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Oxidative Coupling Reaction of Acetylene Compounds in the Solid State

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Oxidative coupling of acetylene compound with cupric salt in the solid state was found to proceed efficiently and selectively. The coupling reaction of α,ω-diacetylenes in the solid state gave the linear oligomers in contrast with the formation of the cyclic products in the solution reaction.

Oxidative coupling reaction of acetylenes with cupric salt in solution is a useful method to obtain diacetylene compounds.[1] During the course of our study on organic solid state reactions,[2] we found that the oxidative coupling reaction of acetylene compounds proceeds in the solid state efficiently and selectively. We also found that the $[\alpha]_D$ value of the linear polymerization product obtained by oxidative coupling of optically active α,ω-diacetylene increases as the helical structure unit increases.

For example, Glaser coupling method of acetylene compounds which is usually carried out in water[3] can be accomplished more efficiently in the solid state. When a mixture of powdered cuprous phenylacetylide (**1a**) and $CuCl_2 \cdot 2H_2O$ was kept at room temperature for 3 h, diphenyldiacetylene (**2a**) was obtained in 60% yield. By the same method, **1b-e** gave **2b-e**. In each case the present method gave better yields than Glaser method.

Table 1. Glaser coupling reaction in the solid state and in water[a)]

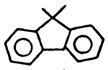
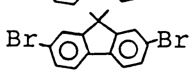
	Ar-C≡CCu (1)	Yield/% of Ar-C≡C-C≡C-Ar (2)[b)]	
	Ar	solid state	water
a	Ph	60	40
b	*p*-Me-C_6H_4-	35	21
c	*p*-Ph-C_6H_4-	67	--
d	2,3,5,6-$(Me)_4$-C_6H-	42	25
e	PhOCH_2-	74	--

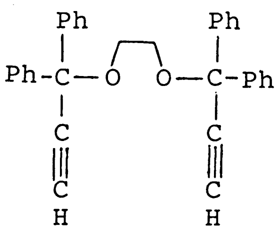
a) The reaction was carried out at room temperature for 3 h.
b) Isolated yield.

Eglinton coupling reaction[4)] could be applied to the reaction of propargyl alcohols in the solid state. When a mixture of powdered propargyl alcohol (**3**) and $CuCl_2$·2Py complex was reacted under the conditions shown in Table 2, the coupling product (**4**) was obtained in 60-92% yields. In the reaction, almost the same result was obtained by using $Cu(OAc)_2$·Py complex. Although the reaction rate was slower in the solid state than in solution, the reaction product in the solid state was different from that in solution. The Eglinton reaction which is usually carried out with $Cu(OAc)_2$ in pyridine, is a good synthetic method for the preparation of cyclic acetylenes from α,ω-diacetylene compounds.[4)] In fact, coupling reaction of α,ω-diacetylene compounds **5**, **7**, and **9a** in pyridine gave the corresponding cyclic dimer (**6**), cyclic monomer (**8**), and *rac*-cyclic dimer (**10**),[5)] respectively (Table 3). When the reaction, however, was carried out in the solid state using $Cu(OAc)_2$·Py complex, the linear coupling product was obtained. The result is also shown in Table 3. However, the optically active α,ω-diacetylene compound (**9b**) gave the optically active linear coupling product both in the solid state and in solution.

Although the coupling of **9b** in pyridine gave a polymer of relatively high molecular weight (*M*n=16,700) which consists of about a hundred monomer units,[6)] that in the solid state gave oligomers of relatively lower molecular weight. From the oligomer mixtures, an optically active linear dimer

Table 2. Oxidative coupling of propargyl alcohols with $CuCl_2 \cdot 2Py$ in the solid state

RR'C(OH)-C≡CH (3) R	R'	Reaction conditions temperature/°C	time/h	Yield/% of RR'C(OH)-C≡C-C≡C-C(OH)RR' (4)
Ph	Ph	50	20	65
Ph	o-Cl-C_6H_4-	50	10	70
p-Me-C_6H_4-	*p*-Me-C_6H_4-	55	22	60
Ph	2,4-$(Me)_2$-C_6H_3-	55	40	54
2,4-$(Me)_2$-C_6H_3-	*o*-Cl-C_6H_4-	80	10	60
Ph	Me	40	16	69
Ph	n-Bu	20	170	92
Ph	n-Bu	45	22	70
		75	2	60
		95	1	60



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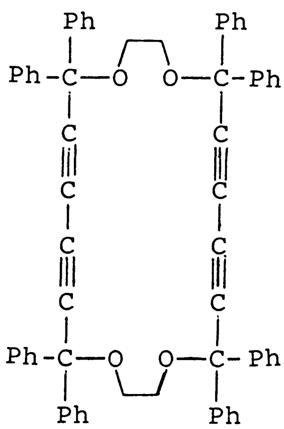

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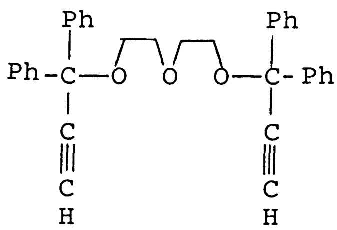

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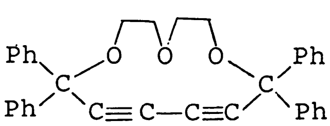

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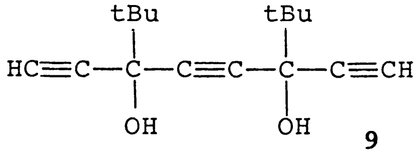

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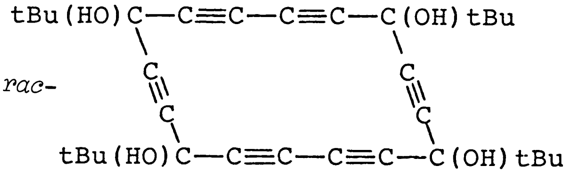

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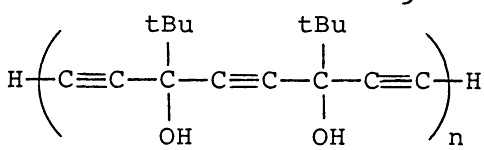

a: *rac*- 11

b: (-)-

Table 3. Oxidative coupling of **5**, **7**, **9a**, and **9b** with $Cu(OAc)_2$ in pyridine and with $Cu(OAc)_2 \cdot Py$ in the solid state

α,ω-Diacetylene compound	Product and yield/%			
	pyridine		solid state	
5	**6**	25	**6**	75
7	**8**	90	**8**	75
9a	**10**	21	**11a**	84
9b	**11b**	75	**11b**	80

(**11b**, n=2) was isolated as crystals (mp 200-202.5 °C, $[\alpha]_D$ -25° (*c* 0.2 in THF)) by chromatography on silica gel ($CHCl_3$). Further oxidative coupling of the **11b** (n=2) in pyridine gave a polymer (*M*n= 8300, $[\alpha]_D$ -123° (*c* 0.2 in THF)). The $[\alpha]_D$ value of **11b** increases as does the molecular weight (*M*n) (Fig. 1). This is probably due to an increase of helical units as the polymer chain extends. Similar tendency has been reported for polypeptides.[7)]

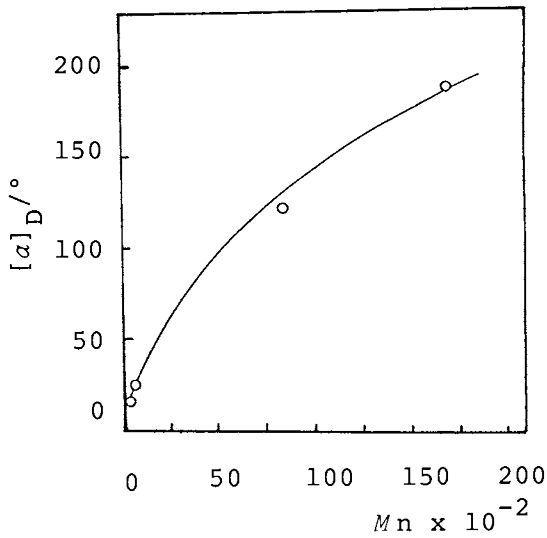

Fig. 1. The relatioship between number-average molecular weight (*M*n) and $[\alpha]_D$ value of **11b**.

References

1) P. Cadiot and W. Chohkiewicz, "Chemistry of Acetylenes," ed by H. G. Viehe, Marcel Dekker, New York (1968), p. 597.
2) F. Toda, Top. Curr. Chem., **140**, 43 (1987); F. Toda, K. Tanaka, and S. Iwata, J. Org. Chem., **54**, 3007 (1989).
3) C. Glaser, Ber, **2**, 522 (1869).
4) G. Eglinton and A. R. Galbraith, Chem. Ind., **1956**, 737.
5) F. Toda, J. Okada, and T. C. W. Mak, Chem. Lett., **1988**, 1829.
6) F. Toda, K. Okada, and K. Mori, Angew. Chem., Int. Ed. Engl., **27**, 859 (1988).
7) M. Goodman and E. E. Schmitt, J. Am. Chem. Soc., **81**, 5507 (1959); M. Goodman, E. E. Schmitt, and D. Yphantis, ibid., **82**, 3483 (1960).

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