

- (28) C. Krüger and E. G. Rochow, *J. Organomet. Chem.*, **1**, 476 (1964).  
 (29) S. A. Vartanyan and A. O. Tosunyan, *Izv. Akad. Nauk Arm. SSR, Khim. Nauki*, **11**, 263 (1958).  
 (30) L. M. Minsk and W. O. Kenyon, U.S. Patent 2 443 167 (1944); *Chem. Abstr.*,

- 42**, 6582 (1948).  
 (31)  $\sigma$  values taken from L. P. Hammett, "Physical Organic Chemistry Reaction Rates, Equilibria, and Mechanisms", 2nd ed, McGraw-Hill, New York, N.Y., 1970, p 356. Best straight line determined by least-squares analysis.

## Stereochemistry of Addition of 2-Cyano-1,3-diphenylallyllithium to *trans*-Stilbene, an Anionic [3 + 2] Cycloaddition

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**Abstract:** Cycloaddition of 2-cyano-1,3-diphenylallyllithium to *trans*-stilbene produces detectable amounts (by NMR) of only two of the ten possible diastereomeric 2,3,4,5-tetraphenylcyclopentane-1-carbonitriles. The structure of the *r*-1,*c*-2,*c*-3,*t*-4,*c*-5 isomer (**1**) was established by x-ray analysis. Treatment of **1** with NaOH in aqueous dioxane inverts its configuration at C(1) to form the *r*-1,*t*-2,*c*-3,*t*-4,*t*-5 isomer (**2**), which is also the other compound formed by cycloaddition. Under identical conditions *cis*-stilbene does not react with 2-cyano-1,3-diphenylallyllithium. This is the first determination of the stereochemical course of cycloaddition of an allyl anion to a carbon-carbon double bond to form a five-membered carbocycle. The observed stereospecific cycloaddition with retention of the configuration of the *trans*-stilbene is predicted for a concerted reaction by conservation of orbital symmetry, but a stepwise cycloaddition mechanism cannot be ruled out.

The number of known examples of cycloadditions of allyl anions to carbon-carbon multiple bonds is small but growing. The oldest examples are the dimerizations of  $\alpha$ -methylstyrene in the presence of an alkylbenzene and sodium or potassium metal,<sup>2</sup> which likely proceed by addition of 2-phenylallyl-sodium and 2-phenylallyl-potassium to  $\alpha$ -methylstyrene. 2-Phenylallyllithium in THF (tetrahydrofuran) and 2-phenylallylmagnesium phenoxide in THF/HMPA (hexamethylphosphoramide) add to *trans*-stilbene to give *r*-1,*t*-2,*c*-4-triphenylcyclopentane.<sup>3</sup> 2-Phenylallylmagnesium phenoxide in THF/HMPA also cycloadds to a variety of other electron-deficient olefins.<sup>4</sup> Treatment of 1,3-diphenylpropyne with lithium diisopropylamide (LDIA) in hexane gives a cyclic dimer.<sup>5</sup> 2-Cyano-1,3-diphenylallyllithium cycloadds to styrene, *trans*-stilbene, 1,1-diphenylethylene, and acenaphthylene.<sup>6</sup> Reaction of a 2-thiomethylenecyclohexanone derivative with LDIA forms a thioallyl anion which adds to ethyl acrylate and to diethyl fumarate to form hydrindanones.<sup>7</sup>

Conservation of orbital symmetry predicts that if these cycloadditions are concerted, they will proceed by a  $\pi_4s + \pi_2s$  mechanism in which the configurations of both the allyl anion and the olefin are retained in the cyclopentyl anion.<sup>8</sup> All previous attempts to determine the stereochemical courses of these reactions have failed because of rapid isomerization of the reactants (and perhaps also isomerization of the products). For example, *cis*-stilbene isomerizes to *trans*-stilbene in 2-phenylallyllithium and 2-phenylallylmagnesium solutions more rapidly than either 2-phenylallylmetal compound adds to *trans*-stilbene,<sup>4</sup> and diethyl maleate apparently isomerizes to diethyl fumarate faster than diethyl fumarate adds to the lithium derivative of a 2-thiomethylenecyclohexanone.<sup>7</sup>

The stereochemical courses of cycloadditions of some heteroatom analogues of allyl anions to electron-deficient double bonds are known. (*E,E*)-1,3-Diphenyl-2-azaallyllithium cycloadds to both *cis*-stilbene and *trans*-stilbene to give different 2,3,4,5-tetraphenylpyrrolidines with "no detectable mutual contamination".<sup>9</sup> The <sup>1</sup>H NMR spectra of the pyrrolidines are consistent with the isomers expected from concerted  $\pi_4s + \pi_2s$  reactions. Several examples of 1,3-dipolar cycloadditions with

complete retention of configuration of both the 1,3-dipole and the dipolarophile are known, and "no exceptions have been observed" to the stereospecificity.<sup>10</sup> Among the 1,3-dipoles known to undergo stereospecific cycloadditions are the azomethine ylides obtained from ring openings of aziridines and the carbonyl ylides obtained from ring openings of oxiranes, both of which are isoelectronic with allyl anions.

Boche and Martens<sup>6</sup> reported previously that 2-cyano-1,3-diphenylallyllithium and *trans*-stilbene form a cycloadduct, but they did not determine which of the ten diastereomeric 2,3,4,5-tetraphenylcyclopentane-1-carbonitriles they isolated. This paper describes the isolation and determinations of structure of the only two of these diastereomers formed in large amounts.

### Results

2-Cyano-1,3-diphenylallyllithium was prepared by treatment of *cis,trans*-2,3-diphenylcyclopropane-1-carbonitrile with 1 equiv of LDIA in THF at  $-78^\circ\text{C}$  followed by warming to room temperature for 1 h to complete electrocyclic opening of the cyclopropyllithium intermediate.<sup>6,11</sup> *trans*-Stilbene (1 equiv) was added, and the disappearance of stilbene was followed by GLC. Only two GLC peaks due to 1:1 adducts were detected after reaction times ranging from 5 to 150 min. Their yields reached constant values of 23 and 25% after 1 h. When the same procedure was employed with *cis*-stilbene, no 1:1 adducts could be detected at any time over a period of 96 h. Cycloaddition clearly occurred only with *trans*-stilbene.

The mixture of 1:1 adducts was purified by liquid chromatography. From the resulting oil one isomer crystallized. Its structure was established as *r*-1,*c*-2,*c*-3,*t*-4,*c*-5-tetraphenylcyclopentane-1-carbonitrile (**1**) by x-ray analysis (provided us by Drs. Chian C. Chiang and Iain C. Paul). A stereoscopic view of **1** is shown in Figure 1.

Treatment of **1** with NaOH in refluxing aqueous dioxane converted it to an oily mixture containing 97.7% of another isomer **2** and 2.3% of **1** by GLC analysis. (Isomer **1** appeared as the peak of shorter retention time. Isomer **2** appeared as the peak of longer retention time.) When the isomerization of **1**

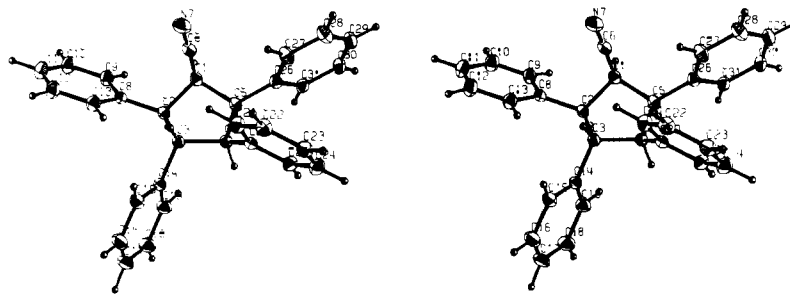
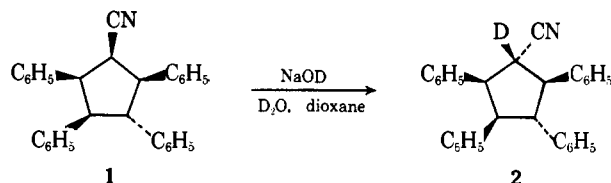


Figure 1. A stereoscopic view of the single molecule of **1**.



was repeated with NaOD in dioxane/ $D_2O$ , the isolated **2** contained 0.97 atom excess D by mass spectrometry. The  $^1H$  and  $^{13}C$  NMR spectra of deuterated **2** indicate that the deuterium is located entirely at the 1-position within the limits of NMR detection. This proves that **1** and **2** differ in configuration only at C(1) and establishes the structure of **2** as *r*-1,*t*-2,*c*-3,*t*-4,*t*-5-tetraphenylcyclopentane-1-carbonitrile. Isomer **2** subsequently was obtained in crystalline form also.

$^1H$  NMR spectra of **1** and **2** were obtained at 220 MHz in the presence and in the absence of shift reagent  $Eu(fod)_3$ . The paramagnetic reagent enabled approximate first-order analysis of each of the five cyclopentane proton multiplets of **1** and **2**. The  $^{13}C$  NMR spectrum of each isomer showed the expected five cyclopentane ring carbon peaks and one cyano carbon peak. In none of the  $^1H$  or  $^{13}C$  NMR spectra were there any notable peaks which could be due to other 2,3,4,5-tetraphenylcyclopentane-1-carbonitrile isomers. The  $^1H$  and  $^{13}C$  NMR spectra of the first-purified, unfractionated reaction mixture contained all of the peaks observed in the individual spectra of **1** and **2**, but no additional peaks. We estimate that no more than 10% of any of the other eight diastereomers of **1** and **2** could have been present in the original reaction mixture.

The 2,3,4,5-tetraphenylcyclopentane-1-carbonitrile originally reported by Boche and Martens had mp 120.0–120.5 °C.<sup>6</sup> Our crystalline **1** had mp 147–148 °C, and crystalline **2** had mp 103–105 °C. Dr. Boche recently informed us that they isolated a compound with mp 145–147 °C four years ago.<sup>12</sup> The IR spectra of their 145–147 °C compound and our **1** are identical. Presumably the 2,3,4,5-tetraphenylcyclopentane-1-carbonitrile they reported earlier was a mixture of **1** and **2** in unknown proportions.

### Discussion

A mechanism for cycloaddition of 2-cyano-1,3-diphenylallyllithium to *trans*-stilbene must explain the formation of only **1** and **2** in quantities large enough to detect in NMR spectra of the product mixture. There are eight more diastereomeric 2,3,4,5-tetraphenylcyclopentane-1-carbonitriles (**3–10**) of which isomers **8** and **10** should be about equal in stability to **2**, isomers **3**, **4**, **6**, **7**, and **9** should be about equal in stability to **1**, and isomer **5** should be less stable than **1**. (These estimates of relative stabilities are based only on the numbers of pairs of vicinal substituents on the cyclopentane cis to one another.)

Formation of only **1** and **2** can be explained by concerted cycloaddition of (*E,E*)-2-cyano-1,3-diphenylallyllithium to *trans*-stilbene as shown in Figure 2. In a concerted mechanism the configurations of both the stilbene and the allyl anion must be retained. At 25 °C in THF the (*E,E*) and (*E,Z*) conformers

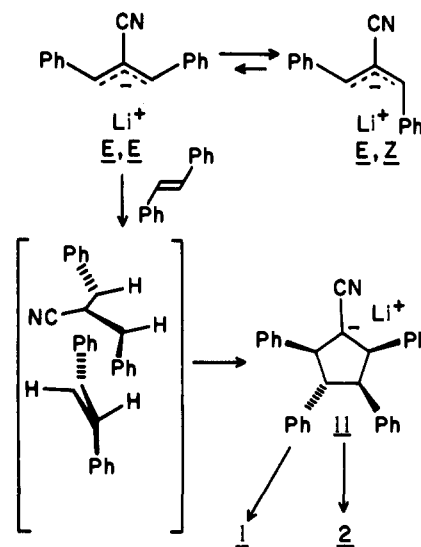
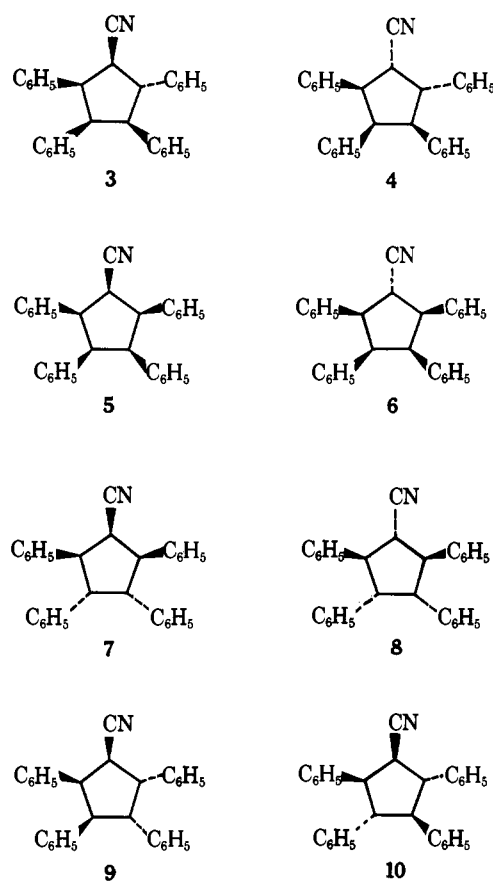


Figure 2. Concerted mechanism for cycloaddition of 2-cyano-1,3-diphenylallyllithium to *trans*-stilbene.



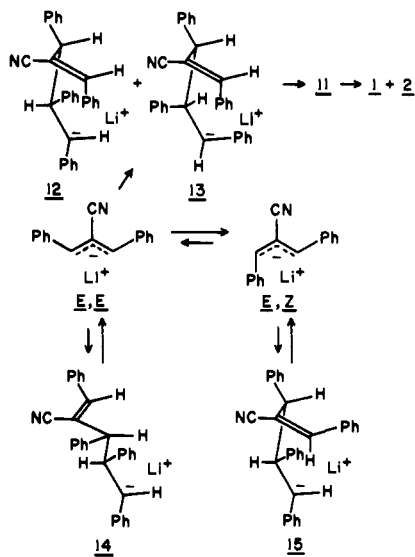
**Table I.**  $^{13}\text{C}$  NMR Spectra of **1** and **2**

Isomer 1		Isomer 2		Assignment
$\delta$ , ppm <sup>a</sup>	Rel peak ht <sup>b</sup>	$\delta$ , ppm <sup>a</sup>	Rel peak ht <sup>b</sup>	
140.3	1.20	140.0	0.65	C(1) of C <sub>6</sub> H <sub>5</sub>
139.2	1.08	138.9	0.50	
136.7	1.05	138.3	0.53	C(2,3,4) of C <sub>6</sub> H <sub>5</sub>
136.2	1.18	138.0	0.63	
129.3	2.20	128.8	3.70	
129.1	2.25	128.4	2.65	
128.2	5.20	128.3	2.74	
127.7	2.41	128.0	2.36	
127.5	2.94	127.7	2.78	
127.1	2.44	127.3	3.00	
126.5	1.48	126.7	1.64	
126.1	1.10	126.2	1.15	
119.7	0.99	121.0	0.24	CN
57.0	0.91	57.1	1.08	CHC <sub>6</sub> H <sub>5</sub>
53.8	0.86	56.9	1.10	
53.1	0.85	56.3	1.05	CHCN
51.0	0.85	53.6	0.90	
42.7	0.80	41.7	0.10 <sup>c</sup>	

<sup>a</sup> Spectra were taken as CDCl<sub>3</sub> solutions with internal tetramethylsilane on a JEOL FX-60 instrument at 15.0 MHz. <sup>b</sup> Normalized to the average peak height of a single aromatic carbon atom with a directly bound proton. <sup>c</sup> Spectrum was taken with deuterated compound.

**Table II.**  $^1\text{H}$  NMR Spectrum of Cyclopentane Hydrogens of Isomer **1**

$\delta$ , ppm	Multiplicity	$J$ , Hz	Rel shift, Eu(fod) <sub>3</sub>	Assignment
3.78	t	6.5, 6.5	1.00	H(1)
3.88	t	10.5, 9.5	0.37	H(3) or H(4)
3.96	d of d	12, 6.5	0.45	H(5) or H(2)
4.19	d of d	10.5, 6.5	0.45	H(2) or H(5)
4.30	d of d	12, 9.5	0.65	H(4) or H(3)

**Figure 3.** Stepwise mechanism for cycloaddition of 2-cyano-1,3-diphenylallyllithium to *trans*-stilbene.

of 2-cyano-1,3-diphenylallyllithium interconvert rapidly on the  $^1\text{H}$  NMR time scale according to Boche and Schneider.<sup>13</sup> At  $-15^\circ\text{C}$  the equilibrium mixture favors the (*E,Z*) conformer by 92/8. Nevertheless the major cycloadducts must be formed from the less stable (*E,E*) conformer. Boche and Martens found earlier that only the (*E,E*) conformer underwent cycloaddition to acenaphthylene.<sup>6,14</sup>

Alternatively cycloaddition could proceed by a stepwise mechanism via **12** or **13** as shown in Figure 3. Many other rotamers of **12** and **13** might also be formed. Many of them, such

as **14**, cannot cyclize, but some, such as **15**, would be expected to cyclize readily. In a stepwise mechanism either **15** is never formed, or it reverts to starting materials much faster than it cyclizes. Because there is no obvious reason why intermediates such as **15**, which lead to isomers **3–10**, should not be formed and should not cyclize, the concerted mechanism appears more likely. But we cannot rule out the stepwise process.

Why does *cis*-stilbene not react at all with 2-cyano-1,3-diphenylallyllithium when *trans*-stilbene cycloadds so readily? Space filling molecular models show that the phenyl rings of *cis*-stilbene are twisted out of the plane of the central double bond so that their ortho hydrogens lie above and below the central carbon atoms. These ortho hydrogens could block attack of nucleophiles at the double bond. Why does only the (*E,E*) conformer and not the (*E,Z*) conformer of 2-cyano-1,3-diphenylallyllithium react with *trans*-stilbene? We have no good answer. Space filling models show no obvious differences in steric hindrance at C(1) and C(3) of the two isomeric anions.<sup>15</sup>

### Experimental Section<sup>16</sup>

**2-Cyano-1,3-diphenylallyllithium and *trans*-Stilbene.** A solution of 2.7 g (15.0 mmol) of recrystallized *trans*-stilbene in 10 mL of dry THF was added at room temperature with stirring under nitrogen to a solution of 15.0 mmol of 2-cyano-1,3-diphenylallyllithium in 50 mL of THF prepared by ring opening of *cis,trans*-2,3-diphenylcyclopropane-1-carbonitrile with LDIA.<sup>6,11</sup> Over a period of 3 h 1.0-mL aliquots were withdrawn by syringe, hydrolyzed in aqueous NH<sub>4</sub>Cl, extracted into ether, and dried. Samples were analyzed on a Varian Model 2700 gas chromatograph equipped with flame ionization detectors and a 1.8 m  $\times$  2 mm i.d. glass column of 3% SE-30 on 100/200 Gas Chrom Q. Besides *trans*-stilbene and 2-cyano-1,3-diphenylpropene, GLC scans programmed from 75 to 290  $^\circ\text{C}$  at 15 $^\circ/\text{min}$  showed two peaks with retention times of 17.5 and 18 min. No additional peaks were detected with OV-1, OV-17, and DC-560 GLC columns. Yields

Table III. <sup>1</sup>H NMR Spectrum of Cyclopentane Hydrogens of Isomer 2

δ, ppm	Multiplicity	J, Hz	Rel shift, Eu(fod) <sub>3</sub>	Assignment
3.60	t	10.5, 9	1.00	H(1)
3.77	t	10.5, 10.5	0.63	H(2) or H(5)
3.83	t	10.5, 10	0.28	H(3) or H(4)
4.02	t	10, 9.5	0.32	H(4) or H(3)
4.19	t	9.5, 9	0.62	H(5) or H(2)

of the compounds in the two peaks were determined relative to *n*-dodecane, but were not corrected by GLC response factors. The yields were 23 and 25%, respectively, from samples isolated after 1.0, 1.5, and 2.5 h. GLC coupled to a Varian MAT CH-7 mass spectrometer showed that both peaks contained compounds with molecular ions at *m/e* 399. Several attempts to isolate these compounds by preparative GLC failed because of decomposition. The compounds in both GLC peaks were isolated as a mixture by liquid chromatography through a 3 × 60 cm column of silica gel with 10% dichloromethane in hexane as eluent. An oil was obtained after evaporation of solvent. Impurities in the reaction mixture badly affected column performance such that the column had to be washed with methanol after every 3–4 runs and repacked with clean silica gel after 12–15 runs. After about 10 days white crystals formed in the oil. They were isolated and washed with hexane: mp 147–148 °C. GLC of the crystalline material showed only the first of the two peaks observed by GLC of the crude reaction mixture. The structure was established as **1** by x-ray analysis. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** are in Tables I and II. GLC of the mother liquors from the crystallization showed both of the original peaks with relative areas of 20/80.

The unfractionated, chromatographed mixture was shown to be a mixture of isomers of 2,3,4,5-tetraphenylcyclopentane-1-carbonitrile by IR, <sup>1</sup>H and <sup>13</sup>C NMR, and mass spectra. The NMR spectra contained all of the peaks and only the peaks listed in Tables I–III for isomers **1** and **2**: IR (KBr) of mixture 3040 (m), 2240 (m), 1600 (m), 1500 (s), 1450 (s), 1080 (m), 1040 cm<sup>-1</sup> (m); mass spectrum (70 eV) *m/e* (rel intensity) 399 (28), 270 (15), 218 (58), 193 (14), 192 (40), 191 (22), 181 (55), 180 (100), 179 (48), 178 (32).

Exact mass calcd for C<sub>30</sub>H<sub>25</sub>N, 399.19885; found, 399.1990.

Anal. Calcd for C<sub>30</sub>H<sub>25</sub>N: C, 90.18; H, 6.31; N, 3.51. Found: C, 89.93; H, 6.50; N, 3.38.

**Isomerization of 1 to 2.** To a solution of 100 mg of crystalline **1** in 10 mL of *p*-dioxane was added 2.0 mL of a solution of 1.0 M NaOH in water. The mixture was heated quickly to reflux in a nitrogen atmosphere, and 0.5-μL aliquots were withdrawn periodically and injected directly into the gas chromatograph. The reaction mixture contained 51.4% of **2** after 5 min, 86.7% of **2** after 15 min, and 97.7% of **2** after 60 and 120 min. The remainder of the reaction mixture was hydrolyzed with 10% aqueous HCl, extracted with dichloromethane, washed with aqueous NaHCO<sub>3</sub> and water, dried, and evaporated to an oil which was dried at 100 °C and 0.1 mm for 24 h.

The isomerization was repeated using NaOD in D<sub>2</sub>O and was apparently complete after 45 min. Samples isolated from the refluxing solution after 2, 7, and 23 h were analyzed for deuterium by mass spectrometry on a Varian MAT CH-5 instrument at low electron voltage. All three samples gave molecular ions which were 2.98% *d*<sub>0</sub>, 97.00% *d*<sub>1</sub>, and 0.02% *d*<sub>2</sub>. The <sup>1</sup>H and <sup>13</sup>C NMR spectra in Tables I and III were obtained with the oily **2** isolated after 23 h. Subsequently crystals of **2** were obtained from absolute ethanol. Recrystallization gave material with mp 103–105 °C.

**Crystal Data:** C<sub>30</sub>H<sub>25</sub>N, mol wt = 399.56, monoclinic, *a* = 8.431 (1), *b* = 10.920 (2), *c* = 25.038 (6) Å, β = 104.23 (2)°, *V* = 2234.4

Å<sup>3</sup>, *Z* = 4, ρ<sub>c</sub> = 1.19 g/cm<sup>3</sup>, μ (Cu Kα) = 5.3 cm<sup>-1</sup>, *F*(000) = 848, space group *P*2<sub>1</sub>/*c*, λ (Cu Kα) = 1.541 78 Å.

A total of 2789 nonzero reflections was collected on a computer-controlled four-angle Syntex P2<sub>1</sub> diffractometer using Cu Kα radiation. The structure was solved by direct methods. Block-diagonal least-squares refinement of the positional and anisotropic thermal parameters for the nonhydrogen atoms and the positional and isotropic thermal parameters for the hydrogen atoms gave final values for *R* and *R*<sub>w</sub> of 0.053 and 0.057, respectively, on all observed reflections.

**Acknowledgments.** We thank Dr. Chian C. Chiang and Dr. Jain C. Paul for carrying out the x-ray analysis at the University of Illinois. Extensive use was made of the Syntex P2<sub>1</sub> Diffractometer and EXTL computer system whose purchase was made possible by the major equipment grant MPS 75-05911. We thank Dr. Gernot Boche for informative correspondence including an IR spectrum of **1** and a preprint of ref 13.

**Supplementary Material Available:** A listing of the final atomic parameters, bond lengths and bond angles from the crystal structure of isomer **1** is given in Table IV (4 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) Address correspondence to W. T. Ford at Rohm and Haas Company, Research Laboratories, Spring House, Pa. 19477.
- (2) J. Shabtai and H. Pines, *J. Org. Chem.*, **26**, 4225 (1961); M. Kolobielki and H. Pines, *J. Am. Chem. Soc.*, **79**, 5820 (1957).
- (3) G. F. Luteri and W. T. Ford, *J. Organomet. Chem.*, **105**, 139 (1976).
- (4) G. F. Luteri and W. T. Ford, *J. Org. Chem.*, **42**, 820 (1977).
- (5) R. Eidschink and T. Kauffman, *Angew. Chem., Int. Ed. Engl.*, **11**, 292 (1972).
- (6) G. Boche and D. Martens, *Angew. Chem., Int. Ed. Engl.*, **11**, 724 (1972).
- (7) J. P. Marino and Wm. B. Mesbergen, *J. Am. Chem. Soc.*, **96**, 4050 (1974).
- (8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim, W. Germany, 1970.
- (9) T. Kauffmann and E. Köpplmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 290 (1972); T. Kauffmann, K. Habersaat, and E. Köpplmann, *ibid.*, **11**, 291 (1972).
- (10) R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976), and references therein.
- (11) M. Newcomb and W. T. Ford, *J. Am. Chem. Soc.*, **96**, 2968 (1974).
- (12) G. Boche, personal communication.
- (13) G. Boche and D. R. Schnelder, *Tetrahedron Lett.*, 3657 (1976).
- (14) G. Boche, D. Martens, and H.-U. Wagner, *J. Am. Chem. Soc.*, **98**, 2668 (1976).
- (15) A referee suggests that steric hindrance to contact ion pairing between the α-cyano carbon atom and the THF-solvated lithium ion raises the energy of the transition state for cycloaddition of the (*E,Z*) conformer. In the transition state for cycloaddition of the (*E,E*) conformer only hydrogen atoms at C(2) and C(5) need lie on the same side of the cyclopentane ring as the lithium ion; for cycloaddition of the (*E,Z*) conformer one hydrogen atom and one phenyl ring at C(2) and C(5) lie on the same side of the cyclopentane ring as the lithium ion.
- (16) All temperatures are uncorrected.