

SYNTHESIS OF A PRESUMED SEX ATTRACTANT OF THE DRIED BEAN BEETLE¹

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(-)-Methyl n-tetradeca-trans-2,4,5-trienoate (1) has been isolated^{3,4} from the male Dried Bean Beetle [Acanthoscelides obtectus (Say)]⁵ and is presumed to be a sex attractant. A synthesis of the racemic ester has recently been reported.⁶ We wish to describe here another synthesis of the racemic ester, using the reaction of a lithium dialkylcuprate with a propargylic allylic acetate to produce the required allene-ene system. Reactions of lithium dialkylcuprates with both isolated allylic acetates (to give alkylated olefins)⁷ and isolated propargylic acetates (to give alkyl allenes)^{8,9} have been reported.

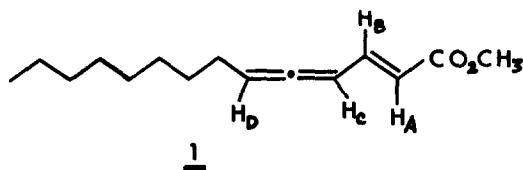


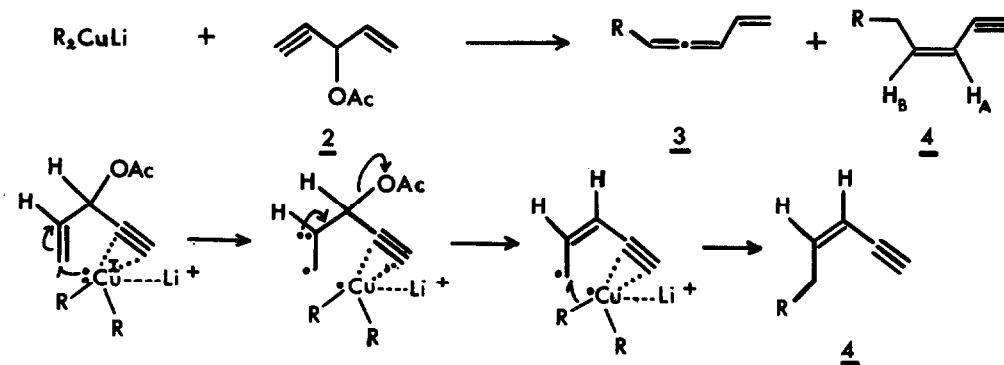


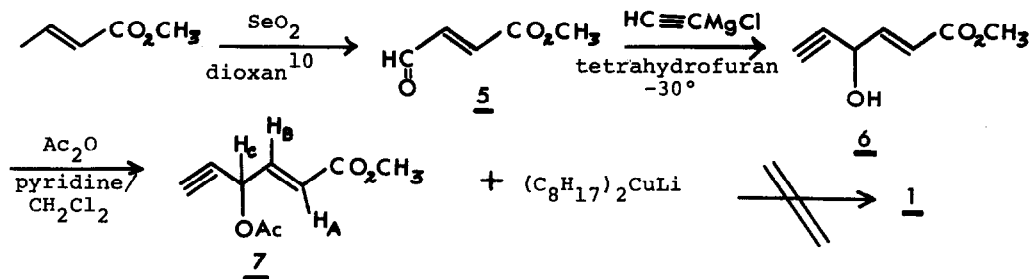
Table I summarizes our exploratory reactions of lithium dialkylcuprates with 3-acetoxy-pent-1-en-4-yne (2). The major product, 3, results from β -addition to the triple bond. The minor product, 4, (separated from 3 by preparative glpc) resulting from the addition to the double bond, has the cis configuration [eg 4b, ir (CS₂) ν_{\max} 740 cm⁻¹, $\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}$; nmr (CCl₄) δ : 5.4 ppm (H_A, J_{AB} \sim 11 Hz)]. The stereoselective formation of 4 suggests the formation of an intermediate complex between the polymeric organocuprate and the triple bond (see below).

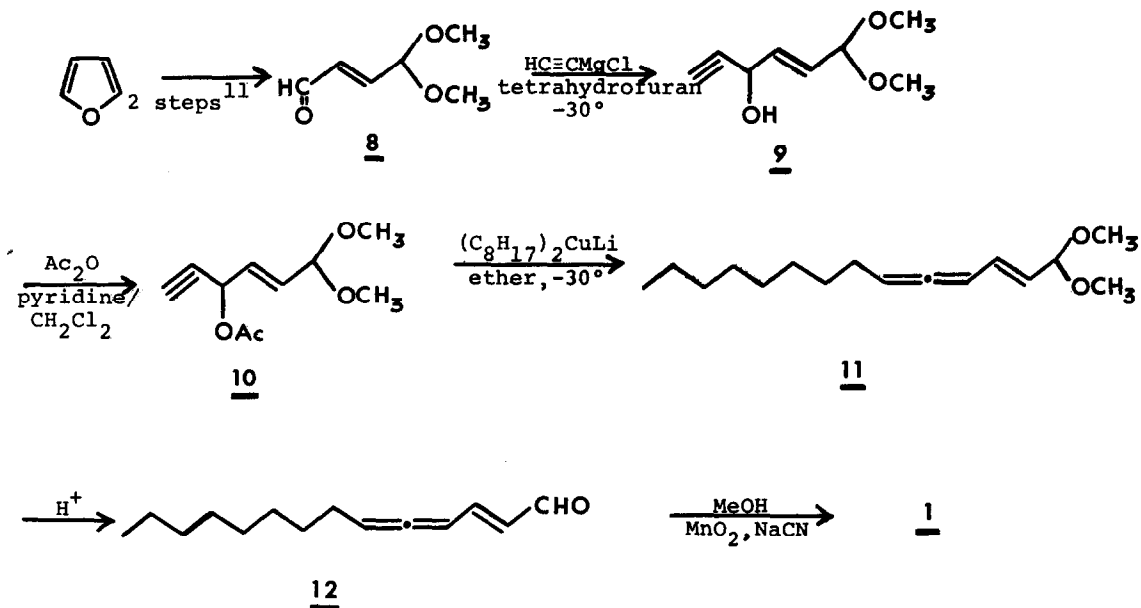
TABLE I

(R) ₂ CuLi	Solvent	Temp	Ratio		Overall Yield % of <u>3</u> + <u>4</u>
			 (<u>3</u>)	 (<u>4</u>)	
a: R = CH ₃	ether	-20°	94	6	42
b: R = C ₄ H ₉	ether	-20°, -30°	80	20	60
c: R = C ₈ H ₁₇	ether	-30°	90	10	52



We attempted to synthesize 1 using the addition of lithium dioctylcuprate in ether (-30°) to methyl 4-acetoxy-hex-2-en-5-ynoate (7) [(prepared as in the reaction scheme); ir (film) ν_{\max} 970 cm^{-1} ; -CH=CH- trans; nmr (CDCl₃) δ : 6.23 (H_A , d, $J_{AB} = 16$ Hz), 6.92 ppm (H_B , q, $J_{AB} = 16$ Hz, $J_{BC} = 5$ Hz)], but the reaction products showed neither allenic absorption in the ir, nor any intense uv absorption; presumably the copper reagent reacted mainly with the $\alpha\beta$ -unsaturated ester double bond.





In contrast, alkylation of the corresponding dimethyl acetal 10 was successful. The latter was prepared by acetylation (90% yield) of the alcohol 9, which resulted from ethynylation (87% yield) of 4,4-dimethoxy-trans-but-2-en-1-al (8) (prepared¹¹ from furan). Reaction of lithium dioctylcuprate with 10 in ether (-30°) gave in 25% isolated yield the allene 11 [purified by preparative tlc; bp_{0.02} 70°; ir (film) ν_{max} 1945, 1685, 1640, 980 cm^{-1} ; nmr (CDCl₃) δ : 6.5-5.1, (m, $\text{H}-\text{C}=\text{C}=\text{H}$ and $-\text{CH}=\text{CH}-$), 4.81 (d, $J=5$ Hz, $-\text{CH}(\text{OCH}_3)_2$), 3.32 (s, 2x OCH_3), 2.05 (m, $\text{CH}_2-\text{C}=\text{C}=\text{C}$), 1.30 (broad s, $-(\text{CH}_2)_6$), 0.90 ppm (broad t, CH_3); mass spectrum, m/e 252 (M^+), 75 (base peak)]. Careful hydrolysis of 11 with 0.1N aqueous HCl in ether at room temperature gave the unstable aldehyde 12 (60% yield) which was oxidized (60% yield) in methanol with MnO_2 -NaCN¹² to the methyl ester 1; ir (film) ν_{max} : 1940, 1720, 1630, 980 cm^{-1} ; λ_{max} (hexane) 253 nm ($\epsilon=24,200$); nmr (CDCl₃) δ : 7.25 (H_B , dd, $J_{AB} \sim 16$ Hz, $J_{BC} \sim 10$ Hz), 6.0 (m, H_C), 5.9 (H_A), 5.48 ppm (m, H_D); mass spectrum, m/e 236 (M^+), 205 ($\text{M}-\text{OCH}_3$), 177 ($\text{M}-\text{COOCH}_3$), 138 ($[\text{C}_8\text{H}_{10}\text{O}_2]^+$), 79 (base peak). The physical constants are in excellent agreement with those obtained by Horler and by Landor.^{4,6,13,14} Investigations of the possible biological properties of 1 are in progress.

References

- (1) Contribution No. 9 from the research laboratory of Zoecon Corporation.
- (2) Zoecon Postdoctoral fellow, 1971-1972.
- (3) J. A. Hope, D. F. Horler and D. G. Rowlands; J. Stored Prod. Res., 3, 387 (1967).
- (4) D. F. Horler, J. Chem. Soc., (C), 859 (1970).
- (5) Coleoptera: Bruchidae.
- (6) P. D. Landor, S. R. Landor and S. Mukasa, J. Chem. Soc. (D)-Chem. Comm., 1638 (1971).
- (7) R. J. Anderson, C. A. Henrick, and J. B. Siddall, J. Amer. Chem. Soc., 92, 735 (1970); P. Rona, L. ~~Tokes~~ Tokes, J. Tremble and P. Crabbé, Chem. Comm., 43 (1969).
- (8) P. Rona and P. Crabbé, J. Amer. Chem. Soc., 90, 4733 (1968).
- (9) P. Rona and P. Crabbé, J. Amer. Chem. Soc., 91, 3289 (1969).
- (10) F. Bohlmann and E. Inhoffen, Chem. Ber., 89, 1276 (1956).
- (11) S. M. Makin and N. I. Telegina, J. Gen. Chem. USSR, 1082 (1962); Chem. Abs. 58, 3308e (1963).
- (12) E. J. Corey, N. W. Gilman, and B. E. Ganem, J. Amer. Chem. Soc., 90, 5616 (1968).
- (13) We are grateful to Dr. Horler for supplying us with copies of the ir and nmr spectra of the natural material for comparison with those of our synthetic 1.
- (14) Satisfactory nmr, ir and mass spectra, and also elemental analyses, were obtained for all new compounds.