

PALLADIUM CATALYZED REGIOSELECTIVE COTRIMERIZATION BETWEEN
DIMETHYL ACETYLENEDICARBOXYLATE AND TWO 1-ALKENE MOLECULES

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In the presence of bis(maleic anhydride)(norbornene)palladium as a catalyst, two 1-alkene molecules, R-CH₂-CH=CH₂, were added regioselectively to dimethyl acetylenedicarboxylate in the syn addition mode to give dimethyl 2-(2-alkenyl)-3-alkylmaleates, R-CH=CH-CH₂-C(COOCH₃)=C(COOCH₃)-CH₂CH₂CH₂-R under moderate condition (40-45°C) in chloroform.

There have been several studies on cyclotrimerization or cyclocotrimerization of various acetylenes under transition metal catalysis.^{2,3} In particular, η⁵-C₅H₅Co species have been reported to be extremely effective to such processes which underwent through metallacyclopentadiene intermediates.^{2b-d} On the other hand, little has been studied on the transition metal catalyzed cotrimerization between one alkyne and two alkene molecules. Wakatsuki, Aoki, and Yamazaki reported for the first time a well-defined linear cotrimerization between two acrylonitrile and diphenylacetylene molecules which proceeded by way of a cobaltacyclopent-2-ene intermediate.⁴ They claimed the formation of the conjugate diene cotrimer, NC-CH=CH-C(Ph)=C(Ph)-CH₂CH₂CN.

During the course of our studies on the Pd(0) catalyzed cyclocotrimerization of two dimethyl acetylenedicarboxylate(DMAD) with various alkenes,³ we have discovered an unexpected formation of the linear non-conjugate cotrimer, 1a-e,⁵ in addition to the expected cyclic cotrimers, 2a-e, when 1-alkenes(R-CH₂-CH=CH₂) with allylic hydrogen atoms were employed(Table 1), as shown below.

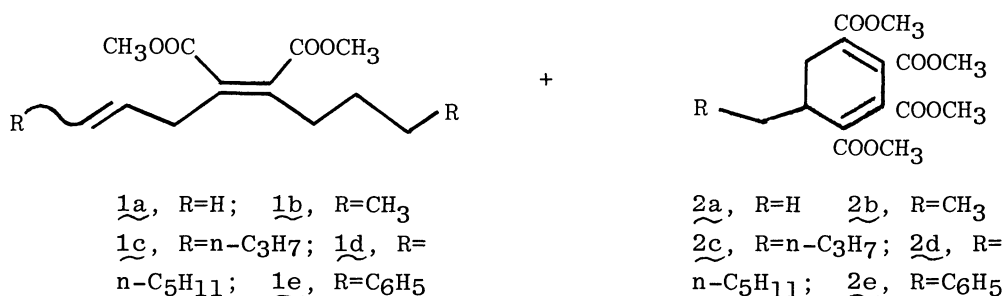
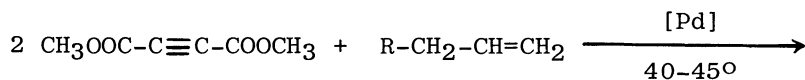


Table 1. Palladium Catalyzed Cotrimerization between DMAD and 1-Alkene

1-Alkene (mmol)	DMAD (mmol)	Catalyst (mmol)	Temp (°C)	Time (day)	Solvent (ml)	Yield of Cotrimer (%) ^a	
						Linear	Cyclic
CH ₃ -CH=CH ₂ (1.5 atom)	13.90	0.042 ^b	40	5	C ₆ H ₆ (60)	<u>1a</u> (54)	<u>2a</u> (45)
C ₂ H ₅ -CH=CH ₂ (1.5 atom)	11.70	0.073 ^b	40	5	C ₆ H ₆ (60)	<u>1b</u> (35)	<u>2b</u> (40)
n-C ₄ H ₉ -CH=CH ₂ (9.13)	3.67	0.038 ^c	45	12	C ₆ H ₆ (3)	<u>1c</u> (37)	<u>2c</u> (55)
n-C ₆ H ₁₃ -CH=CH ₂ (7.16)	1.62	0.022 ^d	45	3	C ₆ H ₆ (3)	<u>1d</u> (32)	<u>2d</u> (67)
(4.00)	1.20	0.030 ^b	40	2	CHCl ₃ (1)	<u>1d</u> (48)	<u>2d</u> (22)
C ₆ H ₅ -CH ₂ -CH=CH ₂ (1.10)	1.10	0.136 ^b	45	10	C ₆ H ₆ (10)	<u>1e</u> (32)	<u>2e</u> (67)

^a Isolated yields based on the charged DMAD. ^b (Ph-CH=CH-CO-C(=CHPh)-CO-CH=CH-Ph)₃Pd₃(CHCl₃)⁶ as the catalyst, in 500 ml autoclave for propene and 1-butene and in sealed tubes for 1-octene and allylbenzene.

^c (PdC₄(COOCH₃)₄)_n + Ph₃P, See ref. 3b. ^d (Ph-CH=CH-CO-CH=CH-Ph)₃Pd₂(CHCl₃)⁷

The formation of the cyclic cotrimers, 2a-2e, is explained by the intermediacy of a palladiacyclopentadiene, $\text{Pd}-\text{C}(\text{COOCH}_3)=\text{C}(\text{COOCH}_3)-\text{C}(\text{COOCH}_3)=\text{C}-\text{COOCH}_3$ 3, which inserts 1-alkene followed by the reductive elimination, as fully investigated by authors in the case of cyclic alkenes.³

At the present stage, the most likely mechanism of the formation of the linear cotrimers, 1a-1e, composed of two 1-alkene and one DMAD moieties, is to postulate a 5-alkyl-1,2-bis(methoxycarbonyl)palladiacyclopent-2-ene intermediate, $\text{Pd}-\text{C}(\text{COOCH}_3)=\text{C}(\text{COOCH}_3)-\text{CH}_2-\text{CH}-\text{CH}_2-\text{R}$ (4), which is generated by the oxidative cyclization of the coordinated DMAD and 1-alkene with a Pd(0) catalyst. In similar cyclizations, the formation of metallacyclopent-2-ene complexes has been claimed in the case of Co⁴ and Rh⁸. The regioselective insertion of the second 1-alkene to the vinyl-palladium bond of 4 yields a symmetric palladiacyclohept-4-ene, $\text{Pd}-\text{CH}(\text{CH}_2\text{R})-\text{CH}_2-\text{C}(\text{COOCH}_3)=\text{C}(\text{COOCH}_3)-\text{CH}_2-\text{CH}-\text{CH}_2\text{R}$, from which the β -elimination of the palladium hydride and subsequent reductive elimination of the resultant alkylhydridopalladium species occur to give 1a-1e. The non-conjugate diene structure of 1a-1e strongly indicates that the β -elimination of the Pd-H takes place selectively from the α -alkyl side chain. A general pattern of the catalytic cycle is shown in Scheme 1.

In order to increase the selectivity of the formation of linear cotrimers, it is necessary to inhibit the formation of the palladiacyclopentadiene(3) at the oxidative cyclization step. Since DMAD is an strongly electron-withdrawing acetylene substrate, the introduction of electron-withdrawing ligands around the Pd(0) catalyst should disfavor its coordination to two DMAD molecules to give 3, but favor that to at least one electron-rich 1-alkene to yield 4.

In fact, bis(maleic anhydride)(norbornene)palladium,⁹ involving two strongly electron deficient maleic anhydride ligands, is extremely effective to increase the selectivity of linear cotrimers as summarized in Table 2.

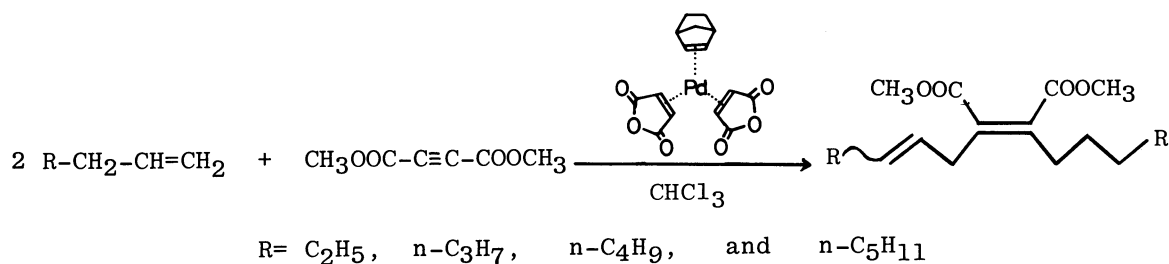
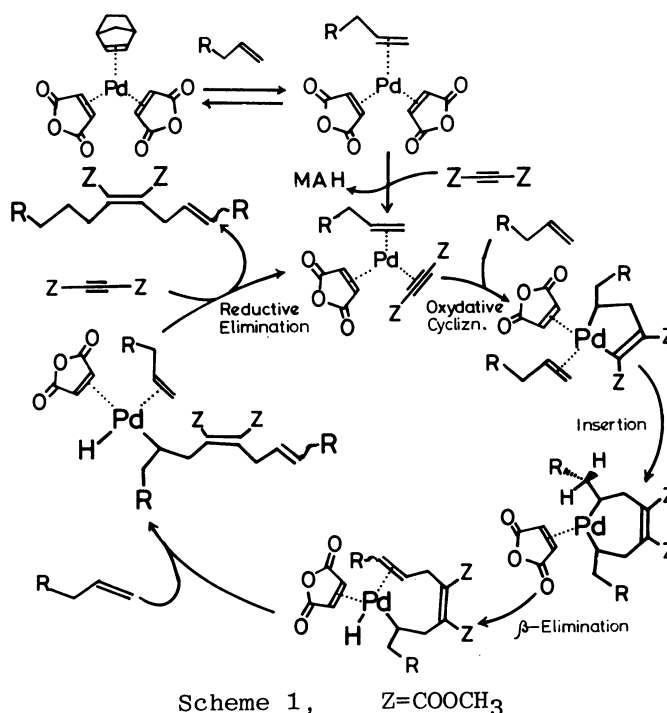


Table 2. Preparation of Dimethyl 2-(2-alkenyl)-3-alkylmaleate, $\text{R-CH=CH-CH}_2\text{-C(COOCH}_3\text{)=C(COOCH}_3\text{)-CH}_2\text{CH}_2\text{CH}_2\text{-R}$ from DMAD and Several 1-Alkenes by Means of Bis(maleic anhydride)(norbornene)palladium.

1-Alkene(mmol) R-CH ₂ -CH=CH ₂	DMAD (mmol)	Catalyst (mmol)	CHCl ₃ (ml)	Temp (°C)	Time (day)	Yield(%) of Di- methyl Maleate ^a
R= C ₂ H ₅ (27.0)	4.97	0.24	18	40	1.5	71
R=n-C ₃ H ₇ (47.2)	8.30	0.50	4	40	2	64
R=n-C ₄ H ₉ (42.4)	7.90	0.44	8	40	4	59
R=n-C ₅ H ₁₁ (4.5)	1.30	0.05	4	45	1.5	78

^a Isolated yield based on the charged DMAD after chromatographic separation with silica gel(n-hexane/ethyl acetate as the eluent). Satisfactory spectroscopic (IR, NMR, and MS, m/e) data and elemental analyses were obtained(see ref.10). The formation of the corresponding cyclic adduct was below 5% in every case.



The mechanism shown in Scheme 1 explains reasonably the dramatic increase in the selectivity of the linear non-conjugate diene cotrimer, the high regioselectivity(both 1-alkene units were added to DMAD in an anti-Markownikov manner), as well as the observed stereoselective syn-addition across the triple bond of DMAD.¹⁰

Active investigation on the synthetic application of these linear cotrimers, dimethyl 2-(2-alkenyl)-3-alkylmaleate, is under progress and will be published in near future.

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References and Notes

- 1) This author(K. H.) contributed at the early stage of this work, when K. I. and K. H. worked at the Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University.
- 2) a) J. P. Collman and L. S. Hegeudus, Principles and Application of Organotransition Metal Chemistry, University Science Book, Mill Valley, Calif., 1980, p.506. b) Y. Wakatsuki, T. Kuramitsu, and H. Yamazaki, Tetrahedron Lett., 4549(1974). c) Y. Wakatsuki and H. Yamazaki, J. Organometal.Chem., 139, 157 and 169(1977). d) R. L. Funk and K. P. C. Vollhardt, J. Am. Chem. Soc., 102, 5254 and 5253(1980).
- 3) a) H. Suzuki, K. Itoh, Y. Ishii, K. Simon, and J. A. Ibers, J. Am. Chem. Soc., 98, 8494(1976). b) L. D. Brown, K. Itoh, H. Suzuki, K. Hirai, and J. A. Ibers, J. Am. Chem. Soc., 100, 8232(1978).
- 4) Y. Wakatsuki, K. Aoki, and H. Yamazaki, J. Am. Chem. Soc., 96, 5284(1974).
- 5) Satisfactory spectroscopic(NMR and IR) data and elemental analyses were obtained for 1a-1e. For example, 1a, NMR(CDCl₃), δ 5.68(1H, m, $J_{trans}=15$, $J_{cis}=9$, $J_{allyl}=5$ Hz), 5.04(1H, m), 4.94(1H, m) as olefinic protons, 3.65 and 3.67(each 3H, s, COOCH₃), 2.99(2H, dt, $J=5$ and 1.5Hz, dienylic), 2.21(2H, t, $J=7$ Hz, allylic), 1.40(2H, m, methylene), 0.93(3H, t, $J=6$ Hz, methyl). IR(CCl₄) 1728 cm⁻¹($\nu_{C=O}$). Anal. Calcd. for C₁₂H₁₈O₄, C, 63.70; H, 8.02. Found. C, 63.54; H, 8.18.
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- 10) NMR(CDCl₃) of 1-hexene cotrimer, 1c, δ 5.40(2H, m, olefinic), 3.72 and 3.68 (each 3H, s, COOCH₃), 3.07(2H, m, dienylic), 1.78-2.58(4H, m, allylic), 1.33 (10H, m, methylene), 0.93(6H, m, methyl). The (Z)-stereochemistry of the maleate part is unequivocally determined by the fact that all cotrimers shown in Table 2 were converted to 3,4-disubstituted furans by an aluminium hydride reduction to diols(86-94%) followed by a dehydrative oxidation with pyridinium chlorochromate(83-91%) as presented at the 43rd Annual Meeting of the Chemical Society of Japan, Tokyo, 2H40, Preprint, Vol. II, p.908. However, the stereochemistry of the alkenyl part could not be determined because of the complexity of NMR spectra. The elimination of Pd-H can occur from either allylic hydrogen atoms to give either (E) or (Z) alkenyl moieties according to Scheme 1.

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