converted to the corresponding nitroso- and/or nitroarenes.

The evolution of a small amount of nitric oxide when sodium nitrite dissolves in trifluoroacetic acid is a fairly reproducible phenomenon and deserves comment. The extent of this reaction does not appear to depend upon the nitric oxide pressure, although detailed measurements have not yet been made. Thus the equilibria that control the formation of NO probably do not involve it. The simplest explanation is suppression of nitrous acid decomposition by water formed in the dehydration of nitrous acid, eq 6-8.

$$NaNO_2 + CF_3CO_2H \rightarrow HNO_2 + Na^+CF_3CO_2^- \quad (6)$$

$$2HNO_2 \rightarrow H_2O + NO + NO_2 \quad (7)$$

$$HNO_2 + CF_3CO_2H \rightarrow H_2O + NO^+CF_3CO_2^- \quad (8)$$

Experimental Section

Experiments except as noted above were conducted or prepared on a vacuum line in which all parts exposed to the reactants were glass, Teflon, Viton, or stainless steel. Pressures were measured by means of an MKS Baratron capacitive pressure gauge that had been calibrated against a laboratory aneroid barometer. The volumes of the various manifolds were determined by pressure, volume, temperature measurements against a calibrated volume sealed into the system. Nitrogen dioxide was measured out by filling a known volume to a pressure calculated by a program for a hand-held calculator that took into account the dimerization to dinitrogen tetroxide and the variation of the equilibrium constant with temperature and then condensing into the reaction mixture. Temperature of a gas was measured by taping a thermocouple to the manifold in which its pressure was measured.

Materials. Trifluoroacetic acid and chloroacetic acid were purchased from Aldrich Chemical Co. Toluene and benzene were ACS reagent grade. These materials were degassed and usually vacuum transferred into the reaction vessel prior to use. Nitrogen dioxide was obtained from Air Products and Chemicals, Inc., and labeled nitrogen dioxide was obtained from Prochem Isotopes. Sodium nitrite was ACS reagent grade purchased from Fisher Scientific and had an assay of 96% by permanganate titration. Palladium acetate and thallium trioxide were obtained from Alfa Inorganics and were used as supplied.

Analysis. Except as noted in the supplementary results, reaction mixtures were worked up by quenching in water, extraction with methylene chloride, reextraction with water to remove TFA, extraction with 1% sodium carbonate to remove acidic byproducts, and drying with calcium sulfate. The sodium carbonate extracts were acidified to pH 1 with sulfuric acid and extracted three or four times with ether. The dried ether solutions were examined by thin-layer and/or liquid chromatography. Nitroarene products were analyzed by gas chromatography on a 25-m dimethylsilicone capillary column using nitrobenzene as internal standard for nitrotoluenes and *p*-nitrotoluene as internal standard for nitrobenzene. Response factors were measured from mixtures approximating the compositions of those analyzed. The internal standard was generally added to the initial reaction mixture. A Finnigan Model OWA GC/MS was used by the Air Products Corporate Research Services Department.

Acknowledgment. I am indebted to Drs. Brian C. Challis and James F. White for helpful discussions and to Fred B. Leh for his capable laboratory assistance. Permission by Air Products and Chemicals, Inc., to publish this work is also gratefully acknowledged.

Registry No. Benzene, 71-43-2; toluene, 108-88-3; nitrosobenzene, 586-96-9; sodium nitrite, 7632-00-0; nitrogen dioxide, 10102-44-0; nitric oxide, 10102-43-9; palladium acetate, 3375-31-3; Wilkinson's catalyst, 14694-95-2; dithallium trioxide, 1314-32-5; benzenediazonium nitrate, 619-97-6; trifluoroacetic acid, 76-05-1.

Supplementary Material Available: Tables of data on the nitration of toluene in TFA, concentration effects on nitration in TFA and acetic acid, and oxidation of nitrosobenzene and a figure (5 pages). Ordering information is given on any current masthead page.

1,1-Dicyclopropylallene: Cycloadditions and Dimerization. Dependence of the Regioselectivity on Solvent Polarity and Lewis Acid Catalysis in the Reactions with Alkoxycarbonyl-Activated Olefins[1]

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1,1-Dicyclopropylallene (**1a**) was found to react with a number of activated olefins (**2**) in a [2 + 2] manner. The reactions with monoactivated **2**, as well as those with 1,2-disubstituted **2**, proceeded at reasonable rates at 200 °C, whereas the reactions with 1,1-disubstituted **2** occured at much lower temperatures. Moreover, the dependence of regioselectivity on the structure of **2** was noted in these reactions. Thus, at 200 °C, methyl acrylate (**2a**), acrylonitrile (**2f**), dimethyl fumarate (**2b**), dimethyl maleate (**2c**), fumaronitrile (**2g**), and maleonitrile (**2h**) yielded the adducts **4** predominantly, if not exclusively. In contrast, the reaction with methylenemalononitrile (**2i**), as well as that with ethenetetracarbonitrile (**2j**), occured at room temperature with overwhelming production of the adducts **3**. The reaction of **1a** with diethyl methylenemalonate (**2d**) required heating to some degree, and its regioselectivity was influenced by solvent polarity. Namely, **4d** predominated in refluxing benzene whereas **3d** was a major product in refluxing acetonitrile. It was further revealed that the Lewis acid catalysis greatly reduced the necessary temperature for the reactions of **1a** with alkoxycarbonyl-activated olefins and brought about a total reversal of the regioselectivity. Thus, **2a-d** gave **3** exclusively at room temperature in the presence of aluminum chloride. These cycloadditions should be stepwise processes since all the reactions that were carried out with **2c** were nonstereospecific. The thermal reaction yielding **4** predominantly appears to be a diradical stepwise process whereas the reaction producing **3** as the principal cycloadduct will involve an intermediate possessing a polar character. Finally, **1a** was found to dimerize at 200 °C. Among the two dimers produced, less crowded **9** rearranged slowly to a spiro compound **11** under the reaction conditions.

The chemistry of allenes has attracted considerable attention for some decades mostly because the allenes exhibit peculiar chemical reactivities.[2] In particular, mechanistic interests have focused on rare, thermal [2 +

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2] cycloadditions which allenes carry out with relative ease.[3]

Among the various allenes, a compound substituted by a cyclopropyl group(s)[4] appears to be an interesting substrate from at least two points of view. On the one hand, the reactivity of allenic multiple bonds will be influenced by the special electronic effects of the cyclopropyl group(s),[5] and, on the other hand, the allene is a kind of vinylcyclopropane capable of undergoing vinylcyclopropane–cyclopentene rearrangements. With regard to the first point, Dewar, Fonken, Jones, and Minter[4c] showed that 1,1-dicyclopropylallene (**1a**) and related compounds have rather low ionization potentials. These results should permit workers to anticipate some characteristic behavior in the chemical reactions of such allenes. As to the second point, Dewar, Fonken, Kirschner, and Minter[4a] demonstrated that the rate of rearrangement of 3-cyclopropyl-1,2-butadiene to 1-methyl-3-methylenecyclopentene is significantly more rapid than that of vinylcyclopropane to cyclopentene, and they showed that the results are supported by MINDO/3 calculations. In a similar study, however, Roth, Schmidt, and Humbert[4b] found that the rate of rearrangement of cyclopropylallene (**1b**) is nearly the same as that of vinylcyclopropane itself. Since the significance of the MINDO/3 calculations has been questioned by Andrews and Baldwin,[6] further studies in related systems appear to be necessary to resolve the disagreement.

In any event, it should be noted that the investigations carried out so far have been restricted mostly to the isomerization of cyclopropylallenes, and no results concerning the [2 + 2] cycloadditions of such allenes have been reported.[4,7] In the present study, we demonstrate that **1a** in fact reacts with a variety of activated olefins (**2**) in the manner anticipated as an allene. It was observed here that the regioselectivity of cycloadditions was uniquely influenced by the pattern of substitution of the activating group in **2** and, in some cases, by solvent polarity.

Table I. Reactions of 1a with Activated Olefins

activated olefin	reaction conditions[a] solvent	temp, °C	time, h	cycloadducts yield,[b] %	3/4 ratio
	Alkoxycarbonyl-Activated Olefins				
2a	benzene	200	4	69	11:89[c]
	acetonitrile	200	4	68	10:90
	CH_2ClCH_2Cl	200	4	66	9:91
2b	benzene	200	6	48[d]	*e*:99
	acetonitrile	200	6	*f*, *g*	*e*:99
2c	benzene	200	32	50[h,i]	*e*:99
	acetonitrile	200	32	*f*, *h*	*e*:99
2d	benzene	200	4	84	5:95[j]
	benzene	80	32.5	81	14:86
	acetonitrile	80	1	85	92:8
2e	acetonitrile	80	4	33	99[c]:*e*
	Cyano-Activated Olefins				
2f	benzene	200	4	*f*	46:54[c]
	neat	200	4	58	37:63
2g	benzene	200	4	68	(12)[k]:88
	acetonitrile	200	4	*f*	(12)[k]:88[l]
2h	benzene	200	4	79	(10)[k]:90[l]
2i	benzene	*m*		66	93:7
	$CDCl_3$	*m*		*f*	97:3
2j	CH_2ClCH_2Cl	*m*		71	99:*e*

[a] Reactions at 200 °C were carried out in the presence of a trace amount of 2,6-di-*tert*-butyl-*p*-cresol. [b] Based on the amounts of products isolated. [c] Mutual isomerization of **3** and **4** was not observed under the reaction conditions. [d] A minor component (0.5%) was detected on GC analysis. [e] Not detected. [f] Not determined. [g] An unidentified product (4%) was also produced. [h] Two additional minor components (total of 10%) were detected on GC analysis. [i] **5** was isolated in 4.7% yield (see text). [j] **3d** isomerized to a significant extent at 200 °C (see text). [k] Not fully characterized (see text). [l] Three additional minor peaks were observed in GC analysis, one of which was found to be **6** (ca. 3% in the reaction of **2h** and a trace amount in the reaction of **2g**). [m] Room temperature.

Moreover, the Lewis acid catalysis greatly influenced the reactions of alkoxycarbonyl-activated **2** with **1a**. These unprecedented results appear to be caused by the special electronic effects[5] of the geminal cyclopropyl groups in **1a**. Furthermore, **1a** was found to undergo dimerization rather than the vinylcyclopropane–cyclopentene-type rearrangement at 200 °C in solution.

Results

The reaction of **1a**[4c,g] with **2** was carried out in an appropriate solvent. Usually, a twofold molar excess of **2** was utilized. In the reactions carried out at 200 °C, a trace amount of 2,6-di-*tert*-butyl-*p*-cresol was added to minimize the polymerization of **1a**. The results are summarized in Table I.

Reaction of 1a with Alkoxycarbonyl-Activated Olefins. At 200 °C, **1a** reacted successfully with methyl acrylate (**2a**), dimethyl fumarate (**2b**), and dimethyl maleate (**2c**) to give the expected cycloadducts, namely, **3**, which is a [2 + 2] cycloadduct of **2** with a double bond substituted by two cyclopropyl groups, and **4**, which is a [2 + 2] cycloadduct with an unsubstituted double bond in **1a**. The adducts were unambiguously characterized with their spectral data. In particular, the differentiation between **3** and **4** could readily be carried out by means of ^1H NMR and UV spectroscopy. *exo*-Methylene hydrogens in **3** gave distinctive signals in the ^1H NMR spectra, whereas a dicyclopropylmethylene unit in **4** exhibited characteristic absorption maximum in the UV region.[8] Stereochemical

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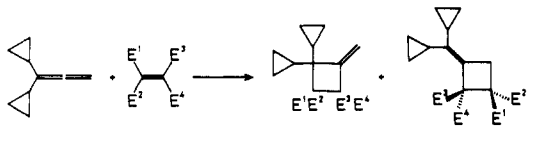
(5) Richey, H. G., Jr. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III, Chapter 25. Wiberg, K. B.; Hess, A., Jr.; Ashe, A. J., III *Ibid.* Vol. III, Chapter 26. Brown, H. C. "The Nonclassical Ion Problem"; Plenum: New York, 1977; Chapter 5 and references cited therein.

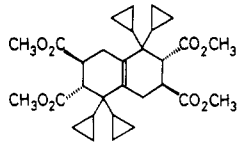
(6) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6706.

(7) Cycloadditions other than [2 + 2] cycloadditions, such as addition of carbenes,[4g] have been examined.



1a 2 3 4

a: $E^1=CO_2CH_3$, $E^2=E^3=E^4=H$
b: $E^1=E^4=CO_2CH_3$, $E^2=E^3=H$
c: $E^1=E^3=CO_2CH_3$, $E^2=E^4=H$
d: $E^1=E^2=CO_2C_2H_5$, $E^3=E^4=H$
e: $E^1=E^3=-CO-O-CO-$, $E^2=E^4=H$
f: $E^1=CN$, $E^2=E^3=E^4=H$
g: $E^1=E^4=CN$, $E^2=E^3=H$
h: $E^1=E^3=CN$, $E^2=E^4=H$
i: $E^1=E^2=CN$, $E^3=E^4=H$
j: $E^1=E^2=E^3=E^4=CN$



5

assignments of the geometrically isomeric adducts were carried out on the basis of the magnitudes in the coupling constants between two vicinal ring hydrogens in the ^1H NMR spectra.[9]

In these reactions, 4 was always produced predominantly. This was true irrespective of solvent polarity (benzene or acetonitrile). It was also true that no appreciable acceleration of the cycloaddition was observed in polar solvents (based on the time required for practical completion of the reaction; see Table I). Control experiments proved that the mutual isomerization of **3** and **4** was unimportant under the reaction conditions, except for one case (see below), indicating that the ratio of **3** and **4** obtained in the reaction can be regarded as a value reflecting the regioselectivity in the cycloaddition.

The reaction of **1a** with **2c** required 32 h of heating at 200 °C for the total consumption of **1a**. Low reactivity of the cis olefin relative to that of the trans isomer in cycloadditions is precedented.[3a,10] From a product mixture, a crystalline compound was separated, and it was characterized as tetramethyl 1,1,5,5-tetracyclopropyl-1,2,3,4,5,6,7,8-octahydronaphthalene-2,3,6,7-tetracarboxylate (**5**, 4.7%). The assignments of the stereochemical relationships in the four ester functions, as well as the positions of cyclopropyl groups, in **5** are tentative, although a trans configuration for both vicinal dicarboxylate units may be assigned on the basis of vicinal coupling constants in the ^1H NMR spectrum of **5**.[11] Thus, in the formation of **5**, two molecules of **2b**, which might be formed by the slow isomerization of **2c**, appear to react with one of the dimers of **1a** in a manner similar to that known in the reactions of the parent allene.[2,12] Some minor components in addition to **3** and **4** were detected in the product mixture in several other reactions as well (see footnotes of Table I), but no further effort was given to isolate and characterize them, since they were so small in quantity.

Table II. Isomer Distributions in the Formation of 4[a]

activated olefin	solvent[g]	4, cis/trans ratio
2b	benzene	*b*:99[c]
	acetonitrile	*b*:99[c]
2c[d]	benzene	70:30[c]
	acetonitrile	57:43
2g	benzene	12:88
	acetonitrile	16:84
2h[e]	benzene	75[f]:25

[a] Isomer distributions in the production of 3 could not be examined (see text). [b] Not detected. [c] No geometrical isomerization was observed under the reaction conditions. [d] Slowly isomerized; 2.3% of **2b** was detected after 32 h heating at 200 °C in benzene. [e] Slowly isomerized; 2.1% of **2g** was produced after 4 h of heating at 200 °C in benzene. [f] A structural isomer, **6** (4.3%), in addition to **4g** (5%) was produced after 4 h of heating at 200 °C in benzene. [g] The temperature was 200 °C in all cases.

Diethyl methylenemalonate (**2d**) reacted with **1a** merely in refluxing benzene, yielding **4d** as a major cycloadduct (**3d**/**4d** ratio of 14:86). Interestingly, the same reaction proceeded more rapidly in refluxing acetonitrile, and the resultant mixture was highly rich in **3d** (**3d**/**4d** ratio of 92:8). It is thus evident that *polar solvents not only accelerated the reaction but also brought about a reversal of the regioselectivity in the cycloaddition* in this case. At 200 °C in benzene, a greater amount of **4d** was produced (**3d**/**4d** ratio of 5:95), but this appears to be caused by the slow isomerization of **3d** to **4d** under the reaction conditions, because it was found in control experiments that **3d** isomerized to **4d** to an extent of 32% after heating at 200 °C for 4 h in benzene.

The reaction of maleic anhydride (**2e**) with **1a** was fruitless in benzene. On mixing of the two components, a light green color developed, and **1a**, but not **2e**, was consumed even at room temperature. A usual workup of the resultant solution did not give any characterizable products. In refluxing acetonitrile, however, the same reaction produced **3e** in 33% yield. No **4e** was detected in the product mixture.

Reaction of 1a with Cyano-Activated Olefins. At 200 °C, the reactions of **1a** with acrylonitrile (**2f**), fumaronitrile (**2g**), and maleonitrile (**2h**) proceeded at reasonable rates to yield the expected cycloadducts, **3** and **4**. It should be noted that **2f** gave a greater amount of **3** (**3f**/**4f** ratio of 46:54) compared to that observed in the reaction of **2a** (**3a**/**4a** ratio of 11:89). In the reactions of **2g** and **2h**, it is presumed that **3g** and **3h** might be produced, but their limited amounts did not permit us to isolate and characterize them. Accordingly, the assignments of **3g** and **3h** were merely carried out by means of ^1H NMR examinations of crude reaction mixtures. It should also be noted here that the reactions of **2f** and **2g** produced **4** predominantly irrespective of solvent polarity. No indication of appreciable rate enhancement by use of polar solvents was noted for the second time.

Methylenemalononitrile (**2i**) reacted with **1a** exothermally at room temperature and produced **3i** as a major cycloadduct even in benzene. The reaction in chloroform-*d*

(8) 1,1-Dicyclopropylalkenes exhibit an absorption maximum in the UV region (Nishida, S.; Moritani, I.; Tsuda, E.; Teraji, T. *J. Chem. Soc., Chem. Commun.* **1969**, 781. Teraji, T.; Moritani, I.; Tsuda, E.; Nishida, S. *J. Chem. Soc. C* **1971**, 3252).

(9) In methylenecyclobutanes, a vicinal coupling constant observed in cis isomers has been shown to be greater than that observed in trans isomers (Baldwin, J. E.; Flemming, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 5261).

(10) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16.

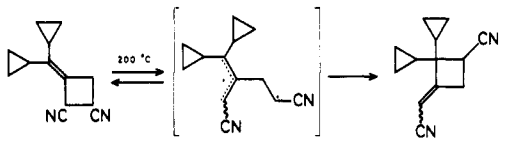
(11) See the Experimental Section. The successful isolation of **5** merely in the reaction of **2c** will be due to the low reactivity of **2c**, which permits **1a** to form dimers to some extent.

(12) Cripps, H. N.; Williams, J. K.; Sharkey, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 2723.

also resulted in an overwhelming production of **3i**. Since **2i** polymerized readily in acetonitrile, reactions in such polar solvents could not be examined. In a similar manner, ethenetetracarbonitrile (**2j**, TCNE) reacted with **1a** in 1,2-dichloroethane at room temperature to give **3j** as the exclusive cycloadduct.

Stereochemical Course of the Cycloaddition. The reactions of **2b**, **2c**, **2g**, and **2h** with **1a** permit us to examine the stereochemical course of the present cycloadditions. Since **3** was produced in a limited quantity, merely the stereochemical consequence of the formation of **4** was examined. The results are summarized in Table II.

Control experiments showed that the isomerization of the initial olefins took place to a negligibly small extent under the reaction conditions. The isomerization of the products was also of negligible importance. Namely, after being heated at 200 °C for 4 h, **4h** isomerized to **4g** to an extent of 5% and **4g** to **4h** to an extent of 2%. Aside from these geometrical isomerizations, a structural isomerization involving a cleavage of the C_1–C_2 bond took place,[13] but no regional isomerization to **3** was observed. Thus, under the same conditions as above, 2,2-dicyclopropyl-3-(cyanomethylene)cyclobutanecarbonitrile (**6**) was produced in



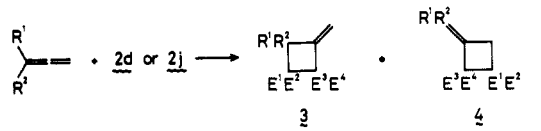
4h or 4g 6

4.3% yield from **4h** and in trace amounts from **4g**. On the basis of the results of the control experiments, it is concluded that the present cycloaddition is nonstereospecific, because the adducts obtained in the reactions of **1a** with **2c**, **2g**, and **2h** were contaminated by the corresponding geometrical isomer in a significant amount, which is hard to explain either by the isomerizations of **2** or those of **4**.

Lewis Acid Catalyzed Reaction. In the reactions of **1a** with alkoxycarbonyl-activated olefins (**2a–d**), addition of aluminum chloride greatly reduced the necessary temperature for the cycloaddition. Since **1a** polymerized with considerable rapidity under the reaction conditions (recovered amounts of **1a** after 1 h in the absence of **2** being merely 12%), a 1.3 times molar excess of **1a** was allowed to react in these cases. A remarkable observation was that the regioselectivity of the cycloaddition was quite different from that observed in thermal reactions. Thus, *the reaction proceeded at room temperature in the presence of aluminum chloride in dichloromethane and* **3** *was the exclusive product* in all these cases.[14] With regard to the stereochemical consequence of this reaction, it was observed that **2c** gave a mixture of **3b** and **3c** in a 27:73 ratio, although **2b** produced only **3b**. Since **2c** isomerized to **2b** only to an extent of 2% and **3c** did not isomerize to **3b** under the reaction conditions, it is apparent that the Lewis acid catalyzed reaction is also nonstereospecific.

In contrast to the reactions of **1a** with **2a–d**, the Lewis acid catalysis operated poorly in the reactions of **1a** with cyano-activated olefins[15] such as **2f** and **2g**. The polymerization of **1a** appears to be more rapid than the cycloaddition with **2**. Thus, the reaction of **1a** (1.7 times in excess) with **2f** in the presence of aluminum chloride produced **3f** only in 40% yield, and the reaction of **1a** with **2g** gave merely a polymeric residue.

Reactions of 1b and 3-Methyl-1,2-butadiene (1c). Since **2d** and **2j** exhibited characteristic behavior in their reactions with **1a**, the reactions of **1b** and **1c** with these activated olefins were examined. The rates of reaction of **1b** with **2d** suffered notable solvent effects, but the regioselectivity of the cycloaddition was not influenced by the solvent polarity. Thus, after 50 h at 80 °C, the consumed amount of **1b** was only 3% in benzene, whereas it



3 4

1b: R^1 = ◁, R^2 = H
1c: R^1 = R^2 = CH_3

k: R^1 = ◁, R^2 = H, E^1 = E^2 = E^3 = E^4 = CN
l: R^1 = R^2 = CH_3, E^1 = E^2 = E^3 = E^4 = CN
m: R^1 = ◁, R^2 = H, E^1 = E^3 = $CO_2C_2H_5$, E^2 = E^4 = H
n: R^1 = R^2 = CH_3, E^1 = E^2 = $CO_2C_2H_5$, E^3 = E^4 = H

was 62% in acetonitrile. The ratios of **3m**/**4m** produced were, however, 37:63 in benzene and 35:65 in acetonitrile. With highly reactive **2j**, **1b** produced a mixture of **3k** and **4k** in a 1:1 ratio (in dichloromethane at room temperature). From the mixture, **3k** could be isolated in a pure form, but **4k** was not.[16] Accordingly, the characterization of **4k** was done by ^1H NMR examinations of crude materials.

In contrast to **1a** or **1b**, **1c** produced exclusively **4** in all cases examined, including the reaction with **2j**. Thus, the results obtained in the reaction with **2j** can be arranged in the following manner; i.e., **1a** gave exclusively **3j**, **1b** appeared to produce both **3k** and **4k**, and **1c** yielded merely **4l**. The Lewis acid catalysis did not operate effectively in the reaction of **1c**, because **1c** appeared to polymerize rapidly in contact with aluminum chloride. Thus, none of the characterizable products was obtained in the attempted Lewis acid catalyzed reaction of **1c** with **2a**, **2b**, **2d**, or **2f**.

Thermal Reaction of the Adducts 3j and 4l. Since cycloadducts of enol ethers with **2j** are known to regenerate zwitterionic intermediates in polar solvents,[17] **3j** and **4l** were heated in such solvents in the hope that the corresponding regioisomer might be produced. However, **3j** showed no indication of producing **4j** in refluxing acetonitrile. In refluxing methanol, on the other hand, **3j** yielded a methanolysis product, 1-amino-5,5-dicyclopropyl-1,5-dimethoxy-4-methylene-1-pentene-2,3,3-tricarbonitrile (**7**), quantitatively, indicating that the zwitterion appeared to be produced and trapped by nucleophilic methanol. In contrast, **4l** did not give any characterizable product on heating in methanol, but it was isomerized to a structural isomer, 2,2-dimethyl-3-(dicyanomethylene)cyclobutane-1,1-dicarbonitrile (**8**), in

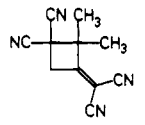
(13) The same type of structural isomerization is known to occur at higher temperature (Doering, W. v. E. 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, UT, June 1969, cited in: Baldwin, J. E.; Flemming, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 5256; **1973**, *95*, 5249, 5261). For the homolytic ring cleavage of methylenecyclobutanes, see: Dryasdale, J. J.; Stevenson, H. B.; Sharkey, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 4908.

(14) The possibility that the unusual results were due to unknown effects of halogen-containing solvents was ruled out, since the reaction of **1a** with **2a** in 1,2-dichloroethane required heating at 200 °C and gave a mixture of **3a** and **4a** in a ratio closely similar to those observed in other solvents (see Table I).

(15) Less effective activation of an enophile by complexation of a Lewis acid to a nitrile than by complexation to an ester was noted also in ene reactions (Duncia, J. V.; Lansbury, P. T., Jr.; Miller, T.; Snider, B. B. *J. Am. Chem. Soc.* **1982**, *104*, 1930).

(16) During the workup, **4k** appeared to decompose to give an intractable residue (see Experimental Section). Reasons for the instability of **4k** are not clear.

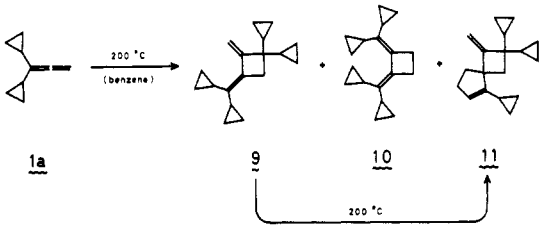
(17) Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171 and references cited therein.



8

chloroform.[13] No change of the results was observed when methanol was added to the chloroform solution in which the isomerization of **41** took place.

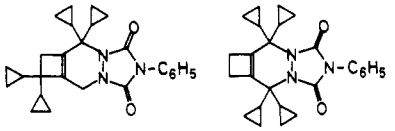
Dimerization. A benzene solution of **1a** in the presence of a trace amount of 2,6-di-*tert*-butyl-*p*-cresol was heated at 200 °C for 32 h. GC analysis of the resultant mixture indicated that there were three dimeric components. In a monomer fraction, several minor components were present but they were very small in their quantities relative to those of the dimers. Each dimer was isolated by means of preparative GC. It was found that two of them were conjugated dienes (λ_{max} = 268 and 278 nm, respectively),[18] but the third dimer was not (λ_{max} < 210 nm). Spectral examinations of these products permited us to assign them to 3,3-dicyclopropyl-1-(dicyclopropylmethylene)-2-methylenecyclobutane (**9**), 1,2-bis(dicyclopropyl-



1a 9 10 11

methylene)cyclobutane (**10**), and 2,2,5-tricyclopropyl-1-methylenespiro[3.4]oct-5-ene (**11**). The combined, isolated yield of these dimers was 35% and the ratio of **9**/**10**/**11** was 1.8:1.7:1.0.[19]

Independent experiments showed that **11** was produced by the rearrangement of **9** under the reaction conditions. In contrast, **10** merely isomerized to **9** gradually at 200 °C. The dimers **9** and **10** reacted smoothly with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to give the expected diene adducts, 2,2,10,10-tetracyclopropyl-5-phenyl-3,5,7-triazatricyclo[7.2.0.0^{3,7}]undec-1-ene-4,6-dione (**12**) and

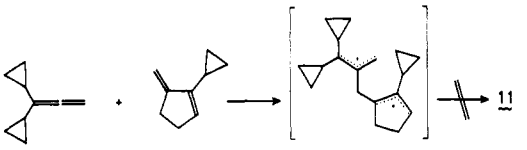


12 13

2,2,8,8-tetracyclopropyl-5-phenyl-3,5,7-triazatricyclo-[7.2.0.0^{3,7}]undec-1-ene-4,6-dione (**13**), but we failed to prepare the authentic **5** in the reaction of **9** with **2b**.

Discussion

Dimerization. Studies so far reported in the literature[4] have demonstrated merely the isomerization of cyclopropylallenes.[7] We have shown here, however, **1a** could produce dimers in fair yield.[19] The vinylcyclopropane–cyclopentene-type rearrangement might also take place, but the dimerization was a more important pathway under the present reaction conditions. The rearranged dimer **11** was derived from **9** but not in the reaction of **1a** with 2-cyclopropyl-3-methylenecyclopentene, a presumed product of the rearrangement of **1a**. If the latter were the case, the reaction should not produce **11**, because an intermediate diradical expected in such reactions would be **14**,[2] which should give an orientation-reversed adduct.



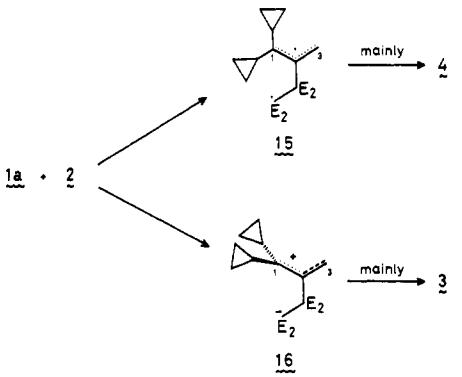
1a 14

Definitive evidence for the above conclusion was provided by the observation that **9** isomerized cleanly to **11** at 200 °C.

Now, the relative inertness of **10** compared to **9** in the vinylcyclopropane–cyclopentene rearrangement appears to be somewhat curious. At present, we prefer to explain the results in the following manner. Since the (*E*)-cyclopropyl groups in both **9** and **10** are in similar surroundings, the rearrangement involving them cannot bring about any difference between **9** and **10**. Accordingly, the (*Z*)-cyclopropyl group should be incorporated in the transformation. Now, the (*Z*)-cyclopropyl group in **10** is highly crowded, and hence it is forced to stretch in an s-trans-like conformation. Thus, **10** can hardly carry out the rearrangement, since it has been well demonstrated that an s-cis conformation of the two functions is a prerequisite to accomplish the transformation.[20] On the other hand, the (*Z*)-cyclopropyl group in **9** is less crowded and appears to be able to take the necessary s-cis-like conformation. Accordingly, **9** rearranges slowly at 200 °C, whereas **10** does not.[21]

It should be worthwhile to note here that no bicyclic product possessing a cycloheptadiene unit was produced in this rearrangement. Apparently, cyclopropylbutadiene–cycloheptadiene rearrangement[22] is an unfa-

Scheme I



(18) As to λ_{max} for related compounds, see: Maurin, R.; Leandri, G.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1971**, 530. Blomquist, A. T.; Verdol, J. A. *J. Am. Chem. Soc.* **1955**, *77*, 1806.

(19) On being heated at 200 °C in benzene, **1b** also gave a fraction (41%) which was a complex mixture (more than 20 components) of dimers and oligomers. The fact that the fraction contained dimeers was proved by the isolation of a head-to-head dimer, tentatively assigned as 1,2-bis[(*Z*)-cyclopropylmethylene]cyclobutane, in low yield.

(20) Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577. Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 122. Doering, W. v. E.; Sachdev, K. *J. Am. Chem. Soc.* **1975**, *97*, 5512. Andrews, G. D.; Baldwin, J. E. *Ibid.* **1976**, *98*, 6705 and references cited therein.

(21) Similar reasonings will account for the nonincorporation of the (*E*)-cyclopropyl groups in the rearrangement. Hydrogens at C_4 are protruding in such a way as to interfere significantly with the (*E*)-cyclopropyl group in the required s-cis-like conformation. In contrast, a group interacting sterically with the (*Z*)-cyclopropyl group in **9** is an *exo*-methylene at C_2. The two hydrogens in the *exo*-methylene group are nearly in plane of the molecular framework, and hence the (*Z*)-cyclopropyl group will be able to rotate to take the s-cis-like conformation in the required unit. Wider bond angles associated with the cyclobutane ring may also help to reduce the steric destabilization in such conformations.

vorable process compared to the vinylcyclopropane–cyclopentene rearrangement, even though all three functions are arranged in a required syn manner as in **9**.

Cycloaddition. In the studies on cycloadditions of allenes,[2] results have been discussed most frequently in terms of either a diradical stepwise mechanism[3b,d,e] or a concerted mechanism.[3a,c,f] In certain special cases, such as the reactions of highly electron-rich allenes with strongly electron-demanding olefins, dipolar processes have also been proposed.[23] Since the present cycloadditions are nonstereospecific, the reactions may most probably be a stepwise process.[24] Lack of significant solvent polarity effects in the thermal reactions of **1a** with **2a–d,f–h** suggests that these reactions are the diradical process. Accordingly, the formation of the cycloadducts in these reactions can be rationalized in terms of the mechanism shown in Scheme I. The initial attack of **2** takes place at the central carbon atom in **1a**,[2] and, as demonstrated by Pasto and his co-workers,[3d,e,25] rotation and bending of the allenic unit occur during the attack of **2** to produce an intermediate, **15**, possessing a delocalized, planar allylic unit. Cyclization then takes place either at C_1 to give **3** or at C_3 to afford **4**. The predominance for the formation of **4** in such reactions is most probably due to relative magnitudes in steric hindrance in the cyclization step.[3d,e] The facts that **2a** gave **3a** and **4a** in a 11:89 ratio and sterically less demanding **2f** produced **3f** and **4f** in a 46:54 ratio provide support for this conclusion.

In contrast to these reactions described just above, the reactions of **2i** and **2j**, as well as that of **2d** (all these olefins have two activating groups on a carbon of the ethylene), in polar solvents yielded **3** predominantly, if not exclusively. The fact that the reaction of **2d** in acetonitrile proceeded considerably more rapidly than that in benzene suggests revelation of polar characters in such reactions. Thus, it may be probable that the reactions proceeding via a polarized intermediate result in the predominant formation of **3**, the adduct with a more highly substituted double bond in **1a**. The results obtained in the Lewis acid catalyzed reactions appear to be in accord with this postulation. Complexation of aluminum chloride on the ester function in alkoxycarbonyl-activated **2** made the reagent active enough to react with **1a** at room temperature. The intermediate produced in such reactions will inevitably be polarized, and it led to the exclusive production of **3**. It can thus be summarized that the present cycloadditions carried out with **1a** are rationalized in terms of either the diradical process, which yielded principally **4**, or the reaction involving a dipolar species, which gave **3** predominantly, if not exclusively.[26]

It is important to note here that the selective formation of **3** was achieved only when the allene carried two cyclopropyl groups on a carbon atom of the allenic unit, as does **1a**. In the reaction of monosubstituted **1b** with **2d**, the reactions proceeded appreciably faster in acetonitrile than in benzene, suggesting that the polar characters might be revealed in the cycloadditions. However, no practical change on the regioselectivity of the cycloadditions was observed in polar solvents. Apparently, a single cyclopropyl group is not effective enough to reveal the abnormality in the cycloadditions in spite of the fact that some charge separations may be taking place in the reaction. Moreover, two methyl groups on a terminal carbon of the allenes was also found to be inefficient to result in the reversal of the regioselectivity of the cycloadditions.

Now, the predominant formation of **3** in the dipolar process[26] may be explained in terms of either i or ii, as described below.

(i) In the first place, it can be argued that the attack of **2** occurs in a manner similar to that which takes place in the diradical process, and an intermediate, which has a nearly planar, largely charge-delocalized allylic unit, will be produced. In a succeeding step, one of the terminal carbon atoms in the allylic unit should rotate to form a bond with a dicyano-substituted carbanion. Such a rotation will inevitably result in the localization of positive charge on the rotating carbon atom. Since the cyclopropyl groups are known to provide a great stabilization to an adjacent, positively charged center,[5] the transition state for the ring closure involving the rotation of the carbon atom carrying the two cyclopropyl groups should be much lower in energy than that derived from the rotation of the unsubstituted carbon atom. Accordingly, **3** was produced as the predominant cycloadduct from the polarized intermediate.

(ii) Alternatively and more simply, however, one may argue that the intermediate takes essentially a twisted, nonplanar structure at the allylic portion as shown in Scheme I. Since the positive charge will be significantly localized at C_1 in such an intermediate, the cyclization will produce **3** predominantly.

Among these alternative explanations, we prefer, at present, to take ii as a possibility. This is because only **1a**, but not **1b**, showed the abnormality in the regioselectivity. If i is the case, even a single cyclopropyl group will influence the regioselectivity to a considerable extent. With explanation ii, it may be argued that the allylic unit in the intermediate derived in the reaction of **1b** will be taking a nearly planar, charge-delocalized structure, and hence the conditions for the ring closure will be similar to those in the diradical process. Accordingly, no striking abnormality in the regioselectivity may be observed.[27]

With regard to the feasibility of the twisted, considerably charge-localized structure for the intermediate, we should

(22) Cf.: Grimme, W.; Doering, W. v. E. *Chem. Ber.* **1973**, *106*, 1765.

(23) Hoffmann, R. W.; Schafer, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 733; *Chem. Ber.* **1972**, *105*, 2437. Gompper, R.; Lach, D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 70. Cf.: Saalfrank, R. W.; Paul, W.; Liebenow, H. *Ibid.* **1980**, *19*, 713.

(24) A possibility that the stereochemical results are an outcome of competing $[2_s + 2_a]$ and $[2_s + 2_s]$ mechanisms (epiotis, N. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 751) may not be ruled out. The fact that no cyclopropane cleaved products were produced in the cycloadditions, which were carried out at 200 °C, appears to be in accord with the concerted processes (Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1974**, *96*, 6451. Shimizu, N.; Ishikawa, M.; Ishikura, K.; Nishida, S. *Ibid.* **1974**, *96*, 6456). However, we observed in several cases that no ring-cleaved products could be obtained in appreciable yields when the radical center of cyclopropylmethyl radicals is stabilized with allylic resonance. Such is also the case in the present reactions. Accordingly, we preferably consider that the cycloadditions proceeded in a stepwise fashion to reveal the nonstereospecificity, as discussed in many precedents.[3]

(25) (a) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* **1981**, *46*, 2837. (b) Pasto, D. J.; Warren, S. E. *Ibid.* **1981**, *46*, 2842.

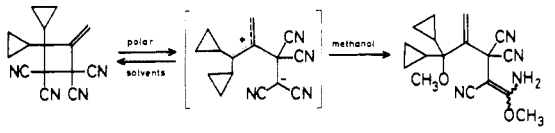
(26) Professor D. J. Pasto suggested in a private communication that there may be gradations in electron distributions between strictly diradical and strictly dipolar intermediates. He in fact demonstrated that the dipolar character in a radical-type transition state was revealed in the reaction of **1c** with benzenethiol.[25b] On the basis of theoretical grounds, there may be no truly "strict diradicals" (Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92). At present, however, we have no proper, quantitative way to evaluate the extents of polar contributions in the intermediates. Accordingly, we prefer to discuss the results simply in terms of mechanisms involving two distinctive intermediates, namely, diradical-like and zwitterion-like species.

(27) Similar striking effects of the substitution of two hydrogens with cyclopropyl groups on a carbon atom were revealed also in the reactions of cyclopropyl-substituted ethylenes with **2j** (Nishida, S.; Moritani, I.; Teraji, T. *J. Org. Chem.* **1973**, *38*, 1878). In fact, the reaction of 1,1-dicyclopropylethylene with **2j**, which involves a simple zwitterionic intermediate, was nearly as rapid as that of **1a** with **2j** (unpublished results).

like to call attention to the results reported by Buss, Gleiter, and Schleyer.[28] Some time ago, they showed that the substitution of hydrogens at a terminal carbon atom in allylic cations by alkyl group(s) greatly reduces the energy barrier for the allylic isomerization. Namely, the energy barrier for the parent allylic cation is 38–43 kcal/mol, whereas that of the methyl-substituted cation is 25–27 kcal/mol, and the 1,1-dimethylallyl cation has a rotational barrier of only 12.5–13.5 kcal/mol. The lowerings of the rotational barrier are due to both electronic and steric effects of the methyl group(s). On the basis of these observations, it is highly probable that the energy barrier for the rotation in the 1,1-dicyclopropylallyl cation is well below that of the 1,1-dimethylallyl cation, because the ability of the cyclopropyl group to stabilize an adjacent cationic center is known to be significantly greater than that of the methyl group.[5,29] With regard to the steric requirement, the cyclopropyl group is considerably larger than the methyl group as well. In the intermediate **16**, there is another alkyl group at the central carbon atom in the allylic unit, which results in an additional steric destabilization for the planar allylic structure. Accordingly, the twisting of the allylic unit in **16** may not be totally unlikely.

It should be pointed out that such a twisted structure for the allylic portion might be feasible only when the intermediate is dipolar in nature. In the diradical intermediate, the cyclopropyl group can provide only a modest stabilization,[30] and hence **15** will be taking a nearly planar, odd-electron-delocalized allylic structure.

No matter which explanation is more adequate, it is concluded that the cyclization of the polarized intermediate produced **3** predominantly. The assumption that the dipolar intermediate cyclizes predominantly at C_1 to give **3** is supported by the observations obtained in the attempted isomerization of **3j**. Although **3j** appears to show



3j 7

no change in refluxing acetonitrile, it produced a solvolysis product, **7**, quantitatively in refluxing methanol. It is thus highly probable that similar heterolysis[17,31] takes place also in acetonitrile, but the intermediate will have no alternative way other than cyclizing back to **3j** in the absence of an effective nucleophile.

The Lewis acid catalysis in allene cycloadditions has been reported in several cases,[32] but the studies are merely related to the possible production of vinyl cations under such conditions. The reversal of regioselectivity by the Lewis acid catalysis is thus an unprecedented observation, and it happens to be the case in the reactions of **1a**.

Conclusion

In spite of the claimed readiness of cyclopropylallenes to undergo the vinylcyclopropane–cyclopentene-type rearrangement,[4a] **1a** dimerized in the manner anticipated as an allene at 200 °C in solution. Both **1a** and **1b** reacted with activated olefins **2** in the expected manner. In thermal reactions, generally, **4** was produced predominantly. However, the reactions of **1a** with geminally bisactivated **2i** and **2j**, as well as with **2d** in polar solvents, produced **3**. Aluminum chloride not only reduced the required reaction temperature for the reactions of **1a** with alkoxycarbonyl-activated **2** but also resulted in the total reversal of the regioselectivity. The predominant formation of **3** may be rationalized in terms of mechanisms involving a polarized intermediate. The cyclopropyl groups play a crucial role in stabilizing the polarized transition state, giving **3**.

Experimental Section[33]

IR spectra were recorded on a Hitachi 215 grating spectrophotometer. UV spectra were taken on a Cary Model 17 spectrophotometer. NMR spectra were recorded on JEOL PS-100 and JEOL FX-100 spectrometers. Mass spectra were determined on a JEOL Model LMS-D300 mass spectrometer. GC analyses were carried out with Hitachi 063 and 163 gas chromatographs. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University. Melting points and boiling points are uncorrected.

Allenes. A 0.83 N ethereal solution of methyllithium (36 mL) was added dropwise to an ethereal solution (100 mL) of 1,1-dibromo-2,2-dicyclopropylcyclopropane[24] (8 g, 28.6 mmol) at 0 °C. After the solution was stirred for an additional 30 min at 0 °C, water (30 mL) was added to it. The resultant ether layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of ether gave an oil, which was distilled to give **1a**:[4c,g] bp 69–71 °C (44 mm); 2.54 g (74%); IR (neat) 3100, 3020, 1960, 1450, 1040, 850 cm^{-1}; ^1H NMR (CCl_4) δ 0.3–0.8 (m, 8 H), 1.0–1.4 (m, 2 H), 4.66 (t, 2 H, J = 3 Hz). The other two allenes, **1b**[4b] and **1c**,[34] were prepared by following the procedures given in the literature.

General Reaction Procedure. A 1:2 mixture of **1a** and **2** was dissolved in a solvent, and a trace amount of 2,6-di-*tert*-butyl-*p*-cresol was added to the resultant solution. After the solution was bubbled with a stream of nitrogen for several minutes, the solution was sealed in a Pyrex tube and heated at 200 °C in an oven. After the required reaction times, the tube was opened, and the solvent and excess **2** were removed by distillation and/or sublimation. The final purification of products was carried out by means of preparative GC. The results are summarized in Tables I and II.

Reaction of 1a with 2a. A benzene solution (3.0 mL) of **1a** (263 mg, 2.2 mmol), **2a** (407 mg, 4.7 mmol), and a small amount of 2,6-di-*tert*-butyl-*p*-cresol was heated at 200 °C for 4 h. The aforementioned workup gave a colorless liquid [bp 90–130 °C (bath temperature, 3 mm)] which was a mixture of methyl 2,2-dicyclopropyl-3-methylenecyclobutanecarboxylate (**3a**) and methyl 3-(dicyclopropylmethylene)cyclobutanecarboxylate (**4a**) in 11:89 ratio (313 mg, 69%). **3a**: IR (neat) 3100, 3020, 1735, 1670, 1060, 1020, 890 cm^{-1}; ^1H NMR (CCl_4) δ 0.1–0.6 (m, 8 H), 0.6–1.3 (m, 2 H), 2.3–3.1 (m, 3 H), 3.50 (s, 3 H), 4.62 (t, 1 H, J = 3 Hz), 4.72 (t, 1 H, J = 3 Hz). Anal. ($C_{13}H_{18}O_2$) C, H. **4a**: IR (neat) 3100, 3020, 1730, 1050, 1010, 810 cm^{-1}; ^1H NMR (CCl_4) δ 0.3–0.8 (m, 8 H), 0.9–1.3 (m, 2 H), 2.97 (br s, 5 H), 3.62 (s, 3 H); UV (hexane) λ_{max} 214 nm (log ϵ 4.01). Anal. ($C_{13}H_{18}O_2$) C, H.

Reaction of 1a with 2b. Reaction of **1a** (380 mg, 3.17 mmol) with **2b** (920 mg, 6.4 mmol) in benzene (15 mL) at 200 °C for 4 h gave a fraction [bp 95–104 °C (bath temperature, 0.005 mm)] which was mostly dimethyl *trans*-3-(dicyclopropylmethylene)-cyclobutane-1,2-dicarboxylate (**4b**; 311 mg, 48%) contaminated by a very small amount (0.5%) of an unidentified component. **4b**: IR (neat) 3100, 3020, 1730, 1430, 1210, 1020 cm^{-1}; ^1H NMR

(28) Buss, V.; Gleiter, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3927.
(29) Brown, H. C.; Cleveland, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 2015. Charton, M. In "The Chemistry of Alkenes"; Zabickey, J., Ed.; Wiley-Interscience: New York, 1970; Vol. II, Chapter 10.
(30) Overberger, C. G.; Lebovits, A. *J. Am. Chem. Soc.* **1954**, *76*, 2722. Martin, J. C.; Timberlake, J. W. *Ibid.* **1970**, *92*, 978.
(31) Kataoka, F.; Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1980**, *102*, 711.
(32) Lukas, J. H.; Kouwenhoven, A. P.; Baardman, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 709. Snider, B. B.; Spindell, D. K. *J. Org. Chem.* **1980**, *45*, 5017. Hoffmann, H. M. R.; Ismail, Z. M.; Weber, A. *Tetrahedron Lett.* **1981**, *22*, 1953.
(33) Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the tables.
(34) Bailey, N. J.; Pfeifer, C. R. *J. Org. Chem.* **1955**, *20*, 95.

(CCl_4) δ 0.2–0.8 (m, 8 H), 0.8–1.4 (m, 2 H), 2.7–3.15 (m, 2 H), 3.2–3.5 (m, 1 H), 3.68 (s, 6 H), 3.97 (d, 1 H, J = 6 Hz); UV (hexane) λ_{max} 210 nm (log ε 3.84). Anal. ($C_{15}H_{20}O_4$) C, H.

Reaction of 1a with 2c. After 32 h at 200 °C, the reaction of **1a** (513 mg, 4.28 mmol) and **2c** (1.20 g, 8.33 mmol) in benzene (10 mL) gave a residue, from which crystals were separated. Recrystallization of the crystals from benzene gave **5**: 53 mg (4.7%); mp 239.5–240 °C; IR (KBr disc) 3100, 3080, 3000, 2955, 1740, 1730, 1435, 1200, 1055, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2–0.7 (m, 16 H), 0.7–1.2 (m, 4 H), 2.2–2.8 (m, 4 H), 3.00 (d, 2 H, J = 5 Hz), 3.3–3.6 (m, 2 H), 3.60 (s, 6 H), 3.67 (s, 6 H); mass spectrum, m/e 528 (M^+, 24.3), 384 (71.3), 59 (100.0). Anal. ($C_{30}H_{40}O_8$) C, H. On an addition of a 0.6-equiv amount of Eu(fod)$_3$ to the chloroform-d solution of **5**, the ^1H NMR signals at δ 2.2–2.8 [C_4 (C_8) protons] were shifted to δ 3.80, those at δ 3.00 [C_2 (C_6) protons] were shifted to δ 5.22, and those at δ 3.3–3.6 [C_3 (C_7) protons] were shifted to δ 4.80. On irradiation of the C_3 (C_7) protons, two multiplets at δ 2.2–2.8 and 3.3–3.6 changed to two singlets. Irradiation of the C_4 (C_8) protons brought about a change of a multiplet signal at δ 3.3–3.6 to a doublet with J = 5 Hz. The magnitude of the coupling constant observed here suggests that the two vicinal methoxycarbonyl groups in **5** are in a trans relationship.[35]

Vacuum distillation of the mother liquor of the crystallization gave a fraction [bp 82–110 °C (bath temperature, 0.05 mm)] which was a mixture of **4b**, dimethyl 3-(dicyclopropylmethylene)cyclobutane-1,2-dicarboxylate (**4c**), and small amounts of two unidentified components (578 mg). **4c**: IR (neat) 3100, 3010, 1740, 1435, 1210, 1020 cm^{-1}; ^1H NMR (CCl_4) δ 0.3–0.7 (m, 8 H), 0.8–1.4 (m, 2 H), 2.78–3.04 (m, 1 H), 3.04–3.40 (m, 2 H), 3.60 (s, 6 H), 4.00 (d, 1 H, J = 9 Hz); UV (hexane) λ_{max} 212 nm (log ε 3.92). Anal. ($C_{15}H_{20}O_4$) C, H.

Reaction of 1a with 2d. A mixture of **1a** (247 mg, 2.06 mmol) and **2d** (630 mg, 3.66 mmol) in benzene (8 mL) was refluxed. GC analysis of the reaction mixture showed that **1a** was totally consumed after 32.5 h. Benzene and excess **2d** were removed under reduced pressure, and the resultant residue was vacuum distilled to give a colorless liquid [bp 140 °C (0.01 mm)] which was found to be a mixture of diethyl 2,2-dicyclopropyl-3-methylenecyclobutane-1,1-dicarboxylate (**3d**) and diethyl 3-(dicyclopropylmethylene)cyclobutane-1,1-dicarboxylate (**4d**) in 14:86 ratio (487 mg, 81%). **3d**: IR (neat) 3100, 3010, 1735, 1105, 1030, 890 cm^{-1}; ^1H NMR (CCl_4) δ 0.2–0.6 (m, 4 H), 0.95–1.25 (m, 2 H), 1.26 (t, 6 H, J = 7.5 Hz), 2.95 (t, 2 H, J = 2.5 Hz), 4.17 (q, 4 H, J = 7.5 Hz), 4.65 (t, 1 H, J = 2.5 Hz), 4.82 (t, 1 H, J = 2.5 Hz). Anal. ($C_{17}H_{24}O_4$) C, H. **4d**: IR (neat) 3100, 3005, 1725, 1260, 1100, 1015 cm^{-1}; ^1H NMR (CCl_4) δ 0.4–0.7 (m, 8 H), 0.95–1.25 (m, 2 H), 1.25 (t, 6 H, J = 7.5 Hz), 3.17 (t, 4 H, J = 1.5 Hz), 4.15 (q, 4 H, J = 7.5 Hz); UV (hexane) λ_{max} 212 nm (log ε 4.18). Anal. ($C_{17}H_{24}O_4$) C, H.

The same reaction was complete after only 1 h in refluxing acetonitrile, and a mixture of **3d** and **4d** in 92:8 ratio was isolated in 85% yield.

Reaction of 1a with 2e. Mixing of **1a** (1.00 g, 8.37 mmol) and **2e** (1.64 g, 16.7 mmol) in benzene produced a light green solution. After a 5-h reflux of the solution, **1a** was completely consumed, but no characterizable material could be isolated from the resultant solution. When the green solution was allowed to stand at room temperature for 7 days, most of **1a** was consumed, but **2e** remained practically intact. **2e** appeared to catalyze the polymerization of **1a**. When **1a** (492 mg, 4.1 mmol) and **2e** (803 mg, 8.2 mmol) were dissolved in acetonitrile (5 mL), no color developed. Refluxing of the solution for 5 h turned it to a dark red. The solution was concentrated, and excess **2e** was recovered by sublimation. Forcing distillation of the resultant residue gave a yellowish green oil [bp 180 °C (bath temperature, 0.02 mm)] which crystallized on when allowed to stand (291 mg, 33%). Recrystallization from hexane gave 2,2-dicyclopropyl-3-methylenecyclobutane-1,2-dicarboxylic anhydride (**3e**): mp 88.5–90 °C; IR (KBr) 3100, 3010, 1860, 1775, 1070, 1030, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.1–0.9 (m, 8 H), 0.9–1.4 (m, 2 H), 3.36 (d, 1 H, J = 7 Hz), 3.84 (dt, 1 H, J = 7, 2 Hz), 4.96 (dd, 1 H, J = 2, 2 Hz), 5.24 (dd, 1 H, J = 2, 2 Hz). Anal. ($C_{13}H_{14}O_3$) C, H.

(35) Sauer, J.; Lang, D.; Weist, H. *Chem. Ber.* **1964**, *97*, 3208.

Reactions of 1a with 2f–h. The reactions were carried out at 200 °C for 4 h, and 2,2-dicyclopropyl-3-methylenecyclobutanecarbonitrile (**3f**), 3-(dicyclopropylmethylene)cyclobutanecarbonitrile (**4f**), *trans*-3-(dicyclopropylmethylene)cyclobutane-1,2-dicarbonitrile (**4g**), and *cis*-3-(dicyclopropylmethylene)cyclobutane-1,2-dicarbonitrile (**4h**) were isolated and characterized.

3f: IR (neat) 3080, 3010, 2240, 1670, 1430, 1020, 890 cm^{-1}; ^1H NMR (CCl_4) δ 0.1–0.8 (m, 8 H), 0.85–1.25 (m, 2 H), 2.7–2.9 (m, 3 H), 4.75–4.90 (m, 2 H). Anal. ($C_{12}H_{15}N$) C, H, N.

4f: IR (neat) 3100, 3010, 2240, 1680, 1420, 1020 cm^{-1}; ^1H NMR (CCl_4) δ 0.3–0.9 (m, 8 H), 0.9–1.25 (m, 2 H), 3.0–3.3 (m, 5 H); UV (hexane) λ_{max} 214 nm (log ε 4.05). Anal. ($C_{12}H_{15}N$) C, H, N.

4g: IR (neat) 3090, 3010, 2240, 1680, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.4–0.95 (m, 8 H), 0.95–1.5 (m, 2 H), 3.1–3.65 (m, 3 H), 4.21 (d, 1 H, J = 5 Hz); UV (hexane) λ_{max} 215 nm (log ε 4.05). Anal. ($C_{13}H_{14}N_2$) C, H, N.

4h: IR (neat) 3090, 3010, 2240, 1680, 1020, 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.5–0.9 (m, 8 H), 0.9–1.5 (m, 2 H), 3.2–3.4 (m, 2 H), 3.52 (ddd, 1 H, J = 9, 9, 6.7 Hz), 4.28 (d, 1 H, J = 9 Hz); UV (hexane) λ_{max} 217 nm (log ε 3.87). Anal. ($C_{13}H_{14}N_2$) C, H, N.

Reaction of 1a with 2i. The reaction of **1a** with **2i** was exothermic and proceeded rapidly at room temperature. Thus, a benzene solution of **1a** (525 mg, 4.38 mmol) was added to a benzene solution of **2i** (704 mg, 9.03 mmol) at room temperature, and solvents and excess **2i** were removed immediately after completion of the addition with a rotary evaporator. Distillation of the resultant oil gave a fraction [bp 110 °C (bath temperature, 0.01 mm)] which was a mixture of 2,2-dicyclopropyl-3-methylenecyclobutane-1,1-dicarbonitrile (**3i**) and 3-(dicyclopropylmethylene)cyclobutane-1,1-dicarbonitrile (**4i**) in a 93:7 ratio (571 mg, 66%). **3i**: IR (neat) 3095, 3020, 2240, 1675, 1430, 1020, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.3–1.0 (m, 8 H), 1.0–1.4 (m, 2 H), 3.22 (t, 2 H, J = 3 Hz), 4.98–5.02 (m, 1 H), 5.02–5.15 (m, 1 H). Anal. ($C_{13}H_{14}N_2$) C, H, N. **4i**: IR (neat) 3100, 3020, 2250, 1690, 1260, 1020, 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.4–0.9 (m, 8 H), 1.0–1.4 (m, 2 H), 3.60 (t, 4 H, J = 1 Hz); UV (95% ethanol) λ_{max} 216 nm (log ε 4.08). Anal. ($C_{13}H_{14}N_2$) C, H, N.

A solution of **2i** in chloroform-d was placed in an NMR tube and a small amount of **1a** was added to it. ^1H NMR examinations of the resultant solution showed that **3i** and **4i** were produced in 97:3 ratio. The same ratio was obtained on GC analyses of the reaction mixture.

Reaction of 1a with 2j. Into a solution of **2j** (256 mg, 2.00 mmol) in 1,2-dichloroethane (70 mL), was added **1a** (240 mg, 2.00 mmol) dropwise. No color developed. The solution was immediately concentrated and the resultant solid residue was recrystallized from benzene–ethanol (1:1) to give 2,2-dicyclopropyl-3-methylenecyclobutane-1,1,2,2-tetracarbonitrile (**3j**): 637 mg (71%); mp 157–158 °C; IR (KBr) 3100, 3020, 2250, 1680, 1430, 875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.3–1.05 (m, 8 H), 1.05–1.4 (m, 2 H), 5.53 (d, 1 H, J = 4 Hz), 5.80 (d, 1 H, J = 4 Hz). Anal. ($C_{15}H_{12}N_4$) C, H, N.

Lewis Acid Catalyzed Reactions of 1a with 2a–d. Under a nitrogen atmosphere was prepared a solution of **2a** (353 mg, 4.1 mmol) and anhydrous aluminum chloride (300 mg, 2.25 mmol) in dichloromethane (7 mL). Then, a solution of **1a** (649 mg, 5.4 mmol) in dichloromethane was added dropwise to it at room temperature. After stirring the resultant red solution at room temperature for 30 min, the mixture was poured into a saturated aqueous solution of sodium hydrogen carbonate (30 mL). An organic layer was separated and washed with water. After the mixture was dried over anhydrous magnesium sulfate, the solvents were removed, and the resultant oily residue was vacuum distilled to give a fraction [bp 120 °C (bath temperature, 3 mm)] which was practically pure **3a** (644 mg, 76%).

In a similar manner, practically pure dimethyl *trans*-2,2-dicyclopropyl-3-methylenecyclobutane-1,2-dicarboxylate (**3b**) was obtained: 82% yield; IR (neat) 3100, 3020, 2960, 1735, 1670, 1435, 1025, 895 cm^{-1}; ^1H NMR (CCl_4) δ 0.2–0.7 (m, 8 H), 0.8–1.3 (m, 2 H), 3.13 (d, 1 H, J = 8 Hz), 3.62 (s, 3 H), 3.65 (s, 3 H), 3.7–3.9 (m, 1 H), 4.78 (d, 1 H, J = 2.5 Hz), 5.08 (d, 1 H, J = 2.5 Hz). Anal. ($C_{15}H_{20}O_4$) C, H. In the reaction of **1a** with **2c**, a mixture of **3b** and dimethyl *cis*-2,2-dicyclopropyl-3-methylenecyclobutane-1,2-dicarboxylate (**3c**) in a 27:73 ratio was obtained (67% yield). GC purification gave crystalline **3c**, which was recrystallized from

hexane: mp 58–59 °C; IR (KBr) 3080, 3020, 2960, 1740, 1730, 1680, 1215, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2–0.6 (m, 8 H), 0.6–1.3 (m, 2 H), 3.30 (d, 1 H, J = 10 Hz), 3.65 (s, 3 H), 3.67 (s, 3 H), 3.7–3.85 (m, 1 H), 4.94 (d, 1 H, J = 3 Hz), 5.23 (d, 1 H, J = 3 Hz). Anal. ($C_{15}H_{20}O_4$) C, H.

The reaction of **1a** with **2d** in the presence of aluminum chloride also produced **3d** exclusively in 30% yield. The yield was low because both **1a** and **2d** polymerized at considerable rates when in contact with aluminum chloride.

Lewis Acid Catalyzed Reactions of 1a with Cyano-Activated Olefins. Under nitrogen was prepared a solution of **2f** (162 mg, 3.1 mmol) and anhydrous aluminum chloride (200 mg, 1.5 mmol) in dichloromethane (10 mL). On an addition of a solution of **1a** (467 mg, 3.9 mmol) in dichloromethane (3 mL), a red color developed. After 1 h at room temperature, GC analyses of the solution indicated the complete consumption of **1a**, but a significant amount of **2f** was still present in the solution. Accordingly, an additional amount of **1a** (142 mg, 1.2 mmol) was added to use up the **2f**. After a workup of the resultant reaction mixture, a fraction [bp 100–140 °C (bath temperature, 2 mm)] was isolated, and it was practically pure **3f** (212 mg, 40%).

The reaction of **1a** (469 mg, 3.9 mmol) with **2g** (233 mg, 3.0 mmol) in dichloromethane (4 mL) in the presence of anhydrous aluminum chloride (200 mg, 1.5 mmol) did not proceed at appreciable rates at room temperature. Accordingly, the solution was refluxed for 5 h. GC analyses showed that **1a** was completely consumed but that a significant amount of **2g** was still present. A standard workup as described above gave no characterizable products.

Reaction of 1b with 2d. A mixture of **1b** (244 mg, 3.05 mmol), **2d** (773 mg, 4.49 mmol), and a trace amount of 2,6-di-*tert*-butyl-*p*-cresol in acetonitrile (4 mL) was heated in a Pyrex tube at 200 °C for 4 h. After removal of the solvents, a residue was vacuum distilled to give a fraction [bp 130 °C (bath temperature, 0.01 mm)] which was a mixture of diethyl 2-cyclopropyl-3-methylenecyclobutane-1,1-dicarboxylate (**3m**) and diethyl 3-(cyclopropylmethylene)cyclobutane-1,1-dicarboxylate (**4m**) in a 39:61 ratio (690 mg, 90%). **3m**: IR (neat) 3080, 2980, 1725, 1265, 885 cm^{-1}; ^1H NMR (a 1:1 mixture of CCl_4 and $CDCl_3$) δ 0.2–0.65 (m, 4 H), 0.65–1.0 (m 1 H), 1.25 (t, 6 H, J = 7.0 Hz), 2.80 (dt, 1 H, J = 16.5, 2.5 Hz), 3.06 (dt, 1 H, J = 8.5, 3 Hz), 3.36 (dt, 1 H, J = 16.5, 2.5 Hz), 4.05–4.4 (m, 4 H), 4.85 (dt, 1 H, J = 2.5, 3 Hz), 4.98 (dt, 1 H, J = 2.5, 3 Hz). Anal. ($C_{14}H_{20}O_4$) C, H. **4m**: (neat) 3090, 2080, 1730, 1265, 1100, 960, 850 cm^{-1}; ^1H NMR (a 1:1 mixture of CCl_4 and $CDCl_3$) δ 0.2–0.5 (m, 2 H), 0.6–0.9 (m, 2 H), 1.25 (t, 6 H, J = 7.5 Hz), 1.2–1.6 (m, 1 H), 3.1–3.2 (m, 2 H), 3.2–3.35 (m, 2 H), 4.20 (q, 4 H, J = 7.5 Hz), 4.66 (d of quintet, 1 H, J = 9, 2 Hz). Anal. ($C_{14}H_{20}O_4$) C, H. The same reaction in benzene at 200 °C or in acetonitrile at 80 °C was investigated merely by GC examinations of the resultant mixtures.

Reaction of 1b with 2j. A yellow solution of **1b** (203 mg, 1.59 mmol) and **2j** (203 mg, 1.60 mmol) in dichloromethane (8 mL) was stirred at room temperature. GC analyses of the solution revealed that 90% of **1b** was consumed after 21 h. Removal of solvents gave a pale yellow oil, which appeared to be a 1:1 mixture of 2-cyclopropyl-3-methylenecyclobutane-1,1,2,2-tetracarbonitrile (**3k**) and 3-(cyclopropylmethylene)cyclobutane-1,1,2,2-tetracarbonitrile (**4k**) on the basis of ^1H NMR examinations of the oil. On an addition of benzene to the oil, crystals were formed and separated. Recrystallization from benzene gave pure **3k**: 123 mg (46%); mp 106–107.5 °C; IR (KBr) 3110, 3030, 2930, 2260, 1870, 1690, 1055, 1035, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.4–1.52 (m, 5 H), 3.38 (dt, 1 H, J = 9, 3 Hz), 5.83 (dd, 1 H, J = 3, 4 Hz), 5.90 (dd, 1 H, J = 3, 4 Hz). Anal. ($C_{12}H_8N_4$) C, H, N. In the ^1H NMR spectrum of the crude oil, a broad singlet ascribed to ring hydrogens at C_4 in **4k** was observed at δ 3.68. Integration of peak areas supported the conclusion that the oil was a 1:1 mixture of **3k** and **4k**. During the recrystallization of **3k**, however, the benzene solution turned red, and **4k** appeared to decompose. A red oil obtained by removal of benzene showed no more peak at δ 3.68, and none of the characterizable products could be isolated from the oil.

Reaction of 1c with 2j. A yellow solution of **1c** (121 mg, 1.78 mmol) and **2j** (228 mg, 1.78 mmol) in 1,2-dichloroethane (5 mL) was stirred at room temperature for 24 h. GC analyses indicated that more than 90% of **1b** was consumed. A solid residue obtained in the evaporation of solvents was examined by ^1H NMR spectroscopy, and it was found that it was practically pure 3-isopropylidenecyclobutane-1,1,2,2-tetracarbonitrile (**4l**). Recrystallization from benzene gave pure **4l**: 246 mg (71%); mp 115–116 °C; IR (KBr) 3020, 2990, 2270, 1720, 1380, 1250, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (t, 3 H, J = 2 Hz), 1.95 (t, 3 H, J = 2.5 Hz), 3.65–3.9 (m, 2 H). Anal. ($C_{11}H_5N_4$) C, H, N.

Reaction of 1c with 2d. A solution of **1c** (271 mg, 4.0 mmol) and **2d** (1.01 g, 5.9 mmol) in acetonitrile (8 mL) was heated in a sealed tube at 80 °C for 50 h. GC analyses showed that 80% of **1c** was consumed. Evaporation of acetonitrile gave a colorless liquid (1.15 g), from which a fraction [bp 50–80 °C (bath temperature, 0.2 mm); 521 mg, 68%] was collected. GC analyses indicated that the fraction was composed of a single component, which was characterized as diethyl 3-isopropylidenecyclobutane-1,1-dicarboxylate (**4n**): IR (neat) 2980, 2930, 1730, 1260, 1150 cm^{-1}; ^1H NMR (CCl_4) δ 1.26 (t, 6 H, J = 7.5 Hz), 1.52 (quintet, 6 H, J = 1.5 Hz), 3.04 (m, 4 H), 4.16 (q, 4 H, J = 7.5 Hz). Anal. ($C_{13}H_{20}O_4$) C, H. The same reaction in benzene either at 80 °C for 50 h (69% consumption of **1c**) or at 140 °C for 50 h (98% consumption of **1c**) produced **4n** as a single product (GC analyses).

Control Experiments. Control experiments were carried out whenever they were necessary. The results are given in either the footnotes of the tables or the text. In a control experiment carried out for **4h**, a new isomer was produced in a small amount (4.3%). In order to obtain the isomer in a larger quantity, we heated a mixture of **4g** and **4h** in a 42:57 ratio in a sealed tube in the presence of a trace amount of 2,6-di-*tert*-butyl-*p*-cresol at 200 °C for 50 h. GC analyses showed that the ratio of **4g**/**4h**/the new isomer was 51:19:30. From this mixture was collected the new isomer by means of preparative GC, and it was characterized as **6**: IR (neat) 3100, 3030, 2250, 2230, 1670, 1420, 1030, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2–0.9 (m, 8 H), 0.9–1.45 (m, 2 H), 2.9–3.3 (m, 3 H), 5.18 (t, 1 H, J = 2 Hz); UV (hexane) λ_{max} 213 nm (log ϵ 4.07). Anal. ($C_{13}H_{14}N_2$) C, H, N.

Methanolysis of 3j. A solution of **3j** (117 mg, 0.47 mmol) in methanol (6 mL) was refluxed for 4 h. TLC analyses of the resultant mixture showed complete consumption of **3j**. Evaporation of methanol gave a colorless solid, which was recrystallized from ethyl acetate to give **7**: 147 mg (quantitative); mp 163.5–166 °C dec; IR (KBr) 3600–2950, 3450, 2240, 1670, 1640, 1405, 1170, 1110, 1080, 1025, 930 cm^{-1}; ^1H NMR (CD_3CN) δ 0.4–0.85 (m, 8 H), 0.95–1.35 (m, 2 H), 3.25 (s, 3 H), 3.35 (s, 3 H), 5.18 (d, 1 H, J = 2.5 Hz), 5.37 (d, 1 H, J = 2.5 Hz), 5.98 (br s, 2 H; disappeared on addition of D_2O). Anal. ($C_{17}H_{20}O_2N_4$) C, H, N.

Refluxing of a solution of **3j** (103 mg, 0.42 mmol) in acetonitrile (10 mL) for 5 h did not bring about any change (TLC), and **3j** was recovered quantitatively by the evaporation of acetonitrile.

Thermal Isomerization of 4l. A chloroform solution of **4l** (237 mg, 1.21 mmol) was refluxed for 5 h. A residual solid obtained in the evaporation of chloroform was recrystallized from chloroform to give colorless needles (130 mg), which were characterized as **8**: mp 163.5–164.0 °C; IR (KBr) 3000, 2950, 2260, 2240, 1655, 1465, 1150 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.84 (s, 6 H), 4.30 (s, 2 H); ^{13}C NMR (acetone-d_6) δ 22.9 (q), 34.9 (s), 41.1 (t), 56.0 (s), 85.0 (s), 110.4 (s), 114.1 (s), 185.3 (s); UV (95% ethanol) λ_{max} 224 nm (log ϵ 3.96), 275 (4.00). Anal. ($C_{11}H_8N_4$) C, H, N. From the mother liquor of the recrystallization were obtained additional amounts of crystals (82 mg), which were **8** and **4l** in a 2.5:1 ratio. Thus, the total amount of **8** was 189 mg (80%), and the recovered amount of **4l** was 23 mg (10%).

Dimerization. A benzene solution (12 mL) of **1a** (2.36 g, 19.6 mmol) in the presence of a trace amount of 2,6-di-*tert*-butyl-*p*-cresol was deoxygenated with bubbling of a nitrogen stream and sealed in a Pyrex tube. The tube was placed in an oven and heated at 200 °C for 32 h. GC analyses of the resultant mixture indicated that more than 95% of **1a** was consumed, and three components were present in the dimer region. In a region for shorter retention times, several very small peaks were observed. Solvents were removed, and the resultant oily residue was distilled to give a pale yellow liquid [bp 85–105 °C (0.01 mm)] which was a mixture of **9**–**11** in a 1.8:1.7:1.0 ratio. Each dimer was separated and purified by means of GC. **9**: IR (neat) 3070, 3000, 1630, 1010, 865, 810 cm^{-1}; ^1H NMR (CCl_4) δ 0.1–0.3 (m, 8 H), 0.3–0.8 (m, 8 H), 0.8–1.2 (m, 3 H), 1.2–1.5 (m, 1 H), 2.18 (br s, 2 H), 4.62 (br s, 1 H), 4.93 (br s, 1 H); UV (hexane) λ_{max} 268 nm (log ϵ 4.19). Anal. ($C_{18}H_{24}$)

C, H. **10**: IR (neat) 3090, 3000, 1630, 1015, 810 cm^{-1}; ^1H NMR (CCl_4) δ 0.1–0.8 (m, 16 H), 0.9–1.2 (m, 2 H), 1.4–1.7 (m, 2 H), 2.46 (s, 4 H); UV (hexane) λ_{max} 278 nm (log ϵ 4.14). Anal. ($C_{18}H_{24}$) C, H. **11**: IR (neat) 3080, 3000, 2930, 2850, 1660, 1015, 880 cm^{-1}; ^1H NMR (CCl_4) δ 0.2–0.55 (m, 8 H), 0.55–1.2 (m, 6 H), 1.2–1.4 (m, 1 H), 1.60 (d, 1 H, J = 12 Hz), 2.12 (d, 1 H, J = 12 Hz), 2.12 (br s, 4 H), 4.63 (s, 1 H), 4.70 (s, 1 H). Anal. ($C_{18}H_{24}$) C, H.

On heating at 200 °C in benzene, **9** rearranged cleanly to **11** (56% rearrangement being observed after 32 h). In contrast, **10** isomerized gradually to **9** (13.6% after 32 h at 200 °C).

In a similar manner, **1b** (1.06 g, 13.2 mmol) gave a fraction [bp 90–180 °C (bath temperature); 434 mg, 41%] which was found to be a mixture of more than 20 components. GC purification permited us to isolate one of the components in a small amount, and it was characterized as a head-to-head dimer:[19] IR (neat) 3100, 3010, 1660, 1430, 1045, 1015, 950 cm^{-1}; ^1H NMR (CCl_4) δ 0.25–0.5 (m, 4 H), 0.5–0.9 (m, 4 H), 1.77 (m, 2 H), 2.40 (s, 4 H), 4.32 (s, 1 H), 4.41 (s, 1 H); UV (hexane) λ_{max} 267 nm (log ϵ 4.14). Anal. ($C_{12}H_{16}$) C, H.

Reactions of 9 and 10 with PTAD. Into a solution of PTAD (42 mg, 0.24 mmol) in dichloromethane (2 mL) was added a solution of **9** (58 mg, 0.24 mmol) in dichloromethane dropwise at room temperature. The evaporation of dichloromethane gave a solid residue, which was recrystallized from benzene to give **12**: 76 mg (76%); mp 122.5–124.5 °C; IR (KBr) 3080, 3000, 2945, 2920, 1765, 1705, 1600, 1500, 1420, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.0–0.8 (m, 16 H), 0.8–1.2 (m, 2 H), 1.4–1.8 (m, 2 H), 2.18 (t, 2 H, J = 3 Hz), 3.97 (t, 2 H, J = 3 Hz), 7.20–7.90 (m, 5 H). Anal. ($C_{26}H_{29}O_2N_3$) C, H, N.

In a similar manner, **10** (79 mg, 0.33 mmol) and PTAD (57 mg, 0.33 mmol) produced a solid residue, which was purified by means of column chromatography followed by recrystallization from ethyl acetate to give **13**: 87 mg (64%); mp 106–109 °C; IR (KBr) 3110, 3030, 2940, 1770, 1705, 1610, 1510, 1410, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.3–1.0 (m, 16 H), 1.4–1.8 (m, 4 H), 2.62 (s, 4 H), 7.20–7.70 (m, 5 H). Anal. ($C_{26}H_{29}O_2N_3$) C, H, N.

The reactions of both **9** and **10** with PTAD proceeded fairly rapidly since a red color of the PTAD solution faded almost instantly on the addition of the solution of **9** or **10**. In contrast, the reaction of **9** with **2b** required heating and gave a complex mixture, from which **5** could not be isolated.

Registry No. **1a**, 60166-70-3; **1b**, 22975-43-5; **1c**, 598-25-4; **2a**, 96-33-3; **2b**, 624-49-7; **2c**, 624-48-6; **2d**, 3377-20-6; **2e**, 108-31-6; **2f**, 107-13-1; **2g**, 764-42-1; **2h**, 928-53-0; **2i**, 922-64-5; **2j**, 670-54-2; **3a**, 82742-61-8; **3b**, 82736-60-5; **3c**, 82736-61-6; **3d**, 85084-70-4; **3e**, 85084-71-5; **3f**, 85084-72-6; **3g**, 85084-73-7; **3h**, 85084-74-8; **3i**, 85084-75-9; **3j**, 85084-76-0; **3k**, 85084-77-1; **3m**, 85084-78-2; **4a**, 82736-55-8; **4b**, 82736-56-9; **4c**, 82736-57-0; **4d**, 85084-79-3; **4f**, 85084-80-6; **4g**, 85084-81-7; **4h**, 85084-82-8; **4i**, 85084-83-9; **4k**, 85084-84-0; **4l**, 85084-85-1; **4m**, 85084-86-2; **4n**, 85084-87-3; **5**, 85084-88-4; **6**, 85084-89-5; **7**, 85084-90-8; **8**, 85084-91-9; **9**, 85084-92-0; **10**, 85084-93-1; **11**, 85084-94-2; **12**, 85084-95-3; **13**, 85084-96-4; PTAD, 4233-33-4; $AlCl_3$, 7446-70-0.

Stereochemistry of Lithiation of *N*-Methylformamide: A Theoretical Study

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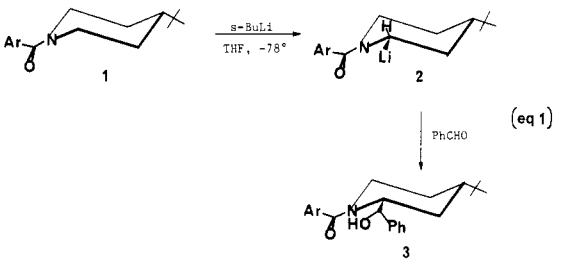
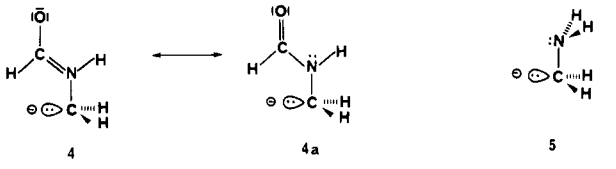
A theoretical examination of the destabilizing effects of a carbanion adjacent to the nitrogen of an amide is presented. When the methyl anion of *N*-methylformamide is placed in conjugation with the amide π system, the molecule is calculated to be 22.3 kcal/mol higher in energy than the ground-state "dipole-stabilized" conformer when a 4-31G basis set is employed. A perturbational molecular orbital (PMO) treatment suggests that the destabilization arises from the increase in energy of the molecular orbital that is largely comprised of the carbanionic center. A similar PMO treatment of formamide provides a rationale for the origin of the barrier to rotation in amides where the energy minimum involves the planar delocalized conformer. The significance of four-electron HOMO–HOMO interactions in both rotational barriers is discussed. A stereoelectronic argument is offered to explain the syn equatorial alkylation of cyclic α-amido anions.

Dipole-stabilized carbanions adjacent to an ester oxygen or the nitrogen of an amide group have recently been shown to be of synthetic utility.[1] For example, Beak[1a] has found that lithiation of the 2,4,6-triisopropylbenzamide **1** followed by reaction with benzaldehyde gave exclusively syn equatorial substitution affording **3**, the thermodynamically *less stable* stereoisomer (eq 1). A sufficient number of related examples[2] of the specificity of metalation have appeared that support the suggestion[1a,3] that syn metalation and substitution of amides is general.



A recent ab initio SCF study[3] presented convincing arguments that the stabilization of such "dipole-stabilized" anions[1a] is relatively high. When the internal dipoles are oriented for maximum stability, as depicted in anion **4**,



extended basis set (4-31+G//STO-3G)[4a] calculations

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