-145 °C [v 1950 cm<sup>-1</sup>; δ <sup>1</sup>H: 6.03 (CH, J ca. 2 Hz); δ <sup>13</sup>C: 91.86 (d), 217.71 (s),

acid<sup>7</sup> or its dimethyl ester.<sup>8</sup> Thus our approach provides a new general method for the synthesis of allene-1,3-dicarboxylic acids.

(Received, 6th November 1978; Com. 1182.)

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