C, 69.06; H, 6.71. Found: C, 69.21; H, 6.86.

Acknowledgment. B.D. and B.P. thank CSIR, New Delhi, for Senior and Junior Research Fellowships. Financial assistance from UGC, New Delhi under COSIST programme is also acknowledged. We are grateful to the reviewers for critical comments and suggestions.

Registry No. **9a**, 137612-32-9; **9b**, 139378-05-5; **9c**, 139378-06-6; **9d**, 139378-07-7; **9e**, 137612-35-2; **9f**, 137612-33-0; **9g**, 137612-36-3; **10a**, 139378-08-8; **10b**, 139378-09-9; **10c**, 139378-10-2; **10d**, 139378-11-3; **10e**, 139378-12-4; **10f**, 139378-13-5; **10g**, 139378-14-6; **11a**, 139378-15-7; **11b**, 139378-16-8; *cis*-**11e**, 139407-35-5; *trans*-**11e**, 139492-52-7; **12a**, 139378-17-9; **12c**, 139378-18-0; **12d**, 139378-19-1; **12e**, 139378-20-4; **13a**, 139378-21-5; **13b**, 139378-22-6; **13c**, 139378-23-7; **13e**, 139378-24-8; **14**, 139378-25-9; **15**, 139378-26-0; **16a**, 139378-27-1; **16e**, 139378-28-2; **17**, 52714-10-0; **18a**, 17649-86-4; **18b**, 17649-87-5; **19a**, 139378-29-3; **19b**, 139378-30-6; **20a**, 139378-31-7; **20b**, 139378-32-8; **21**, 139378-33-9; **22**, 139378-34-0; **23**, 139378-35-1; **25**, 139378-36-2.

Bis(2-acetoxyacrylonitrile) and Its Phenylene and Alkylene Bis Homologues. Preparation, Isomerization, and Intramolecular [2 + 2] Photocycloaddition

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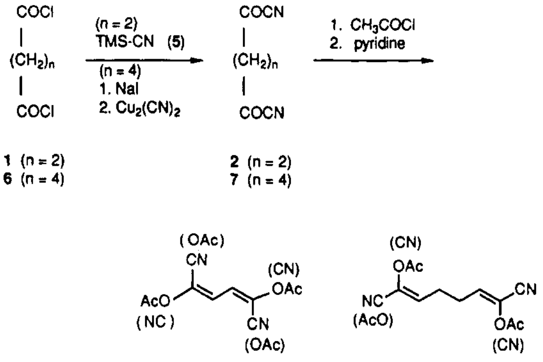
Received March 13, 1990 (Revised Manuscript Received November 22, 1991)

The title compounds, 1,4-diacetoxy-1,4-dicyano-1,3-butadiene (**3**), 1,6-diacetoxy-1,6-dicyano-1,5-hexadiene (**8**), 1,2-bis(2-acetoxy-2-cyanovinyl)benzene (**13**), and 1,4-bis(2-acetoxy-2-cyanovinyl)benzene (**17**) were prepared by acetylation of the corresponding diacyl dicyanides. Dicyanides were prepared from diacyl chlorides by reaction with cyanotrimethylsilane or the NaI-$Cu_2(CN)_2$ reagent. Among the three geometrical isomers of the title compounds, the *Z,Z* diene predominated in **8** whereas *E,E* dienes predominated in conjugated dienes **3**, **13**, and **17**. Conjugated *E,E* dienes underwent photoisomerization to *E,Z* and *Z,Z* isomers much faster than unconjugated diene **8**. Prolonged irradiation on **13** yielded intramolecular [2 + 2] cycloadducts *endo,exo*- and *exo,exo*-5,6-diacetoxy-5,6-dicyano-2,3-benzobicyclo[2.1.1]hex-2-ene (**22**). Photochemistry in the formation of **22** is discussed.

While ketenes have been considered useful compounds in organic synthesis, their instability limits their utility in many ways. Consequently, several synthetic equivalents for ketenes have been developed.[1] One example is 2-acetoxyacrylonitrile, which is useful as a dienophile,[2] Michael acceptor,[3] carbene acceptor,[4] and monomer[5] for polymer synthesis. The few synthetic methods available produce mainly nitriles unsubstituted at the 3-position.[6] However, acylation of the enolates of acyl cyanides[7] enabled us to prepare a number of 3-substituted 2-(acyloxy)acrylonitriles. In the present report syntheses of bis(2-acetoxyacrylonitrile)s bearing either a conjugated or unconjugated diene are described as well as their photochemical isomerization and photochemical intramolecular [2 + 2] cycloaddition reactions.

Results and Discussion

Preparation of Aliphatic Dienes. A synthetic route to 1,4-diacetoxy-1,4-dicyano-1,3-butadiene (**3**) is shown in eq 1. The first attempt to prepare bis(acyl cyanide) **2** by the reaction of succinyl chloride (**1**) with sodium iodide[8] followed by the treatment with cuprous cyanide was unsuccessful and 4,4-dicyano-γ-butyrolactone (**4**) was obtained. The formation of **4** can be explained in analogy to the dimer formation of simple acyl cyanides.[9] However, the use of cyanotrimethylsilane (**5**)[10] was found to successfully give **2** in 63% yield. The reaction of **2** with acetyl chloride and pyridine finally afforded the expected butadiene **3** (63% yield), which consisted only of the *E,E* isomer.[11]



1 (n = 2)
6 (n = 4)

2 (n = 2)
7 (n = 4)

(1)

3 (n = 2) (E,E), (Z,E), (Z,Z) **8** (n = 4) (Z,Z), (Z,E), (E,E)

The choice of cyanation reagents is important.[12] When adipyl chloride (**6**) was treated with cyanosilane **5**, tetra-

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[1] (a) Corey, E. J.; Welnshenker, N. M.; Schaff, T. K.; Huber, W. *J. Am. Chem. Soc.* **1969**, *91*, 5675. (b) Ranganathan, S.; Ranganathan, D.; Mehrotra, A. K. *Synthesis* **1977**, 289. (c) Bartlett, P. D.; Tate, B. T. *J. Am. Chem. Soc.* **1956**, *78*, 2473.

[2] (a) Evans, D. A.; Scott, W. L.; Truesdale, K. *Tetrahedron Lett.* **1972**, 21. (b) Oku, A.; Hasegawa, H.,; Shimadzu, H.; Nishimura, J.; Harada, T. *J. Org. Chem.* **1981**, *46*, 4152.

[3] Oku, A.; Horiie, N.; Harada, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 609.

[4] Oku, A.; Yokoyama, T.; Harada, T. *J. Org. Chem.* **1981**, *48*, 5333.

[5] (a) Ohta, T. *Kogyo Kagaku Zasshi*, **1968**, *71*, 1542. (b) Miyashita, Y.; Shimada, N.; Yamamoto, Y.; Kohjiya, S.; Yamashita, S.; Oku, A. *Chem. Soc. Jpn., 45th Ann. Meeting*, Tokyo (1982), Abstract II, 1J11.

[6] (a) Baker, J. W. *J. Chem. Soc.* **1942**, 520. (b) Johnston, F. U.S. Patent 2395930, 1946.

[7] (a) Oku, A.; Arita, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3337. (b) Oku, A.; Nakaohji, S.; Kadono, T.; Imai, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2966.

[8] THF was inadequate as the solvent because it underwent a ring-cleavage reaction by the intermediate acyl iodide to give bis(4-iodobutyl) succinate. Oku, A.; Harada, T.; Kita, K. *Tetrahedron Lett.* **1982**, *23*, 681.

[9] Tate, D. E. *J. Am. Chem. Soc.* **1956**, *78*, 5575.

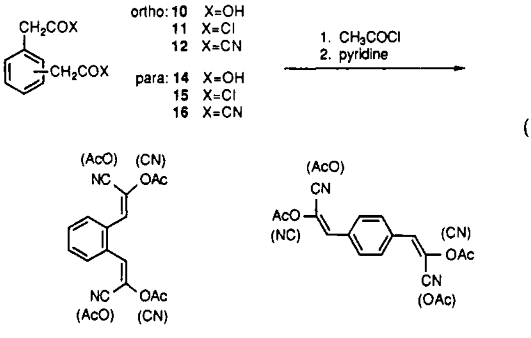
[10] (a) Zubrik, J. W.; Dubar, B. L.; Durst, H. D. *Tetrahedron Lett.* **1975**, 71. (b) Herrman, K.; Simdren, G. *Synthesis* **1979**, 204.

[11] For the NMR spectra see the Experimental Section and for the details of structure determination see the supplementary material pages (S-1) for **3**, (S-2) for **8**, (S-3) for **13**, (S-4) for **17**, (S-5) for **22**, and also from (S-1-1) to (S-5-1) for spectra charts.

[12] Hünig, S.; Schaller, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 36.

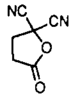
cyanide 9[13] was formed (14%) but cyanide 7 was not found.[14] To prepare cyanide 7 successfully,[15] 6 we treated with sodium iodide followed by the cyanation with cuprous cyanide in the presence of phosphorus pentoxide. Without isolation of 7 the reaction mixture was treated with acetyl chloride–pyridine reagent to give a mixture of three geometric isomers of 1,6-diacetoxy-1,6-dicyano-1,5-hexadiene (8) in 67% yield.[11]

Preparation of Divinylbenzene Derivatives. 1,2-Bis(2-acetoxy-2-cyanoethenyl)benzene (13) was prepared from 1,2-benzenediacetic acid (10) (eq 2). All the procedures were carried out in one-pot operation using sodium iodide–cuprous cyanide reagent in the same way as was mentioned above for 8. The acetylation of 12 gave 13 in 34% yield. 4-Cyano-1,2-dihydro-2-oxo-6-benzo-3-oxepine (18) was the second product (19%), which became the sole product (71%) in a prolonged acetylation for 18 days. Use of 5[16] as the cyanation reagent was unsuccessful.



(2)

13 (E,E), (Z,E), (Z,Z) 17 (E,E), (Z,E), (Z,Z)



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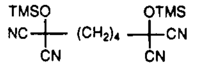

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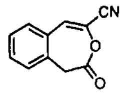


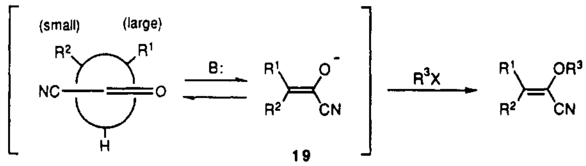
18

1,4-Bis(2-acetoxy-2-cyanoethenyl)benzene (17) was also prepared in 34% yield from 1,4-benzenediacetic acid (14) via dichloride 15 and dicyanide 16 in the same way as was adopted for 13.

The rates of diene formation are remarkably different among the four dienes. Conjugated dienes 3, 13, and 17 are formed relatively fast with one isomer always predominating, whereas unconjugated diene 8, which consists of three isomers, is formed as slowly as 2-acetoxy-3-methylacrylonitrile was.[7b] Therefore, we assume that both the formation of the monoenolate and the consecutive formation of bisenolate proceeded much faster with 2, 12, and 16 than with 7 as a consequence of the formation of a conjugated diene (eq 4).

Photochemical Isomerization. Butadiene 3 obtained from the acetylation of 2 consisted of one isomer (A). It was transformed either thermally or photochemically to other geometrical isomers B and C: Heating A without solvent, or exposing its acetone solution to sunlight, or irradiating its $CDCl_3$ solution with a medium pressure Hg lamp yielded a mixture of A, B, and a trace of C. On the basis of the ^1H NMR analysis, A, B, and C are assigned to 3(*E*,*E*), 3(*Z*,*E*), and 3(*Z*,*Z*), respectively.[10]

Hexadiene 8 formed by the acetylation of 7 consisted of three isomers D, E, and F in the ratio 88/11/1. The ratio changed to 43/51/6 after irradiating the mixture for 42 h with a medium pressure Hg lamp. The assignment of the second major isomer E was done based on the appearance of two acetyl protons with different chemical shifts but equivalent intensities. The assignment of the major isomer D to either 8(*E*,*E*) or 8(*Z*,*Z*) by a simple NMR analysis seemed difficult because the olefinic protons of both D and E appear within 6.05–6.10 ppm. NOESY spectra of the mixture (ca. 1:1) of D and E were measured to solve this problem. While the acetyl methyl of D as well as one of two methyls of E appearing at a lower field does not show any appreciable NOE interaction, the methyl appearing at higher field does with two olefinic protons. Therefore, we assigned D as the *Z*,*Z* isomer. The assignment is in accord with the predominant formation of the *Z* isomers for simple 3-alkyl-substituted 2-acetoxyacrylonitriles.[7b,12] Hünig and co-workers explained this selectivity in terms of conformational control in cyano enolate (19 in eq 3). Hence, isomer F must be 8(*E*,*E*).[11]



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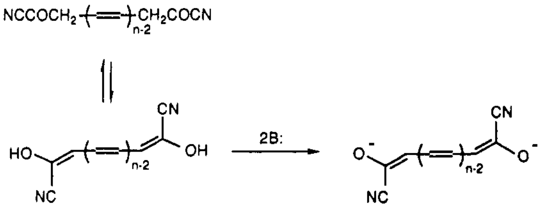
(3)

o-Divinylbenzene 13 which initially consisted of one isomer (G) underwent photoisomerization to give a mixture of three isomers (G, H, and I). They are assigned structures 13(*E*,*E*), 13(*E*,*Z*), and 13(*Z*,*Z*), respectively, by ^1H NMR (NOESY) analysis: Isomer H shows two pairs of singlets for methyl and olefinic protons in which an appreciable NOESY is observed between the higher counterpart of each pair. Therefore, these signals are ascribable to the *E* moiety of the *E*,*Z* isomer. In comparison with this observation isomer G is assigned to the *E*,*E* structure.[11,17] *p*-Divinylbenzene 17 consisting also of one isomer (J) underwent photoisomerization to give a mixture of three isomers (J, K, and L). On the basis of a similar reasoning made for 13, the three isomers are assigned respectively structures 17(*E*,*E*), 17(*E*,*Z*), and 17(*Z*,*Z*).[11] The dominance of *E*,*E* configuration in conjugated dienes indicates that the corresponding *E*,*E* isomer of dienol 20 or dienolate 21 (eq 4) may be preferable to the *Z*,*Z* isomer.



20 21

(4)

Similarly to their rapid photoisomerization, conjugated dienes also underwent thermal isomerization readily at 150 °C, whereas unconjugated diene 8 isomerized quite slowly under the same conditions.

Intramolecular [2 + 2] Photocycloaddition of Diene 13. Nonsensitized photolysis of 13(*E*,*E*) for 6 h first produced a mixture of G, H, and I (the ratio of *E* to *Z* groups = 69/31). Further irradiation changed the product com-

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[13] Hertenstein, U.; Hünig, S.; Reichelt, H. *Chem. Ber.* **1982**, *115*, 261.

[14] The reaction of 6 with 5 for 9 days at 20 °C followed by treatment with AcCl/pyridine gave 8 in only 2% yield.

[15] (a) Asinger, F.; Saus, A.; Offermanns, H.; Hahm, H. D. *Justus Liebigs Ann. Chem.* **1966**, *92*, 691. (b) Haase, K.; Hoffmann, H. M. R. *Angew. Chem.* **1982**, *94*, 80.

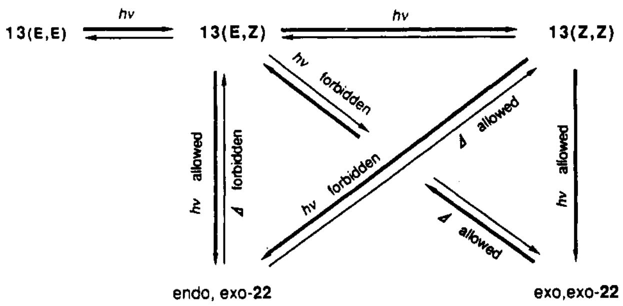
[16] Hünig, S.; Lucke, E.; Brenninger, W. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 533.

[17] Structural determination on the basis of empirical methods proposed in the following reports was not adequate for those compounds: (a) Pascual, C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164. (b) Tobey, S. W. *J. Org. Chem.* **1969**, *34*, 1281.

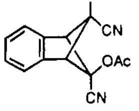
Table I. Time-Dependent Change in the Isomer Distribution of Dienes during Irradiation

		isomer ratio *Z,Z*/*Z,E*/*E,E*		
time (h)	diene 3	diene 8	diene 13	diene 17
0	0/0/100	88/11/1	0/0/100	0/0/100
6	16/43/41		65/35/0	10/30/60
18	22/41/37		**22** appeared	complex
42	22/45/33	43/51/6	**13** disappeared	complex

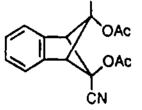
Scheme I



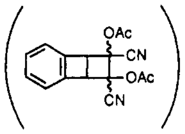
position to form two intramolecular [2 + 2] cycloadducts **22**. On the basis of spectroscopic analysis,[11] the structures were elucidated to be endo,exo and exo,exo isomers of 2,3-benzobicyclo[2.1.1]hex-2-ene (**22**), the head-to-tail cycloadducts of **13**. Bicyclo[2.2.0]hexene **23**, benzobicyclo[2.1.1]hexene,[18] benzobicyclo[3.1.0]hexene,[19] and dimers[20] were not detected in the product mixture.



endo, exo -**22**



exo, exo -**22**



23

The photochemical interconversion of the isomers of **13** and their photocyclizations to **22** were examined. The time-dependent photochemical changes in the isomer distribution (Table I) and also the independent photochemical as well as thermal reactions[21] of the isolated isomers of **13** showed that the *E,E* isomer first isomerizes to *E,Z* and then to *Z,Z*, both undergoing further photochemical cyclization to give *endo,exo*- and *exo,exo*-**22** at a slower rate than the isomerization. In contrast, the *E,E* isomer hardly undergoes cyclization. The endo,exo photoproduct was formed from the *Z,Z* diene more selectively (endo,exo:exo,exo = 6:1) than from the *Z,E* isomer (the ratio was 3:1). This implies that a direct cyclization path of the *Z,Z* diene to *endo,exo*-**22** must exist without the intervention of the *Z,E* isomer. Scheme I illustrates the observed transformations.

According to the orbital symmetry rule, photocyclization of **13**(*Z,Z*) may produce either *exo,exo*- or *endo,endo*-**22** via a supra–supra or antara–antara route, respectively. However, the photochemically symmetry-forbidden product *endo,exo*-**22** was the major product. Analogously, thermal ring-opening of *endo,exo*-**22** gave the symmetry-forbidden product *E,Z* together with the symmetry-allowed product *Z,Z*. A reasonable explanation for the results is that a biradical intermediate derived from a triplet excited state must be involved as the major reacting species in the unsensitized photocyclization of **13**. [2 + 2] photocycloadditions of *o*-divinylbenzene derivatives[18-20] and styrenes[22] have been reported to proceed in a stepwise manner via diradicals. In addition, photosensitized reactions of 1,5-hexadienes give bicyclo[2.1.1]hexanes efficiently.[23] In the direct irradiation of **13**, a triplet process producing five-membered bicyclic structures dominates both kinetically and thermodynamically over the concerted process owing to the highly substituted conjugated structure of **13**.

Experimental Section

General. ^{1}H NMR spectra were measured at 60 or 300 MHz in $CDCl_3$ unless otherwise stated. ^{13}C NMR spectra were recorded on a 75-MHz spectrometer. Low-resolution (LRMS) and high-resolution (HRMS) mass spectra were measured at 70 eV. Temperatures are not corrected.

Succinyl (**1**) and adipyl chloride (**6**) were prepared by the method reported.[24] 1,2-Benzenediacetyl chloride (**11**) was prepared by the reaction of the diacid **10** with $SOCl_2$. 1,4-Benzenediacetyl chloride (**15**) was prepared by the method of Titley.[25] NaCN and $Cu_2(CN)_2$ were dried at 120 °C under vacuum for 24 h. Pyridine and acetonitrile were dried over CaH_2 and distilled. For photolysis, a $CDCl_3$ solution of the diene under N_2 was irradiated at 25 °C with a Ushio 453B medium pressure Hg lamp equipped with a Pyrex filter.

Succinyl Dicyanide (2). Under an N_2 atmosphere succinyl chloride (**1**) 16.3 g (105 mmol) was added to cyanotrimethylsilane (**5**) at room temperature. The reaction progress was monitored by IR spectroscopy [**1** (1800 cm^{-1}) and cyanide **2** (1740 cm^{-1})]. After 7 days, dicyanide **2** was obtained in 63% yield by distillation.

1,4-Diacetoxy-1,4-dicyano-1,3-butadiene (3). Freshly distilled cyanide **2** (9.06 g, 6.66 mmol) was mixed with acetyl chloride (AcCl, 14.6 g, 186 mmol) in benzene (17 mL), and to this mixed solution was added a benzene solution (80 mL) of pyridine (14.6 g, 186 mmol). After 1 h, the mixture was worked up with water and EtOAc. After removing the solvent, the remaining solid was recrystallized from benzene to give **3** (9.19 g, 63%). **3(*E,E*)**: mp 165–170 °C; ^{1}H NMR 2.22 (6 H, s), 6.65 (2 H, s); ^{13}C NMR 20.189 (CH_3CO), 113.069 (CN), 121.775 (=CH), 123.874 (=C), 166.216 (C=O); IR (KBr) 3080, 2220, 1773, 1610, 1380, 1200, 1140, 1020, 920, 900, 800 cm^{-1}; LRMS, *m/z* 220 (M^+, 0.085), 178 (2), 109 (1.7), 54 (1.8), 43 (100); UV λ_{max} (nm, EtOH) 351 (3330), 274 (20000).

Anal. Calcd for $C_{10}H_8N_2O_4$: C, 54.53; H, 3.66; N, 12.72. Found: C, 54.81; H, 3.55; N, 12.75.

3(*Z,E*): ^{1}H NMR 2.22 (3 H, s), 2.26 (3 H, s), 6.72 and 6.83 (2 H, d × 2, $J = 18$ Hz).

1,6-Diacetoxy-1,6-dicyano-1,5-hexadiene (8) by the Reaction of Adipyl Chloride (6) with NaI–$Cu_2(CN)_2$. Chloride **6** (13.1 g, 71 mmol) was added to a mixture of $Cu_2(CN)_2$ (12.8 g, 142 mmol), NaI (12.8 g, 142 mmol), and P_2O_5 (1 g) in CH_3CN (40 mL) at rt. The consumption of **6** (1800 cm^{-1}) and the formation of cyanide **7** (1740 cm^{-1}) were monitored by IR measurement. After 4 days, AcCl (15.7 g, 200 mmol) and pyridine (15.8 g, 200 mmol) were added, and the mixture was stirred for an additional 40 h. A column chromatographic separation followed by distillation (203 °C/0.27 Torr) yielded a mixture of three isomeric hexadienes **8** in 67% yield (*Z,Z*/*Z,E*/*E,E* = 88/11/1). **8**: mp 89–100 °C (mixture of three isomers). **8(*Z,Z*)** (separated from a mixture of *Z,Z* and *Z,E*): ^{1}H NMR 2.24 (6 H, s), 2.28 (4 H, d × 2, $J = 7.5$ Hz), 6.05 (2 H, bt); ^{13}C NMR 19.94 (CH_3), 24.20 (CH_2), 113.30 (CN), 122.15 (=CH), 134.39 (=C), 167.03 (CO); IR 2220, 1790, 1670, 1200, 1120 cm^{-1}; UV λ_{max} (EtOH) 223 (12900); LRMS, *m/z* 248 (M^+, 0.43), 206 (1.54), 55 (9.39), 43 (100), 42 (3.66).

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(19) Pomerantz, M. *J. Am. Chem. Soc.* **1967**, *89*, 694.

(20) Tavares, D. F.; Ploder, W. H. *Tetrahedron Lett.* **1970**, 1567.

(21) Heating a dioxane solution of *exo,exo*-**22** at 90 °C for 24 h afforded only **13**(*Z,E*) (72%) whereas *endo,exo*-**22** gave both *Z,E* and *Z,Z* (30 and 3%, respectively, at 90 °C, 41 and 14% at 100 °C). Also the acid hydrolysis of **22** at 90 °C gave 1,2-benzenediacetyl cyanide **12**, indicating that **22** underwent retrocyclization to diene **13** and further hydrolysis to give **12**. **12**: ^{1}H NMR 3.70 (s, 4 H), 7.28 (s, 4 H); IR ($CDCl_3$) 1720, 2240 cm^{-1}.

(22) Nishimura, J.; Doi, H.; Ueda, E.; Ohbayashi, A.; Oku, A. *J. Am. Chem. Soc.* **1987**, *109*, 5293.

(23) (a) Review: Dilling, W. L. *Chem. Rev.* **1969**, *69*, 845. (b) Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 4936. (c) Charlton, J. L.; deMayo, P.; Skattebøl, L. *Tetrahedron Lett.* **1965**, 4579.

(24) Ruggli, P.; Maeder, A. *Helv. Chim. Acta* **1943**, *26*, 1486.

(25) Titley, A. F. *J. Chem. Soc.* **1926**, *128*, 508.

8(*Z*,*E*): ^{1}H NMR 2.19 (3 H, s), 2.23 (3 H, s), 2.36 (2 H, bq, J = 7.5 Hz), 2.48 (2 H, bq, J = 7.5 Hz), 5.98 (1 H, t, J = 7.5 Hz), 6.10 (1 H, t, J = 7.5 Hz).

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.28. Found: C, 58.14; H, 4.92; N, 11.32.

1,2-Bis(2-acetoxy-2-cyanoethenyl)benzene (13). To a mixture of $Cu_2(CN)_2$ (0.85 g, 9.5 mmol), NaI (1.42 g, 9.5 mmol), and P_2O_5 (0.1 g) in CH_3CN (10 mL) was added a solution of 1,2-benzenediacetyl chloride (**11**) (1.04 g, 4.5 mmol) in CH_3CN (5 mL) at 0 °C. After stirring for 2 h at rt (for the ^{1}H NMR data for intermediate cyanide **12** see ref 21 for the hydrolysis of **13**), AcCl (0.85 g, 10.8 mmol) and pyridine (0.86 g, 10.8 mmol) were added successively. After 3 days the precipitated solids were removed and the AcCN solution of the filtrate was concentrated under vacuum and worked up with a mixture of water and AcOEt. Purification on a silica gel column afforded crystalline **13** in 34% yield. **13(*E*,*E*)**: mp 140–142 °C; ^{1}H NMR 2.22 (6 H, s), 6.90 (2 H, s), 7.42 (2 H, m), 7.55 (2 H, m); ^{13}C NMR 20.27 (CH_3), 113.89 (CN), 121.70 (=CH), 129.65, 129.70, 130.01, 130.11 (two sets of aromatic =CH, one set each of aromatic =C and olefinic =C), 166.78 (CO); IR (KBr) 2220, 1790, 1650, 1200, 1160 cm^{-1}; UV λ_{max} (EtOH) 251 (14 000), 281 (11 600), 209 (6100); LRMS, m/z 296 (M$^+$, 1.91), 254 (5.0), 227 (15.5), 212 (18.3), 185 (100), 158 (23.6).

Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.45. Found: C, 64.72; H, 3.93; N, 9.34.

Other isomers were obtained from the pyrolysis.[26] **13(*Z*,*E*)**: ^{1}H NMR 2.21 (3 H, s, AcO of the *E* moiety), 2.32 (3 H, s), 6.91 (1 H, s, =CH— of the *E* moiety), 7.08 (1 H, s), 7.45–7.55 (1 H, m), 7.75–7.87 (1 H, m); **13(*Z*,*Z*)**: ^{1}H NMR 2.27 (6 H, s), 7.07 (2 H, s), 7.57 (4 H, m).

1,4-Bis(2-acetoxy-2-cyanoethenyl)benzene (17). The preparative procedure which was similar to that described for **13** gave **17** in 34% yield. **17(*E*,*E*)**: mp 140–142 °C; ^{1}H NMR 2.35 (6 H, s), 6.73 (2 H, s), 7.55 (4 H, s); ^{13}C NMR 20.544 (CH_3), 114.25 (CN), 121.06 (=CH), 130.42 (aromatic =CH), 130.81 (aromatic =C), 132.86 (=C), 166.49 (CO); IR (KBr) 2220, 1770, 1640, 1210, 1150 cm^{-1}; UV λ_{max} (EtOH) 315 (26 900), 327 (21 300), 226 (9300).

Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.45. Found: C, 64.96; H, 4.04; N, 9.24.

Irradiation of the *E*,*E* isomer for 6 h afforded two other isomers. **17(*Z*,*E*)**: ^{1}H NMR 2.23 (3 H, s), 2.27 (3 H, s), 6.72 (1 H, s), 6.97 (1 H, s), 7.70 (4 H, m). **17(*Z*,*Z*)**: ^{1}H NMR 2.27 (6 H, s), 6.97 (2 H, s), 7.78 (4 H, s).

General Procedure for the Photoisomerization of Dienes. Under an N_2 atmosphere, a $CDCl_3$ solution (0.4 mL) of a diene (11 mg) was placed in an NMR sample tube (Pyrex) which was then irradiated with a medium pressure Hg lamp. Time-dependent changes of the components in the solution were examined by NMR and the results for **3**, **8**, **13**, and **17** are summarized in Table I.

Photocyclization of 13. A $CDCl_3$ solution of **13(*E*,*E*)** was irradiated without sensitizers through a Pyrex filter for 18 h. Cyclization products *endo*,*exo*- and *exo*,*exo*-5,6-diacetoxy-5,6-dicyano-2,3-benzobicyclo[2.1.1]hex-2-enes (*endo*,*exo*-**22** and *exo*,*exo*-**22**) appeared in the reaction mixture in addition to *Z*,*E* and *Z*,*Z* isomers of **13**. After 42 h, isomers of **13** disappeared and only two isomers of **22** remained in the solution. ***endo*,*exo*-22** (65%): mp 120 °C; ^{1}H NMR 1.71 (3 H, s, *endo*-AcO), 2.31 (3 H, s), 4.51 (2 H, s), 7.32 (2 H, m), 7.38 (2 H, m); ^{13}C NMR 19.65 and 20.75 (CH_3), 61.22 (CH), 84.52 and 85.18 (AcOCCN), 113.77 and 115.48 (CN), 123.33, 128.21, and 128.89 (three sets of aromatic C), 168.07 and 168.75 (CO); IR (KBr) 2230, 1770 cm^{-1}; LRMS, m/z 296 (M$^+$), 254, 212, 194, 167. Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; 9.45. Found: C, 64.38; H, 3.93; N, 9.44. ***exo*,*exo*-22** (18%): mp 133–135 °C; ^{1}H NMR 2.20 (6 H, s), 4.45 (2 H, s), 7.45 (2 H, m), 7.52 (2 H, m); ^{13}C NMR 20.40 (CH_3), 59.58 (CH), 88.87 (AcOCCN), 114.40 (CN), 123.27 and 129.61 (two sets of aromatic =CH), 138.77 (aromatic =C), 168.17 (C=O); IR (KBr) 2230, 1770 cm^{-1}; LRMS, m/z 296 (M$^+$), 254, 227, 212, 194, 167; CI-MS m/z 297 (MH$^+$). Anal. Found: C, 64.72; H, 4.05; N, 9.40.

Independent irradiation of a $CDCl_3$ solution of **13(*Z*,*E*)** or **13(*Z*,*Z*)** for 30 min gave a mixture of three isomers of **13** containing a small amount of **22**, whereas that of *E*,*E* formed only a mixture of three isomers of **13**. After 1 h, the formation of **22** from *Z*,*E* was first observed. After 3 h, a mixture of two isomers of **22** containing no diene isomers was formed from both *Z*,*E* and *Z*,*Z*, whereas in the irradiated product mixture starting from *E*,*E* the diene isomers remained to some extent and later disappeared after 6 h.

Acknowledgment. Support by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 01649510) is greatly appreciated.

Registry No. **1**, 543-20-4; **2**, 63979-84-0; (*E*,*E*)-**3**, 139131-43-4; (*Z*,*E*)-**3**, 139131-44-5; **6**, 111-50-2; **7**, 80317-75-5; (*Z*,*Z*)-**8**, 139131-45-6; (*Z*,*E*)-**8**, 139131-46-7; (*E*,*E*)-**8**, 139131-47-8; **10**, 7500-53-0; **11**, 41640-86-2; **12**, 139131-48-9; (*E*,*E*)-**13**, 139131-49-0; (*Z*,*E*)-**13**, 139131-50-3; (*Z*,*Z*)-**13**, 139131-51-4; **14**, 7325-46-4; **15**, 21062-19-1; **16**, 139131-52-5; (*E*,*E*)-**17**, 139131-53-6; (*Z*,*E*)-**17**, 139131-54-7; (*Z*,*Z*)-**17**, 139131-55-8; *endo*,*exo*-**22**, 139166-26-0; *exo*,*exo*-**22**, 139240-39-4; Me_3SiCN, 7677-24-9.

Supplementary Material Available: Spectral data for dienes **3**, **8**, **13**, and **17** and cycloadducts **22** and explanations for structure determination (22 pages). Ordering information is given on any current masthead page.

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[26] Under an N_2 atmosphere in sealed tubes without solvent, **3**(*E*,*E*), a mixture of **8** (*Z*,*Z*/*Z*,*E*/*E*,*E* = 88/11/1), **13**(*E*,*E*), or **17**(*E*,*E*) was heated at 150 °C for 8 h except **3**(*Z*,*Z*) which was heated at 170 °C for 1 h. Isomer ratios were analyzed by ^{1}H NMR.

The Ortho–Para Ratio and the Intermediate in the Persulfate Oxidation of Aromatic Amines (the Boyland–Sims Oxidation)

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Received December 10, 1990

The previous belief that the persulfate oxidation of aromatic amines gives the *o*-sulfate exclusively is untrue; substantial quantities of the para isomer are produced. Kinetic studies on 2,4- and 2,6-disubstituted aromatic amines show that the rate of reaction with persulfate is nearly the same for both isomers. The probable intermediate in this reaction is the arylhydroxylamine-*O*-sulfonate. This was demonstrated by showing that the reaction between *N*,*N*-dimethylaniline *N*-oxide and the sulfur trioxide–pyridine complex gives material which rearranges to a mixture of *N*,*N*-dimethylaniline *o*- and *p*-sulfates in the same ratio as is given by the persulfate oxidation of *N*,*N*-dimethylaniline. The ortho–para ratio is unaffected by dilution. This leads to the conclusion that the degree of intramolecularity of the rearrangement is the same for the formation of both the ortho and para isomers.

Persulfate ions have been reported to react with aromatic amines in neutral or basic aqueous solutions to form *o*-amino aryl sulfates exclusively with the exception that small amounts of the para isomers were reported for the

0022-3263/92/1957-2266$03.00/0