

crystallization of the photolysis intermediates from acetone-water also effected their conversion to 7. The infrared absorption of the photolysis product is not that of 5 or 7; its molecular weight and nmr spectrum are consistent with that of a mixture of isomers 6a and 6b. Hydrolysis of 6a and 6b at 40° in aqueous acetonitrile (quartz nmr tubes) is accelerated by irradiation. It is thus apparent that in the unique photochemical hydrations of acetylenes such as 1 and 5, participation of the *o*-amido group plays a very important role. Work is in progress to characterize more fully and establish the mechanisms of formation and hydrolysis of intermediates such as 2 and 6a,b. It is also likely that photochemical neighboring group participation will be a most important effect in other electrophilic, nucleophilic, or related addition systems.

Study of the photochemical reactions of acetylenes with other nucleophiles has been initiated. Photolysis of diphenylacetylene (8) in pure methanol occurs slowly and results primarily in addition to give methyl *trans*- (major, 9) and *cis*- (minor, 10) 1,2-diphenylvinyl ethers (Table I); photochemical reduction of 8 by methanol is

ments was there addition of methanol to 8 resulting in diphenylallyl alcohols. The processes leading to reduction and to addition may be related to either singlet or triplet excited states and/or vibrationally excited ground state. Linear and distorted triplets of different electronic energies may also play a role.⁸ Studies now under way are designed to elucidate which of these excited intermediates are involved.

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(9) National Science Foundation Undergraduate Research Participant, 1968.

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Table I. Photolysis of Diphenylacetylene and Methanol^a

Time, hr	% reaction	9	10	11	12	13
10	33 ^b	62	1	21	10	6
20	35	60	2	19	11	8
40	73	63	3	17	6	10
88	88 ^c	62	6	13	6	14

^a Aliquots were removed at the designated time periods and analyzed by glpc techniques. ^b The unidentified nonvolatile components amount to 8% of the total product. ^c Unidentified nonvolatile components, 15%.

a competitive process in that *cis*- (11) and *trans*-stilbenes (12) are also found. Phenanthrene (13) is also obtained, presumably by photolysis of 11.⁶ Irradiation of 8 (0.01 *M*) in methanol-benzene (1:1 v/v) yielded the same products as in Table I. When 2 equiv of 5,5-dimethyl-1,3-cyclohexanedione (14) was added to the solvents which had been distilled from these reaction mixtures, formal dimethone (mp 189°, lit.⁷ 189, 191°) resulted in high yield. Photolysis of 8 (0.01 *M*) in methanol-mesitylene (1:1 v/v) yields only 11 and 12; upon addition of 14 to the distilled solvent only traces of formal dimethone are formed. Thus addition of methanol is arrested while transfer of hydrogen from mesitylene is noted. In none of the photochemical experi-

(6) F. R. Stermitz in ref 1b, p 248 ff.

(7) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, New York, N. Y., 1957, p 583.

Stereospecific Addition of Alkylcopper Reagents to α,β -Acetylenic Acids. The Nature of the Vinylc Enolate

Sir:

Two communications were published recently on the stereospecific conjugate addition of dimethylcopper-lithium to α,β -acetylenic esters^{1,2} at low temperatures and on the fast isomerization (5 min) of the adduct at 0° in ether solution. We obtained similar,³ although not identical, results when a phenyl was one of the β groups in the product. However, addition of methylcopper⁴ to phenylpropionic acid (1a) gave an enolate that retained its configuration at room temperature for prolonged periods and yielded on protonation mostly⁵ *cis*-

(1) E. J. Corey and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, **91**, 1851 (1969).

(2) J. B. Siddall, M. Biskup, and J. H. Fried, *ibid.*, **91**, 1853 (1969).

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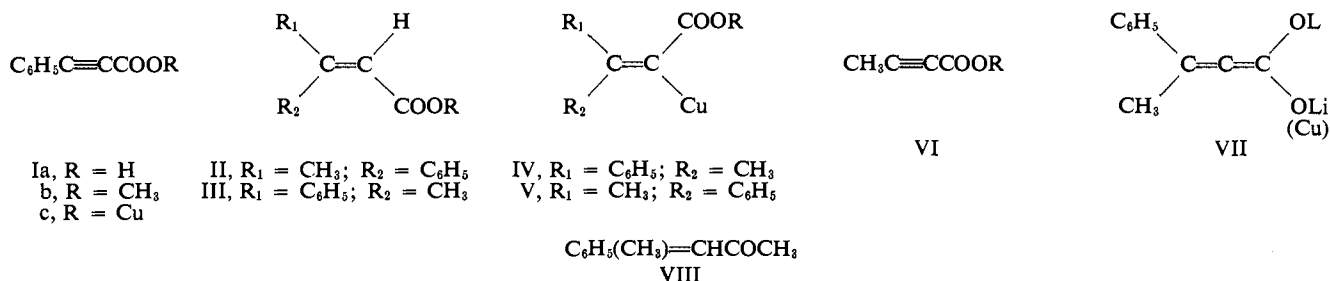
Table I. Reaction of Organocopper Reagents with Conjugated Acetylenic Acids^a

Run	Organometallic reagent	RC≡CCOOR (mmoles)	Cu:C≡C-	Starting material	Yield, %			
					II	III	VIII	Over-all
73	CH ₃ Cu ^b	Ia (20)	2.3:1	0	82	18	0	90
	CH ₃ Li ^c			0	7	90	3	
77	(CH ₃) ₂ CuLi ^b	Ia (20)	2.3:1	0	7	93	<1	84
	CuI ^c			0	15	85	<1	
88	C ₆ H ₅ Cu ^b	VIa (20)	2.3:1	12	11	77	0	75
	C ₆ H ₅ Li ^c			4	12	84	0	
91	(C ₆ H ₅) ₂ CuLi ^b	VIa (20)	2.3:1	4	10	86	0	88
	CuI ^c			4	16	80	0	
80	CH ₃ Cu ^b	Ib (30)	1.5:1	11	36	53	0	72
	CH ₃ Li ^c			0	0	0	53 ^d	
50	(CH ₃) ₂ CuLi	Ib (30)	1.5:1	4	19	35	7 ^d	73 ^c

^a A solution of the acetylenic compound in 20 ml of ether was added with a syringe during 30 min under nitrogen to the copper compound in 70 ml of ether cooled at -60° . The reaction mixture was stirred at -60° for 1 hr and left for 20 hr at room temperature. ^b Half of the solution or supernatant was withdrawn and poured on ice and HCl. ^c The remainder of the reaction mixture was cooled to -60° and this reagent was added in an equivalent amount to the organocopper compound. The mixture was left for 24 hr at room temperature, then poured on ice and HCl. ^d A mixture of unidentified additional products containing also a small amount of dimethylcarbinol was obtained.

β -methylcinnamic acid (IIa). Addition of methyl-lithium (equivalent amount to the copper reagent) to this enolate caused an isomerization of the enolate, and

ity that the lithium in these enolates is near the oxygen (VII) and the stereochemistry of the product is determined by the protonation step. A lithium enolate is



the *trans*- β -methylcinnamic acid (IIIa) was obtained on protonation (Table I). A similar product was obtained on addition of the dimethylcopper-lithium reagent to Ia. The larger amount of IIa in the methylcopper addition is not due to the stabilization of the *cis*-enolate (IVc) by the larger relative amount of Cu in the solution, since addition of CuI to the product of reaction of dimethylcopper-lithium with Ia did not change essentially the ratio of the products. Moreover, addition of phenylcopper to tetrolic acid (VIa) and subsequent hydrolysis gave predominantly the product of over-all *cis* addition IIIa. The same product was obtained in the diphenylcopper-lithium addition to VIa.

The addition of methylcopper to Ia or VIa is not 100% stereospecific despite the fact that the enolate IVc did not change its configuration for several days at room temperature. This is probably due to a temperature effect during the step of addition itself. Our reactions were carried out at -60° whereas the reported additions to the esters^{1,2} were carried out at -78 and -100° . The isomerization may be due to the transformation of the copper enolates to lithium enolates or to a rapid equilibrium between these species. The lithium enolates of the salts undergo probably a rapid inversion of configuration. There is also the possibil-

also probably obtained during the dimethylcopper-lithium additions.⁶

It is not clear whether the steric course of the methylcopper addition to the ester Ib is due to a lower specificity during the addition to esters at the temperature of our study or to an equilibration of the copper enolates of the esters⁷ that could be faster than in the case of the acids. No data are known on the equilibration of these enolates.

It is of interest that addition of methylcopper to Ib gives an anion whose ester function is attacked by added excess methylolithium to give the ketone VIII.

(6) A distinct possibility is the formation of a copper enolate with a methyl group on the copper. This enolate is expected to dissociate more easily than the enolate formed in the methylcopper addition, where the copper is probably coordinated with less basic groups, such as ether or halide anions.

(7) We are investigating this point.

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A Planar Azetidinium Compound

Sir:

Questions about the planarity or nonplanarity of saturated organic four-membered ring systems are the

(5) The composition of the product was analyzed by nmr³ and in several cases by glpc³ (after transformation of the acids into their methyl esters).