biradical cannot be just the transition state for epimerization of the bicyclo[2.1.0]pentanes.

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Nickel(0)-Catalyzed Alternating Copolymerization of Carbon Dioxide with Diynes to Poly(2-pyrones)

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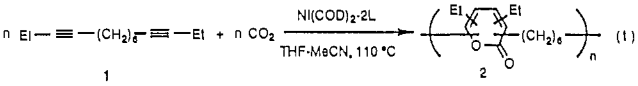
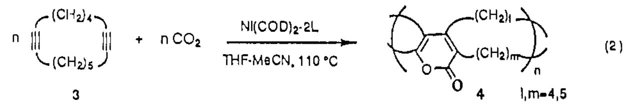
Use of CO_2 as a comonomer for polymer synthesis is an attractive approach to chemical utilization of CO_2, which is of great concern at the present time in relation to carbon resources and environmental problems, but there are few reports of CO_2 copolymerization which satisfy both alternating copolymerization and degree of polymerization. To our knowledge, alternating copolymerization of CO_2 with epoxides involving C–O bond formation is the only example to be cited.[1]

Recently we reported that diynes such as 1,6-heptadiyne, 1,7-octadiyne, and substituted diynes act as reactive substrates in nickel(0)-catalyzed CO_2 fixation into unsaturated hydrocarbons to afford bicyclic 2-pyrones fused with five- and six-membered carbocycles by intramolecular cyclization of diynes involving CO_2.[2] Here we report efficient alternating copolymerization of CO_2 with acyclic and cyclic diynes, which do not readily undergo intramolecular cyclization, to produce a new class of polymer, poly(2-pyrones), by nickel(0)-catalyzed intermolecular cyclization of diynes involving CO_2 (eqs 1 and 2). These are the first examples of alternating copolymerization of CO_2 with an unsaturated hydrocarbon and also one involving C–C bond formation.





When 3,11-tetradecadiyne (**1**) was treated with CO_2 under pressure in a mixed solvent of THF–MeCN[3] at 110 °C in the presence of a Ni(0) catalyst (10 mol %) generated from $Ni(COD)_2$ and 2 equiv of a tertiary phosphine ligand, a copolymer **2** was obtained by concentration of the reaction mixture under vacuum followed by precipitation with ether (eq 1, Table I).

Copolymers are pale yellow to brown solids. They are soluble in methylene chloride and chloroform, but are insoluble in ether, benzene, and hexane. Copolymers show IR and ^1H NMR absorptions assignable to a 2-pyrone ring. The most useful diagnosis of the 2-pyrone ring is by ^{13}C NMR spectroscopy.[4] The copolymers prepared in THF-MeCN exhibit five groups of ^{13}C NMR C=C and C=O absorptions characteristic of the 2-pyrone ring (Figure 1d).

Table I. Nickel(0)-Catalyzed Alternating Copolymerization of Diyne with CO_2 to Poly(2-pyrone)[a]

diyne, mmol	ligand (L)	solvent	poly(2-pyrone) yield,[b] %	M_n[c]	M_w/M_n
1					
1	PEt_3	THF	50	3300	4.4
		THF–MeCN	42	8400	2.3
			59	6500	2.4
				(5600)[d]	
			55[g]	8200	2.9
2			86	13300	2.3
1	$P(n\text{-}C_8H_{17})_3$	THF	34	9300	3.5
		THF–MeCN	58	11400	2.4
			63	8600	3.0
				(8100)[d]	
2			72	17900	3.2
1			61[e]	8100	2.7
	$P(c\text{-}C_6H_{11})_3$		0		
3					
1	PEt_3	THF	27	2900	2.1
		THF–MeCN	33	4600	3.9
				(4200)[d]	
			49[e]	3800	3.0
	$P(n\text{-}C_8H_{17})_3$	THF	11	2100	1.7
		THF–MeCN	30	3700	3.6
2			30[f]	5300	2.9
1			53[e]	5200	3.1
				(4200)[d]	
	$P(c\text{-}C_6H_{11})_3$		~0		

[a] Ni/diyne = 0.10; L/Ni = 2; CO_2, 50 kg/cm^2 (initial pressure at room temperature); solvent, 5 mL THF/MeCN = 1–2 (v/v); temperature, 110 °C; time, 20 h. [b] Based on the formation of a 1:1 alternating copolymer of diyne with CO_2. [c] Determined by GPC with polystyrene standards in chloroform. [d] Determined by VPO in chloroform. [e] L/Ni = 3. [f] Time, 40 h. [g] Temperature, 90 °C.

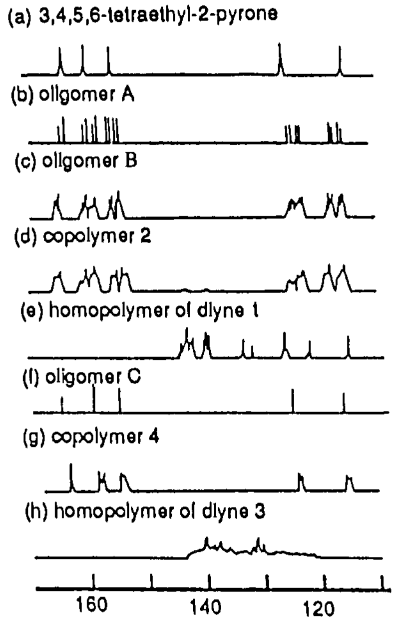


Figure 1. ^{13}C NMR spectra of copolymers and related compounds (δ, ppm).

To define a copolymer structure, preparation of co-oligomers and homopolymers of **1** were carried out. Ether-soluble co-oligomers A (15%) and B (10%) along with ether-insoluble copolymers (11%) were obtained by shortening the reaction time to 20 min. Spectroscopic data and elemental analyses demonstrate

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[1] (a) Inoue, S. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Kodansha: Tokyo, 1981; p 153. (b) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8.

[2] (a) Tsuda, T.; Sumiya, R.; Saegusa, T. *Synth. Commun.* **1987**, *17*, 147. (b) Tsuda, T.; Morikawa, S.; Sumiya, R.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 3140. (c) Tsuda, T.; Morikawa, S.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1989**, 9. (d) Tsuda, T.; Morikawa, S.; Hasegawa, N.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2978.

[3] (a) Walther, D.; Schønberg, H.; Dinjus, E.; Sieler, J. *J. Organomet. Chem.* **1987**, *334*, 377. (b) Behr, A.; He, R.; Juszak, K.-D.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1986**, *119*, 991.

[4] Staunton, J. *Comprehensive Organic Chemistry*; Pergamon: Oxford, UK, 1979; Vol. 4, p 629.

0002-7863/92/1514-1498$03.00/0

J. Am. Chem. Soc. 1992, 114, 1499-1500 1499

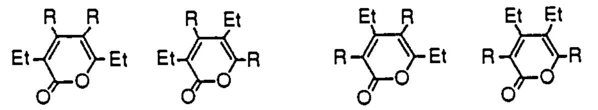

Figure 2. Four regioisomers of the co-oligomer A (R = $(CH_2)_6C{\equiv}C$—Et).

that A and B consist of one CO_2 molecule plus two diyne molecules and two CO_2 molecules plus three diyne molecules, respectively. The co-oligomer A exhibits 16 ^{13}C NMR absorptions with almost equal intensities (Figure 1b) assignable to the $C{=}C$ bonds of the 2-pyrone ring, which indicates that A is composed of nearly equal amounts of four regioisomers shown in Figure 2. Homopolymerization of **1** without CO_2 gave methanol-insoluble polymers (35%, $M_n = 1800$)[5] whose ^{13}C NMR spectrum (Figure 1e) is quite different from those of copolymers.

Agreement of a pattern of the ^{13}C NMR $C{=}C$ absorptions of copolymers **2** almost free from the $C{=}C$ absorptions of homopolymers with those of co-oligomers A and B (Figure 1) indicates that alternating copolymerization of CO_2 with **1** occurs to produce poly(2-pyrone) **2**,[6] and its repeating unit[7] corresponds to the structure of the 2-pyrone ring of A.

The alternating copolymerization of diynes with CO_2 depends upon the relative reactivity of inter- to intramolecular cyclization of diynes. Thus, the reaction of 3,9-dodecadiyne and CO_2 under the standard reaction conditions of Table I produced a corresponding bicyclic 2-pyrone[2] fused with a six-membered ring as a main product (~40%) together with a small amount of polymers (~10%).

1,7-Cyclotridecadiyne (**3**), a cyclic diyne, also underwent facile alternating copolymerization with CO_2 to produce poly(2-pyrone) **4**[8] with a unique ladder structure (eq 2, Table I). Copolymers **4** are white powders.[9] They show a solubility similar to that of the copolymer **2**. Formation of alternating copolymers **4**[7] from CO_2 and **3** is demonstrated by agreement of a pattern of the ^{13}C NMR $C{=}C$ absorptions of **4** (Figure 1g) free from the $C{=}C$ absorptions (Figure 1h) of methanol-insoluble homopolymers[5] of **3** (22%, $M_n = 840$) with that (Figure 1f) of a co-oligomer C composed of one CO_2 molecule and two molecules of the diyne **3**.[10]

The TGA curve for the copolymer **2** or **4** run under nitrogen shows a rapid weight loss around 420 °C.

The present study suggests that numerous unprecedented poly(2-pyrones) can be prepared by changing the structure of diynes, for example, $RC{\equiv}C(CH_2)_mC{\equiv}CR$ ($m \geq 7$, $m \leq 2$). Their preparations, characterizations, and reactions utilizing a variety of chemical reactivities of the 2-pyrone ring[4] are interesting further subjects.

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Supplementary Material Available: Experimental section including characterization data of copolymers and co-oligomers (3 pages). Ordering information is given on any current masthead page.

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(5) A structure of the homopolymer has not been determined at the present time. As to the structure of acetylene oligomers, see, for example, ref 3a.

(6) The copolymers **2** produced at 90 °C in THF–MeCN show no ^{13}C NMR $C{=}C$ absorptions of homopolymers of **1**. The copolymers **2** produced in THF without MeCN show weak but distinct ^{13}C NMR $C{=}C$ absorptions of homopolymers of **1** along with those of the 2-pyrone ring.

(7) Orientation of 2-pyrone rings along the polymer chain is reasonably assumed to be random.

(8) The copolymers **4** obtained in THF alone exhibit negligible ^{13}C NMR $C{=}C$ absorptions of homopolymers of **3**.

(9) The copolymers **2** and **4** did not show satisfactory elemental analysis results. It was found that ashes were formed after combustion analyses of the copolymers. This finding suggests that nickel salts contaminate the copolymers, which was further confirmed by X-ray fluorescence analysis. Their removal by washing chloroform solutions of the copolymers with water or dilute hydrochloric acid was unsuccessful.

(10) One regioisomer among four possible regioisomers.

Exo-Lone-Pair Effect on Hetero-Diels-Alder Cycloaddition Stereochemistry

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In hetero-Diels–Alder reactions, we have discovered that the interactions of lone pairs on N or O with π systems can exert powerful stereochemical control. The n–π repulsion which causes this phenomenon should be very important in controlling stereochemistry in many complexation and reactivity events as well.

Hetero-Diels–Alder reactions are often key steps in stereoselective syntheses of natural products.[1,2] To learn about the transition structures of such processes, we investigated reactions of 1,3-butadiene with formaldehyde, formaldimine, diazene, and nitrosyl hydride with ab initio quantum mechanical methods. Geometry optimizations were performed at the RHF level using GAUSSIAN 86 and 88.[3] Structures were fully optimized with the 3-21G basis set, followed by vibrational frequency calculations. MP2/6-31G* calculations on 3-21G geometries were performed to evaluate the activation energies. A concerted, but nonsynchronous, reaction mechanism was presumed. The RHF/3-21G transition structure for the reaction of butadiene with ethylene is very similar to those at higher levels of theory, including MCSCF.[4] The MP2/6-31G* activation energy for this reaction is about 10 kcal/mol lower than the experimental value,[5] but substituent effects are reproduced well.[6] Predicted activation energies for hetero-Diels–Alder reactions are given in Table I, and transition structures are shown in Figure 1.

The transition structure for the reaction of butadiene with formaldehyde, **1**, resembles that for the reaction of butadiene with ethylene,[4a] with a 0.08 Å shorter C–C forming bond. The C_6–O_1 bond is 0.14 Å shorter than the C_2–C_3 bond, differing from MINDO/3 predictions.[7] Our results reflect the shorter C–O than

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(1) Boger, D. L.; Weinreb, S. N. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987. Weinreb, S. M.; Staib, R. R. *Tetrahedron* **1982**, *38*, 3087. Hamer, J., Ed. *1,4-Cycloaddition Reactions*; Academic Press: New York, 1967.

(2) (a) Jung, M. E.; Shishido, K.; Light, L.; Davis, L. *Tetrahedron Lett.* **1981**, 4607. (b) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 6376. (c) Nader, B.; Bailey, T. R.; Franck, R. W.; Weinreb, S. M. *J. Am. Chem. Soc.* **1981**, *103*, 7573. (d) Le Coz, L.; Veyrat-Martin, C.; Wartski, L.; Seyden-Penne, J.; Bois, C.; Philoche-Levisalles, M. *J. Org. Chem.* **1990**, *55*, 4870. (e) Danishefsky, S. J.; Larson, E.; Askin, D.; Kato, N. *J. Am. Chem. Soc.* **1985**, *107*, 1246.

(3) (a) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. GAUSSIAN 86, Gaussian, Inc., Pittsburgh, PA 15213. (b) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. GAUSSIAN 88, Gaussian Inc., Pittsburgh, PA 15213.

(4) (a) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554. (b) Bach, R. D.; McDouall, J. J. W.; Schlegel, H. B.; Wolber, G. J. *J. Org. Chem.* **1989**, *54*, 2931 (c) Loncharich, R. J.; Houk, K. N. Unpublished results on the MP2/6-31G* transition structure for butadiene + ethylene. (d) Bernardi, F.; Bottini, A.; Field, M. J.; Guest, M. F.; Hillier, I. H.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1988**, *110*, 3050. Bernardi, F.; Bottini, A.; Robb, M. A.; Field, M. J. *J. Chem. Soc., Chem. Commun.* **1985**, *15*, 1051.

(5) (a) Krause, M.; Vavruska, M.; Bazant, V. *Collect. Czech. Chem. Commun.* **1957**, *22*, 484. (b) Kuchler, L. *Trans. Faraday Soc.* **1939**, *35*, 874. (c) Lewis, D. K.; Bergman, J.; Manjoney, R.; Paddock, R.; Kalra, B. L. *J. Phys. Chem.* **1984**, *88*, 4112. (d) Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198. (e) Smith, S. R.; Gordon, A. S. *J. Phys. Chem.* **1961**, *65*, 1124. (f) Tardy, D. C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508. Tsang, W. J. *Chem. Phys.* **1965**, *42*, 1805; Tsang, W. J. *Int. J. Chem. Kinet.* **1970**, *2*, 311. (h) Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878.

(6) (a) Houk, K. N.; Loncharich, R. J.; Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 9172. (b) Loncharich, R. J.; Brown, F. K.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 1129. (c) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127. (d) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem.*, in press.

0002-7863/92/1514-1499$03.00/0