umn, giving, among others, 5 g of dinitrile as a colorless liquid; bp 138 °C (0.4 mm); IR 3.01, 3.28, 3.42, 3.49, 4.51, 6.09, 7.23 μm; NMR ($CDCl_3$/Me_4Si) δ 1.59 (s, NH), 1.88, 2.02 (d, J = 7 Hz, CH_3), 3.41 (s, CH_2), 6.48, 6.60 (q, J = 7 Hz, m, J = 1 Hz, =CH). Anal. Calcd for $C_{10}H_{13}N_3$: C, 68.5; H, 7.4; N, 24.0. Found: C, 68.0; H, 7.7; N, 24.8.

2-Cyano-2-butenylamine (23a). The fraction, bp 68–75 °C (2.1 mm) (17.5 g), showed: IR 3.0, 3.5, 3.6, 4.5, 6.1, 6.2, 6.9, 7.3 μm; ^1H NMR (CCl_4/Me_4Si) δ 1.21 (s, 2 NH), 2.00 (d, J = 7 Hz, t, J = 1.5 Hz, CH_3), 3.38 (m, J = 1.5 Hz, CH_2), 6.39 (q, J = 7 Hz, t, J = 1.5 Hz, =CH). Elemental analyses were unsatisfactory because the ammonia addition is apparently reversible.

Bis(2-cyano-2-butenyl)methylamine (24). To a solution of 5 g of methylamine in 25 mL of EtOH at 0 °C was added dropwise a solution of 28 g of 2-cyanobutadiene in 25 mL of EtOH over a 0.5-h period. The red solution was refluxed overnight and distilled, giving 20 g of colorless liquid: bp 113–120 °C (0.05 mm); IR 3.25, 3.37, 3.48, 3.55, 4.49, 6.07 μm; ^1H NMR δ 1.91, 2.05 (d, J = 6 Hz, CH_3CH), 2.30 (s, CH_3N), 3.20 (s, CH_2N), 6.48, 6.60 (q, J = 6 Hz, br, =CH). Anal. Calcd for $C_{11}H_{15}N_3$: C, 69.8; H, 8.0; N, 22.2. Found: C, 70.0; H, 8.0; N, 22.5.

Bis[2-(aminomethyl)butyl]methylamine (25). A slurry of 15 g of dinitrile **24**, 60 mL of THF, 25 g of NH_3, and 20 g of Raney nickel was shaken under 2000 psi of H_2 at 135 °C/8 h. The catalyst was separated, solvent was removed on a rotary evaporator, and the product was distilled through a small spinning-band column; bp 75–77 °C (0.02 mm); yield 9 g; IR 2.99, 3.06, 3.44, 3.49, 3.58, 6.26, 7.26 μm; ^1H NMR (CCl_4/Me_4Si) δ 2.13 (s, CH_3), 2.05–2.7 (m, CH_2N), 0.9 (t, J = 6 Hz, CH_3CH_2), 1.05–1.8 (m, CH_2). Anal. Calcd for $C_{11}H_{27}N_3$: C, 65.6; H, 13.5; N, 20.9. Found: C, 66.4; H, 13.2; N, 20.1.

3,5-Bis(dimethylamino)valeronitrile (26) was prepared by the addition of dimethylamine to 1-cyanobutadiene:[1] ^1H NMR (CCl_4/Me_4Si) δ 1.62 (q, J = 6.5 Hz, CH_2CN), 2.19, 2.30 (s, s, NCH_3), 2.42 (m, CH_2N), 2.90 (m, CHN).

1,3-Bis(dimethylamino)-5-aminopentane (27). A slurry of 18 g of nitrile **26**, 50 mL of THF, 20 g of NH_3, and 10 g of Raney cobalt was shaken under 1000 psi of H_2 at 135 °C/6 h. Distillation gave 7 g of triamine, bp 84–90 °C (2 mm); IR primary aliphatic amine; ^1H NMR δ 1.12 (s, NH_2), 1.2–1.8 (m, 4 H), 2.11, 2.17 (s, s, NCH_3), 2.27–2.79 (m, 5 H). Anal Calcd for $C_9H_{23}N_3$: C, 62.4; H, 13.4; N, 24.2. Found: C, 62.2; H, 13.4; N, 24.2.

1,3,5-Tris(dimethylamino)pentane (28). To 17 g of **27** at 0 °C was added 40 g of formic acid and then 40 g of formalin. The solution was refluxed, giving off 4.5 L of CO_2 in 2 h. After the addition of 5 mL of concentrated HCl, the solution was stripped on the rotary and poured onto ice. The solution was made basic with 50% NaOH, and the organic phase was extracted into ether, dried, and distilled, giving 12 g of colorless liquid: bp 68–70 °C (0.6 mm); IR saturated tertiary amine; NMR ($CDCl_3$/Me_4Si) δ 1.30 (m, $CH_2CH_AH_BCH$), 1.57 (m, $CH_2CH_AH_BCH$), 2.13 (s, 12 H, CH_3N), 2.19 (s, 6 H, CH_3N), 2.20 (m, J = 6 Hz, CH_2N), 2.40 (pentet, J = 6, CHN). Anal. Calcd for $C_{11}H_{27}N_3$: C, 65.6; H, 13.5; N, 20.9. Found: C, 66.1; H, 13.5; N, 21.0.

Registry No.—**1**, 64413-80-5; **2**, 64413-76-9; **3a**, 64413-74-7; **3c**, 64413-75-8; **4**, 59821-81-7; **5**, 13035-19-3; **6**, 64413-73-6; **7a**, 64414,07-9; **7b**, 64414-06-8; **8a**, 64414-05-7; **8b**, 64414-09-1; **9a**, 64413-85-0; **9b**, 64413-84-9; **10a**, 64413-83-8; **10b**, 64413-82-7; **11**, 64414-08-0; **12** isomer 1, 64413-81-6; **12** isomer 2, 64413-79-2; **13**, 64413-78-1; **14**, 64413-77-0; **15**, 64398-03-4; **16**, 64398-02-3; **17a** isomer 1, 64398-01-2; **17a** isomer 2, 64397-86-0; **17b** isomer 1, 64398-00-1; **17b** isomer 2, 64397-85-9; *cis*-**18a**, 64397-99-5; *trans*-**18a**, 64397-98-4; **18b** isomer 1, 64414-30-8; **18b** isomer 2, 64397-84-8; **19**, 64397,87-1; **20**, 64397-97-3; **21**, 64397-96-2; **22**, 64397-95-1; **23a**, 64397-94-0; **23b**, 64397,93-9; **24**, 64397-92-8; **25**, 64397-91-7; **26**, 64397-90-6; **27**, 64397-89-3; **28**, 64397-88-2; hydrazine, 302-01-2; 1-cyanobutadiene, 1615-70-9; benzaldehyde, 100-52-7; phenyl isocyanate, 103-71-9; isobutyl chloroformate, 17462-58-7; benzoyl chloride, 98-88-4; methyl isocyanate, 624-83-9; maleic anhydride, 108-31-6; phthalic anhydride, 85-44-9; succinic anhydride, 108-30-5; dimethyl acetylene dicarboxylate, 762-42-5; hexafluorobutyne, 692-50-2; methyl vinyl ketone, 78-94-4; acetylacetone, 123-54-6; phenylhydrazine, 100-63-0; methylhydrazine, 60-34-4; 2-cyanobutadiene, 5167-62-4; methylamine, 74-89-5; formalin, 50-00-0.

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(6) Research Disclosure 11516, Nov., 1973.

Reactions of 1,1-Disubstituted Olefins Containing Electron-Attracting Substituents with Methylphenyldiazomethanes

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Reactions of 1,1-disubstituted olefins **3** which carry cyano, carboalkoxy, halogen, etc. as a substituent with methyl-para-substituted-phenyldiazomethanes (**2**) in dichloromethane at −5–0 °C produce 1,1-disubstituted-3-phenyl-1-butene (**4**) and 1,1-disubstituted-2-methyl-2-phenylcyclopropane (**5**). Product ratios of **4** to **5** seem to depend upon the substituents on **3**. In the case of **3** with both cyano and carboalkoxy groups, product **4** is more favorable than **5**; on the other hand, when using **3** with both either a cyano or carboalkoxy group and either a halogen or hydrogen, product **5** is more favorable than **4**. The product ratios of **4** to **5** also depend upon the substituents of **2**; e.g., when the substituent is an electron-attracting group product **4** is more favorable than **5**, and when the substituent is an electron-donating group **5** is more likely than **4**.

It has been reported[1-3] that the reactions of 2-cyano-3-phenylacrylates with diazomethane give various products, including 2-cyano-3-methyl(or ethyl)-3-phenylacrylates, 2-cyano-3-methyl-3-benzylacrylates, and 1-cyano-2-methyl-2-phenylcyclopropanecarboxylates (**5a,b**). **5** (X = NO_2, R = H, Y = CN, Z = COOMe) has been isolated in pure form[4] but **5a** and **5b** have not.[5] We wished to obtain **5b** in its pure form and tried the following reactions.

Methylphenyldiazomethane (**2a**)[6,7] reacted with 2-cyanoacrylates **3a,b** in dichloromethane at −5–0 °C readily, and the crude products obtained were applied to a column of silicic acid (eluted with chloroform) and afforded 2-cyano-4-methyl-4-phenylcrotonates **4a,b**. In the case of **2a** with **3b**, **5b** was afforded, mp 105–106 °C, in 9.8% yield together with **6b** (X = H), mp 160–161 °C, in 2.7% yield. From its NMR, **6** was recognized as a geometrically simple compound.

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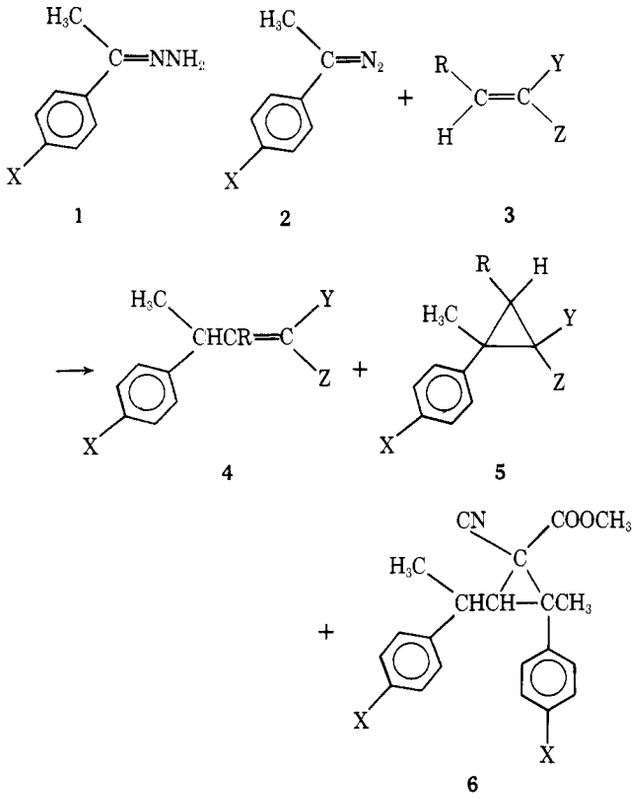
Table I. Product Yields and Geometric Isomer Ratios of the Reactions

2		3				4							5						
Compd 2	X	Compd 3	R	Y	Z	Compd 4	X	R	Y	Z	Yield %	c:t	Compd 5	X	R	Y	Z	Yield %	c:t
a	H	a	H	CN	COOEt	a	H	H	CN	COOEt	29.3	1:3.3	a	H	H	CN	COOEt	None	
	H	b	H	CN	COOMe	b	H	H	CN	COOMe	27.8	Only t	b	H	H	CN	COOMe	9.77	Only t
	H	c	H	CN	Cl	c	H	H	CN	Cl	None		c	H	H	CN	Cl	33.7	1:1
	H	d	H	Br	COOMe	d	H	H	Br	COOMe	None		d	H	H	Br	COOMe	25.9	1:1.5
	H	e	H	H	COOMe	e	H	H	H	COOMe	7.81	Only t	e	H	H	H	COOMe	21.5	Only t
	H	f	CH_3	CN	COOMe	f	H	CH_3	CN	COOMe	16.4	1:10	f	H	CH_3	CN	COOMe	23.8	1:1.8
b	Cl	b	H	CN	COOMe	g	Cl	H	CN	COOMe	33.5	1:6.7	g	Cl	H	CN	COOMe	None	
	Cl	c	H	CN	Cl	h	Cl	H	CN	Cl	None		h	Cl	H	CN	Cl	39.5	1:1.2
c	CH_3	b	H	CN	COOMe	i	CH_3	H	CN	COOMe	3.9	Only t	i	CH_3	H	CN	COOMe	14.8	Only t



To obtain **5** in a better yield, we varied the substituents Y or Z of the olefin **3**, and their reactions gave the products **4a–i** and **5b–i**. The yields (%) based on acetophenone hydrazones **1**[8] and isomeric ratios[9] of these products are shown in Table I. The products **4–6** were characterized on the basis of their MS, IR, NMR, and UV spectra and analyses. Table II shows NMR spectral data of **4**, Table III shows NMR spectral data of **5**, and Table IV shows UV spectral data of **4** and **5**.[10] (For Tables II–IV, see paragraph concerning supplementary material.)

The differences between **4** and **5** have been apparently recognized on NMR and UV spectra. From the NMR spectra of these compounds, **4b** and **5b** are geometrically simple, and the constitution of the trans form only was estimated. A vinyl proton of **4b** appears at δ 7.63 (d), but two hydrogens of the cyclopropane ring of **5b** appear at δ 2.40 (d) and 2.01 (d). On the UV absorption curve, **4b** shows a marked variation with a change in the acidity of the medium, as shown by a new absorption maximum at 340 nm (log ϵ 3.85) in alkaline medium, but the UV spectra of **5b** does not show a marked variation (Figure 1). The UV spectra of **4a** and **4g** are similar to that of **4b**, and those of **5c–i** are similar to that of **5b**.

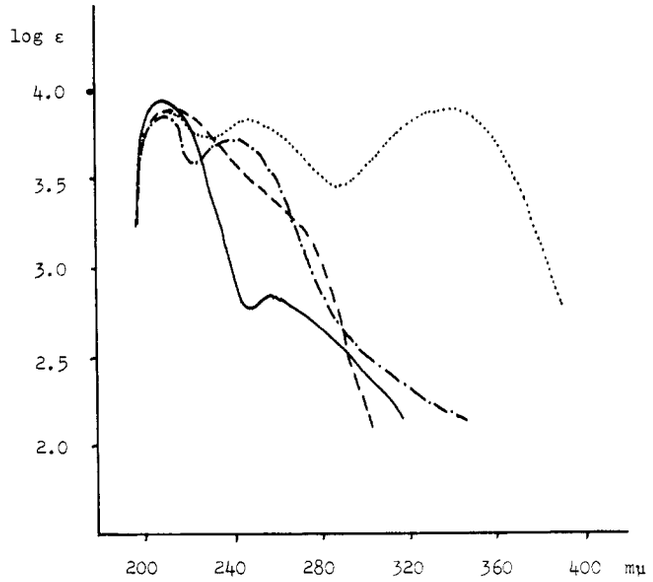
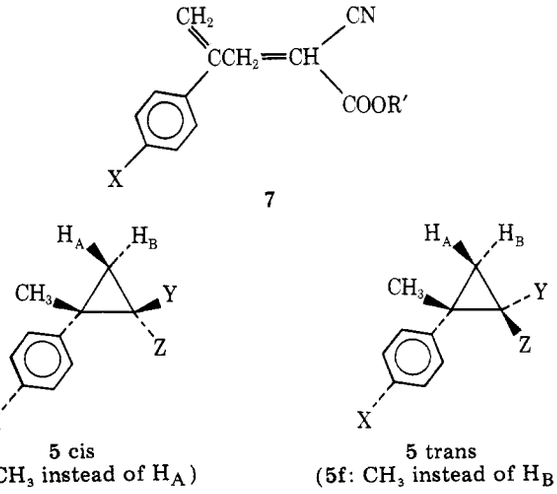


Figure 1. UV spectra of **4b** and **5b:** (- - -) **4b** in neutral medium; (· · ·) **4b** in basic medium; (– • –) **4b** in acidic medium; (—) **5b** in neutral medium.



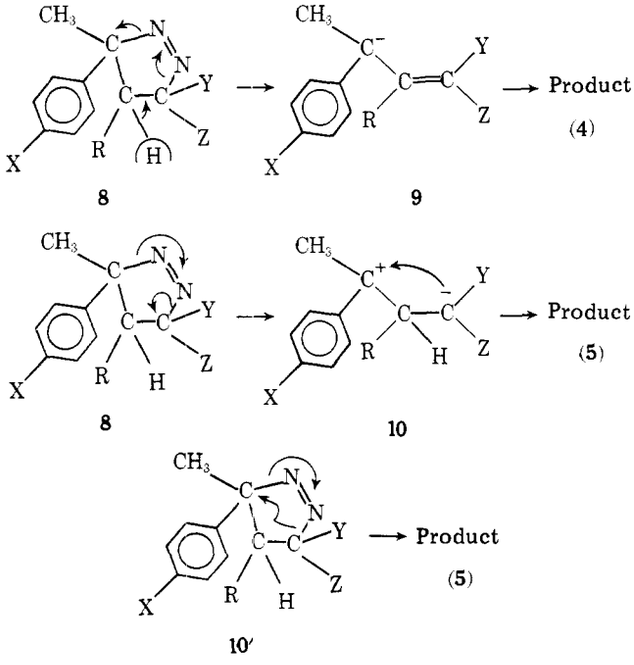
When **5b** is kept at 180 °C for 3 h it changes completely to **7b** (X = H; R′ = Me): NMR ($CDCl_3$) δ 5.30 and 5.42 (nearly two s, 2 H), δ 3.5 (ABX type, 1 H), 3.2 (ABX type, 2 H, J_{AX} = 8.6 Hz, J_{BX} = 6.4 Hz, J_{AB} = 13.6 Hz), 3.72 (s, 3 H). This fact suggests that **4** has not been produced from **5**; the products **4** and **5** have been produced via a separate route.

Reaction of methyl-*p*-chlorophenyldiazomethane (**2b**) with

3b only produces olefin compound **4g**, but reaction of **2b** with 2-chloroacrylonitrile (**3c**) only produces cyclopropane compound **5h**. On the other hand, reaction of methyl-*p*-methylphenyldiazomethane (**2c**) with **3b** produces both olefin compound **4i** and cyclopropane compound **5i**, mp 103–104.5 °C,[11] with the result that the latter will give a better yield than the former. In this case, the products were refined carefully with a column of silicic acid (eluted with chloroform and petroleum ether) to produce **4i** and **5i** in their pure forms, respectively; in spite of refining which was repeated four to five times, **4i** was obtained as an equivalent mixture with **6i**.

The IR spectrum of **5e** agrees with that of the product from the reaction of α-methylstyrene with diazoacetic ester.[12] On the UV spectra of **4f** a marked variation has never been shown with a change in the acidity of the medium, because the CH_3 group attaching to the C=C bond decreases the acidity of the vinyl hydrogen. In comparing the mass spectra of **4** with those of **5**, it is observed that all base peaks of **4** are made of $M^+ - R'OH$ but those of **5** are made of the fragments which lack a substituent in the cyclopropane ring.

From the reports of Carrie et al.[13] concerning pyrazoline compounds, we guess that these reactions which are treated under no irradiation at low temperature proceed by way of the pyrazoline compounds **8**. McGreer et al.[14] have suggested that the pyrolyses of pyrazolines at 70 or 140 °C proceeded through ionic mechanisms and were affected by the polarity of solvents. Also, we guess that when **8** loses nitrogen through an ionic mechanism, according to the nature of the substituent X, Y, and Z, they take either a path to product **4** easily or the other path to produce **5** easily. From the above results, 1,1-disubstituted olefin which carries the electron-attracting substituents such as COOR′ and CN conjugated with C=C is ordinarily unfavorable for cyclopropane ring formation, but our experiments show that it proceeded together with chain-extended olefin formation. The ratios of **4** to **5** in the reaction products seem to depend upon the substituents (Y, Z) of **3**; namely, in the case of **3** with both CN and COOR′ groups, product **4** is more favorable than **5**; on the other hand, in the case of **3** with both either a CN or COOR′ group and either a halogen or hydrogen, product **5** is more favorable than **4**. The details are as follows: **3** (R = H, Y = CN, Z = COOR′), **4** > **5**; **3** (R = H, Y = H, Z = COOR′), **4** < **5**; **3** (R = CH_3, Y = CN, Z = COOR′), **4** < **5**; **3** (R = H, Y = Br, Z = COOR′), **4** ≪ **5**; **3** (R = H, Y = CN, Z = Cl), **4** ≪ **5**.



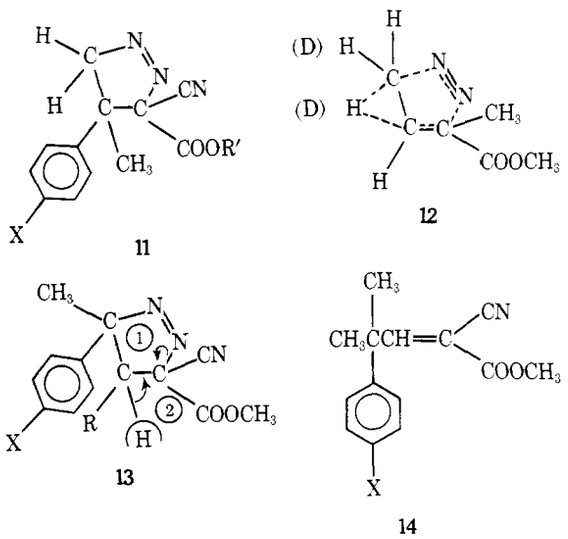
8 **9** **8** **10** **10′**

On the reaction of methyl-para-substituted-phenyldiazomethanes (**2**) with methyl α-cyanoacrylate (**3b**), the substituents (X) of **2** control the product ratios of **4** to **5** in the reaction products as follows: **2** (X = Cl), **4** ≫ **5**; **2** (X = H), **4** > **5**; **2** (X = CH_3), **4** < **5**.

In the case of **8** (X = Cl, R = H, Y = CN, Z = COOR′), the carbanion at the benzyl site is stable. When, therefore, a nitrogen molecule misses from **8**, a hydrogen on the allyl site of Y or Z will leave off **8** as a proton, and then the residue will produce **4** through an intermediate **9**. In the case of **8** (X = CH_3, R = H, Y = CN, Z = COOR′), the carbonium ion at the benzyl site is stable. When, therefore, a nitrogen molecule misses from **8**, the residue will produce the carbanion at the α position of Y or Z in **10**. If the carbanion has a certain stability, though a zwitter ion **10** is difficult to exist, it will produce **5** by way of a concerted mechanism (**10′**).

Discussion

Hamelin et al.[15] and McGreer et al.[16] considered the mechanisms of olefin formation by pyrolyses of the pyrazolines **11**, and they suggested that the driving force which was caused by the formation of the zwitter ion of $^+$N-2 and $^-$C-3 (shifting ① in **13**) was the result of an aromatic or methyl



11 **12** **13** **14**

group migrating from C-4 to C-5. From the kinetic study[16,17] using the deuterated pyrazolines, McGreer et al. suggested that the olefin formation proceeded by way of the concerted mechanism which transformed the σ bond between N-2 and C-3 into the π bond between C-3 and C-4 in **12**. They also suggested that the olefin formation was a stereospecific reaction, but that the cyclopropane formation was not.[16-18] Their products-yield data[4] showed that **11** (X = NO_2) produced much more corresponding cyclopropane compound than **11** (X = MeO) did, but, in both cases, more olefins were produced than cyclopropane compounds, but these facts are opposite to our results, and their data were obtained regardless of whether C-4 was charged negative or positive in the transition state of the decomposition reaction of **11**.

In the case of our study, the bond shifting in the decomposition reactions of pyrazoline takes place in the reverse direction to the cases in the study of Hamelin et al. and McGreer et al. In our case, the formation of olefin **4** from pyrazoline **8** occurred through intermediate **9** owing to the bond shifting (**13**, ② →), and a hydrogen at C-4 came off as a proton. Consequently, it is difficult to consider that a hydrogen at C-4 migrates to C-5 in the form of a hydrogen atom or a hydride ion. A methyl migration from C-4 to C-5 is also difficult to consider because the olefin of the type **14** is not given.

In our study, when a pyrazoline **8** produced a zwitterion **10**

of ^{+}C and ^{-}C, the bond shifting (**13**, ← ①) which is also shown by Hamelin et al. and McGreer et al. occurred; but in our case it should be considered that a pyrazoline **8** produces a cyclopropane compound **5**.

Experimental Section[19]

Methyl α-Cyanoacrylate (3b). In a 200-mL round-bottomed flask with a reflux condenser a mixture of 25 g (0.25 mol) of methyl cyanoacetate, 10 g of paraformaldehyde, and 3 drops of piperidine was heated and stirred on a oil bath at 80 °C for 1 h. The content of the flask became a pale-yellow resinous material. The material was cooled down to room temperature and was dissolved into 300 mL of dichloromethane, into which 100 g of anhydrous sodium sulfate was added for dryness. This solution contained 0.92 g (0.0082 mol) of methyl α-cyanoacrylate per 10 mL. Ethyl α-cyanoacrylate (**3a**) was prepared in the same way.

Methyl 2-Cyano-4-methyl-4-phenylcrotonate (4b), Methyl 1-Cyano-2-methyl-2-phenylcyclopropanecarboxylate (5b), and Methyl 1-Cyano-2-α-methylbenzyl-3-methyl-3-phenylcyclopropanecarboxylate (6b). To the stirred mixture of 8 g (0.06 mol) of acetophenone hydrazone (**1**, X = H), 60 mL of dichloromethane, and 6.2 g of anhydrous magnesium sulfate, cooled in an ice bath, 28 g of active manganese dioxide[20] was added portionwise in 20 min, and then the whole material was stirred for 1 h at room temperature. The inorganic salts were filtered off with a Buchner funnel packed with hyflo super-cel (Johns-Manvills Sales Corp.), being washed with 30 mL of dichloromethane. The combined filtrates were cooled down to −35 °C, and then a small amount of precipitates was separated off by decantation. The deep red-purple solution contained methylphenyldiazomethane (**2a**). To this cooled dichloromethane solution of **2a** in a 200-mL round-bottomed flask, 70 mL of a dichloromethane solution of **3b** (0.0574 mol) was added and stirred at −5–0 °C for 1 h, the solution changed its color to yellow, and stirring was continued overnight at room temperature. The solvent was distilled off under reduced pressure at 40–50 °C. Fourteen grams of crude oily products was obtained. A solution of 14 g of the crude products in the minimum volume of chloroform was applied to a column of silicic acid (500 g, 100 mesh), and the column was eluted with chloroform. The crude products resolved into four or five bands in the column; the pale-yellow fastest moving band (500 mL of chloroform solution) gave 5 mL of oily product. When 3 mL of 95% ethanol was added to this product, 5.72 g of **6b** was given as the crystals which gave 0.51 g (yield 2.7%) of the colorless prisms of **6b**, mp 160–161 °C, by recrystallization from ethanol, and the mother liquid, being applied to a column of silicic acid (three times chromatographied), gave the solution of **4b**.

The second fastest moving band (500 mL of chloroform solution) gave 3 mL of oily product. Two milliliters of 95% ethanol was added to this product and then 1.303 g of **5b** as the colorless prisms, mp 105–106 °C, was given. These prisms gave 1.25 g (yield 9.8%) of **5b**: mp 105–106 °C; NMR ($CDCl_3$) δ 2.17 (d, H_A), 2.10 (d, H_B, J_{AB} = 6 Hz), 1.67 (s, CH_3); MS *m/e* (rel intesity) 215 (27), 200 (4), 183 (70), 156 (100); IR (nujol) 2248 (CN), 1764 cm^{-1} (C=O), by recrystallization from ethanol; Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.37; H, 5.98; N, 6.68. The mother liquid, being applied to a column of silicic acid (three times chromatographed), gave the solution of **4b**.

A combined solution of **4b** gave 3.56 g (yield 27.8%) of pure **4b** as a pale-yellow oil: n^{20}_D 1.5396; NMR ($CDCl_3$) δ 4.16 (m, H_A), 7.62 (d, H_B, J_{AB} = 11 Hz), 1.53 (d, CH_3); MS *m/e* (rel intensity) 215 (47), 183 (100), 155 (37); IR (neat) 2230 (CN), 1740 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.29; H, 5.90; N, 6.23. From the third and fourth bands, 0.7 g of acetophenonazine, mp 122 °C (lit.[21] mp 121 °C), was given.

6b: mp 160–161 °C; IR (nujol) 2218 (CN), 1740 cm^{-1} (C=O); UV (EtOH), λ_{max}, nm (log ε), in neutral medium 213 (4.05), 252 (2.16), 260 (2.38), 264 (2.38); UV absorption spectrum of **6b** does not show a marked variation with a change in the acidity of the medium; NMR ($CDCl_3$) δ 7.32 (arom, 5 H), 7.12 (arom, 5 H), 3.49 (s, 3 H), 2.72 (d, 1 H, J_{AB} = 12 Hz), 2.51 (m, 1 H, $J_{A\text{-}CH_3}$ = 6 Hz), 1.35 (d, 3 H), 1.50 (s, 3 H). Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.96; H, 6.58; N, 4.39. Found: C, 78.84; H, 6.60; N, 4.48.

In the same way the above **4a** was given as oil: n^{20}_D 1.5292; NMR (Me_2SO-d_6) cis form δ 7.05 (d, H_B, J_{AB} = 11 Hz, H_A is obscure), 1.51 (d, CH_3, $J_{A\text{-}CH_3}$ = 7 Hz); trans form δ 4.00 (m, H_A), 7.77 (d, H_B, J_{AB} = 11 Hz), 1.49 (d, CH_3, $J_{A\text{-}CH_3}$ = 7 Hz); MS *m/e* (rel intensity) 229 (46), 183 (100), 156 (50). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.28; H, 6.56; N, 6.07.

Methyl 2-Cyano-4-methyl-4-*p*-methylphenylcrotonate (4i), Methyl 1-Cyano-2-methyl-2-*p*-methylphenylcylopropanecarboxylate (5i), and Methyl 1-Cyano-2-α-methyl-*p*-methylbenzyl-3-methyl-3-*p*-methylphenylcyclopropanecarboxylate (6i). Methyl-*p*-methylphenyldiazomethane (**2c**) was prepared from 9.4 g (0.06 mol) of *p*-methylacetophenone hydrazone (**1**, X = CH_3), 6.2 g of anhydrous magnesium sulfate in 70 mL of dichloromethane, and 28 g of active manganese dioxide. In the same way as the reaction of **2a** with **3b**, **2c** reacted with 90 mL of a dichloromethane solution of **3b** (0.06 mol) and gave 12.6 g of the crude products. The solution of the crude products in the minimum volume of chloroform was applied to a column of silicic acid (400 g, 100 mesh) and eluted with chloroform. From the faster moving bands, 1 L of chloroform solution gave 10.3 g of an orange-yellow oily substance. The oily substance was applied repeatedly (five times) to a column of silicic acid (each 400 g, 100 mesh) and eluted at first with petroleum ether only (boiling range 30–70 °C) and then with the solvent which was gradually changed to the mixture of petroleum ether and chloroform (10:1).

The fastest moving band, being distilled off the solvent under reduced pressure at 40 °C, gave 1.514 g of a pale-yellow oil. From NMR, this oil (1.514 g) proved to consist of 0.536 g (yield 3.9%) of **4i** and 0.978 g (yield 4.7%) of **6i**. The second fastest moving band, being distilled off the solvent under reduced pressure at 40 °C, gave white crystallines, which gave 2.03 g (yield 14.8%) of **5i** by recrystallization from a mixed solvent of petroleum ether and methanol (1:1): mp 103–104.5 °C; NMR ($CDCl_3$) δ 2.11 (d, H_A), 2.05 (d, H_B, J_{AB} = 6 Hz), 1.57 (s, CH_3); MS *m/e* (rel intensity) 229 (41), 197 (48), 170 (100); IR (nujol) 2250 (CN), 1732 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.46; H, 6.56; N, 6.03. The third and fourth fastest moving bands gave 3.15 g of *p*-methylacetophenonazine, mp 131–132 °C (lit.[21] mp 131 °C). **4i:** NMR ($CDCl_3$) δ 4.00 (m, H_A), 7.40 (d, H_B, J_{AB} = 11 Hz), 1.45 (d, CH_3, $J_{A\text{-}CH_3}$ = 7 Hz). **6i:** NMR ($CDCl_3$) δ 6.98 (arom, 4 H), δ 6.83 and 6.70 (A_2B_2, 4 H, J = 9 Hz), 3.80 (s, 3 H), 2.58 (d, 1 H), 2.46 (m, 1 H, J_{AB} = 10.8 Hz, $J_{A\text{-}CH_3}$ = 6.3 Hz), 2.34 (s, 3 H), 2.20 (s, 3 H), 1.45 (s, 3 H), 1.18 (d, 3 H).

Methyl 1-Bromo-2-methyl-2-phenylcyclopropanecarboxylate (5d). Methylphenyldiazomethane (**2a**) was prepared, in the above-mentioned method, from 0.06 mol of acetophenone hydrazone (**1**, X = H). To the dichloromethane solution of **2a**, 13 g (0.08 mol) of methyl α-bromoacrylate[22] was added under stirring at −5–0 °C, and stirring was continued overnight at room temperature. When the solvent was distilled off under reduced pressure at 40–50 °C, 19.8 g of crude products was given, and then they were applied to a column of silicic acid (500 g, 100 mesh) and eluted with chloroform. That is to say, for the purification of the products, column-chromatography was applied repeatedly six times with silicic acid columns. The fastest moving band gave 1.4 g (yield 5.93%) of the orange-red colored crystals of ω,ω′-dibromoacetophenonazine (**15**):[23] mp 151–152 °C; NMR ($CDCl_3$) δ 4.51 (s, 2 H), 8.0 and 7.5 (arom, 5 H); MS *m/e* (rel intensity) 396 (27), 394 (51), 392 (27), 315 (41), 313 (44), 314 (99), 312 (99), 234 (100). Anal. Calcd for $C_{16}H_{14}N_2Br_2$: C, 48.75; H, 3.55; N, 7.11; Br, 40.61. Found: C, 48.68; H, 3.51; N, 7.03; Br, 40.66. A combined solution of the faster moving bands of each column chromatogram, especially the fastest moving band, gave 4.15 g (yield 25.9%) of **5d** (NMR pure substance, this sample was six times column chromatographed): n^{20}_D 1.5444; NMR ($CDCl_3$) cis form δ 2.02 (d, H_A), 1.70 (d, H_B, J_{AB} = 6 Hz), 1.45 (s, CH_3); trans form δ 2.49 (d, H_A), 1.34 (d, H_B, J_{AB} = 6 Hz), 1.70 (s, CH_3); MS *m/e* (rel intensity) 270 (4), 268 (4), 189 (23), 157 (19), 192 (100); IR (neat) 1730 cm^{-1} (C=O);[24] and any olefin compound was not given.

Methyl 4-Methyl-4-phenylcrotonate (4e) and Methyl 2-Methyl-2-phenylcyclopropanecarboxylate (5e). In the above-mentioned method, from 4 g (0.03 mol) of acetophenone hydrazone (**1**, X = H) was prepared **2a**, which was reacted with 2.2 g (0.025 mol) of methyl acrylate (**3e**) in dichloromethane at −5–0 °C. Crude products (2.1 g) were applied to a column of silicic acid and eluted with chloroform. The fastest moving band (column chromatographed repeatedly two times) gave 0.863 g of a pure oil of **5e**: n^{20}_D 1.5196; NMR (CDl_3) δ 1.36 (dd, H_A), 1.53 (dd, H_B), 1.96 (dd, H_X, J_{AB} = 5 Hz, J_{AX} = 7 Hz, J_{BX} = 8 Hz), 1.51 (s, CH_3); MS *m/e* (rel intensity) 190 (25), 159 (17), 131 (100); IR (neat) 1725 cm^{-1} (C=O). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.64; H, 7.36. The second fastest moving band (column chromatographed repeatedly six times) gave 0.842 g of mixed oil; from NMR, the oil proved to consist of **4e** and **5e** in the ratio 1:0.9. **4e**: NMR ($CDCl_3$) δ 3.55 (m, H_A), 7.66 (dd, H_B), 5.78 (d, H_C, J_{AB} = 11 Hz, J_{AC} = 2 Hz, J_{BC} = 15 Hz), 1.62 (d, CH_3, $J_{A\text{-}CH_3}$ = 7 Hz). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 75.22; H, 7.44.[25] The third and fourth fastest moving bands gave 1.69 g of acetophenonazine, mp 122 °C. As a result, the reaction of **2a** with **3e** gave eventually 12.2 g (yield 21.5%) of **5e** and 0.44 g (yield 7.81%) of **4e**.

Methyl 2-Cyano-3,4-dimethyl-4-phenylcrotonate (4f) and Methyl 1-Cyano-2,3-dimethyl-2-phenylcyclopropanecarboxylate (5f). In the above-mentioned method, from 4 g (0.03 mol) of acetophenone hydrazone (**1**, X = H) was prepared **2a**, which was reacted with 5.1 g (0.042 mol) of methyl α-cyanocrotonate (**3f**) in dichloromethane at −5–0 °C. There was 8.5 g of crude products given, and they were applied to a column of silicic acid and eluted with chloroform. The fastest moving band (column chromatographed repeatedly two times) gave 1.12 g (yield 16.4%) of **4f:** n^{20}_D 1.5427; NMR ($CDCl_3$) cis form δ 1.62 (d, CH_3, $J_{A\text{-}CH_3}$ = 7 Hz, H_A is obscure); trans form δ 5.84 (m, H_A), 1.49 (d, CH_3, $J_{A\text{-}CH_3}$ = 7 Hz), 1.99 (s, CH_3); MS *m/e* (rel intensity) 229 (35), 197 (100), 170 (40); IR (neat) 2220 (CN), 1722 and 1730 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.16; H, 6.62; N, 5.91. The second fastest moving band (column chromatographed repeatedly two times) gave 1.63 g (yield 23.8%) of **5f:** n^{20}_D 1.5298; NMR ($CDCl_3$) cis form δ 1.24 (d, CH_3), 2.30 (q, H_B, $J_{B\text{-}CH_3}$ = 7 Hz); 1.46 (s, CH_3); trans form δ 1.42 (d, CH_3), 2.63 (q, H_B, $J_{B\text{-}CH_3}$ = 7 Hz), 1.69 (s, CH_3); MS *m/e* (rel intensity) 229 (55), 197 (100), 170 (79); IR (neat) 2230 (CN), 1735 and 1740 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.35; H, 6.59; N, 6.11. Found: C, 73.64; H, 6.57; N, 6.02. The third and fourth fastest moving bands gave 0.6 g of acetophenonazine.

1-Chloro-1-cyano-2-methyl-2-phenylcyclopropane (5c). In the above-mentioned method, from 4 g (0.03 mol) of **1** (X = H) was prepared **2a**, which was reacted with 2.2 g (0.025 mol) of α-chloroacrylonitrile (**3c**) and gave 4.12 g of crude products which contained some yellow crystals. The crude products gave 0.46 g of acetophenonazine by filtration, and then the mother liquid was applied to a column of silicic acid (eluted with chloroform), giving a pure oil, 1.94 g (yield 33.7%), of **5c** (column chromatographed repeatedly two times): n^{20}_D 1.5737; NMR ($CDCl_3$) cis form δ 2.10 (d, H_A), 1.42 (d, H_B, J_{AB} = 6 Hz), 1.64 (s, CH_3); trans form δ 1.78 (d, H_A), 1.72 (d, H_B, J_{AB} = 6 Hz), 1.62 (s, CH_3); MS *m/e* (rel intensity) 191 (32), 156 (100), 129 (99); IR (neat) 2220 cm^{-1} (CN). Anal. Calcd for $C_{11}H_{10}NCl$: C, 68.93; H, 5.26; N, 7.31; Cl, 18.50. Found: C, 69.01; H, 5.09; N, 7.52; Cl, 18.79. Any olefin product was not given.

Methyl 2-Cyano-4-methyl-4-*p*-chlorophenylcrotonate (4g). In the above-mentioned method, from 8.5 g (0.05 mol) of *p*-chloroacetophenone hydrazone (**1**, X = Cl), was prepared **2b**, which was reacted with 50 mL of a dichloromethane solution of **3b** (0.04 mol) at −5–0 °C. The reaction gave 12.7 g of crude products as a mixture of oil and crystals. From the crude products, 1.27 g of *p*-chloroacetophenonazine, mp 148–149 °C (lit.[21] mp 151 °C), was given by filtration, and the mother liquid was applied to a column of silicic acid and eluted with chloroform. The fastest moving band (column chromatographied repeatedly two times) gave 4.22 g (yield 33.5%) of **4g:** n^{20}_D 1.5555; NMR (CCl_4) cis form δ 1.33 (d, CH_3, $J_{A\text{-}CH_3}$ = 7 Hz), 3.93 (s, CH_3); trans form δ 4.09 (m, H_A); 7.49 (d, H_B, J_{AB} = 11 Hz), 1.51 (d, CH_3, $J_{A\text{-}CH_3}$ = 7 Hz), 7.22 (arom), 3.82 (s, CH_3); MS *m/e* (rel intensity) 249 (30), 217 (100); IR (neat) 2220 (CN), 1740 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{12}NO_2Cl$: C, 62.51; H, 4.81; N, 5.61; Cl, 17.03. Found: C, 62.75; H, 4.77; N, 5.56; Cl, 17.42; and the slower moving bands gave 2.86 g of **3b**.

1-Chloro-1-cyano-2-methyl-2-*p*-chlorophenylcyclopropane (5h). In the above-mentioned method, from 8.5 g (0.05 mol) of **1** (X = Cl) was prepared **2b**, which was reacted with 4.4 g (0.05 mol) of **3c** in a dichloromethane solution at −5–0 °C. Crude products (7.39 g) were applied to a column of silicic acid and eluted with chloroform. The fastest moving band gave 4.23 g (yield 39.5%) of **5h** (column chromatographied repeatedly three times): n^{20}_D 1.5526; NMR (CCl_4) cis form δ 2.11 (d, H_A), 1.47 (d, H_B, J_{AB} = 8 Hz), 1.67 (s, CH_3); trans form δ 1.80 (d, H_A), 1.70 (d, H_B, J_{AB} = 8 Hz), δ 1.64 (s, CH_3); MS *m/e* (rel intensity) 225 (7), 190 (100); IR (neat) 2233 cm^{-1} (CN). Anal. Calcd for $C_{11}H_9NCl_2$: C, 58.43; H, 4.01; N, 6.20; Cl, 31.36. Found: C, 58.21; H, 3.84; N, 6.18; Cl, 31.18. The slower moving bands gave 0.21 g of *p*-chloroacetophenonazine.

Isomerization of Methyl 1-Cyano-2-methyl-2-phenylcyclopropanecarboxylate (5b). In a glass tube, for the NMR measurement, 50 mg of **5b** was kept at 180 °C for 3 h on an oil bath. The content became a light brown oil, and it was cooled down to room temperature and dissolved into 0.4 mL of chloroform-*d* for the NMR measurement. From NMR, **5b** changed completely to 4-cyano-4-methoxycarbonyl-2-phenyl-1-butene (**7b**).

Registry No.—1 (X = H), 13466-30-3; 1 (X = CH_3), 64242-53-5; 1 (X = Cl), 40137-41-5; **2a**, 22293-10-3; **2b**, 61185-76-0; **2c**, 64252-52-4; **3a**, 7095-85-0; **3b**, 137-05-3; **3c**, 920-37-7; **3d**, 4519-46-4; **3e**, 96-33-3; **3f**, 51977-58-3; *cis*-**4a**, 64252-51-3; *trans*-**4a**, 38323-11-4; **4b**, 64252-50-2; **4e**, 64252-40-9; *cis*-**4f**, 64252-47-7; *trans*-**4f**, 64252-45-5; *trans*-**4g**, 64252-46-6; **4i**, 64252-44-4; **5b**, 64252-43-3; *cis*-**5c**, 64265-07-2; *trans*-**5c**, 64252-38-6; *cis*-**5d**, 62360-17-2; *trans*-**5d**, 62360-16-1; **5e**, 64252-37-5; *cis*-**5f**, 64252-36-4; *trans*-**5f**, 64312-48-7; *cis*-**5h**, 64252-35-3; *trans*-**5h**, 64252-42-2; **5i**, 64252-41-1; **6b**, 64265-06-1; **6i**, 64252-40-0; **7b**, 64252-39-7; **15**, 35635-90-6; methyl cyanoacetate, 105-34-0; paraformaldehyde, 30525-89-4; *p*-methylacetophenonazine, 21399-33-7; acetophenonazine, 729-43-1; *p*-chloroacetophenonazine, 5326-15-8.

Supplementary Material Available. Full NMR data (Tables II and III) and UV spectral data (Table IV) for compounds **4** and **5** (3 pages). Ordering information is given on any current masthead.

References and Notes

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(5) In the report[2] by J. Hamelin et al., the reaction products were applied to distillation so that the NMR data were shown as a mixture of **5** (X = CH_3 or CH_3O, R = H, Y = CN, Z = COOEt) and **7** (X = CH_3 or CH_3O, R′ = Et). McGreer et al.[4] isolated **5** (X = NO_2, R = H, Y = CN, Z = COOMe) in pure form by means of preparative thin-layer chromatography, but they obtained **5** (X = H or CH_3O, R = H, Y = CN, Z = COOMe) which still remains as a mixture with the cinnamates.
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(7) Simmon-Smith's reaction for 2-cyano-3-phenylcrotonate was not successful because of a stable resonance system of the starting materials [see E. Simmon and D. Smith, *J. Am. Chem. Soc.*, **86**, 1337 (1964)].
(8) Yields are for the NMR pure substances which were purified two or three times (or if circumstances require five or six times) by means of the column of silicic acid. One cause of a poor yield is due to the production of phenonazines.
(9) In the compounds *cis*-**4**, CH_3CHPh groups are cis geometry for substituent Z; and the ratios cis/trans are determined from the peak areas of the NMR signals of the products. For determination of the geometry of the compound **5c**, we referred to the following literatures: C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **32**, 1378 (1960); B. P. Dailey, A. Gawer, and W. C. Neikam, *Discuss. Faraday Soc.*, **34**, 18 (1962); G. Allen, D. J. Blears, and K. H. Welf, *J. Chem. Soc.*, 810 (1965). For determination of the geometry of the compound **5d**, we referred to the literature: L. M. Jackmann and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, New York, N.Y., 1969, p 228.
(10) In the case of the isomeric mixture, the isomeric ratios are shown in Table I.
(11) In the report[2] by J. Hamelin et al., **5** (X = CH_3, R = H, Y = CN, Z = COOEt) was described as an oil, bp 169–171 °C (2 mmHg); we suppose it would be a mixture of **5** and the corresponding **7**.
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(19) Microanalyses were performed by the Microanalytical Laboratory of Kyoto University, infrared spectra were determined by means of a Perkin-Elmer 180 spectrometer, ultraviolet spectra by means of a Perkin Elmer 202 spectrometer, NMR spectra by means of a Hitachi R-22 (90 MHz) spectrometer, and mass spectra (70 eV) by means of a Shimazu GC-MS 7000 spectrometer and Hitachi RMU-6 mass spectrometer.
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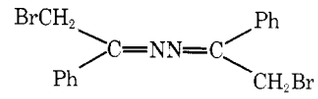
(23) Compound **15** has the structure:



(24) For **5d** Anal. Calcd for $C_{12}H_{13}O_2Br$: C, 53.53; H, 4.83. Found: C, 52.66; H, 4.87; the sample was column chromatographied six times, but these data are no good because **5d** is unstable.
(25) Mixed sample of **4e** and **5e** in the ratio 1:0.9.