Reaction of 2-Substituted Acrylonitriles with Diazoalkanes. Preparation of Cyclopropanone Cyanohydrins[1]

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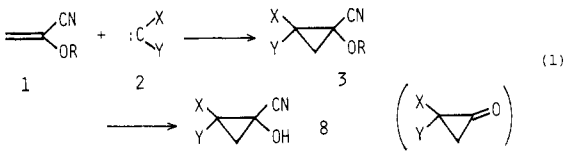
The preparation of cyclopropanone cyanohydrins was investigated. The reaction of 2-acetoxyacrylonitrile (1) with carbenes, e.g., diphenylcarbene, phenylcarbene, fluorenylidene, and methylene, gave the corresponding 1-acetoxy-1-cyanocyclopropanes (3). Similarly, the 1,3-dipolar addition of 1 with diazoalkanes, e.g., diphenyldiazomethane, phenyldiazomethane, diazofluorene, and 1-phenyldiazoethane, gave the corresponding pyrrazoline derivatives, which were decomposed to give 3. These adducts were then hydrolyzed by aqueous HCl to the corresponding cyanohydrins 8. The reactions of 2-((trimethylsilyl)oxy)acrylonitrile (10) with carbenes gave the cyclopropanation products 11. Adducts 11 were easily hydrolyzed in aqueous methanol to produce 8. The 1,3-dipolar addition of 10 with diazoalkanes also yielded cyanohydrins 8 after hydrolysis.

Cyanohydrins and their derivatives have been regarded as the synthetic equivalents of the corresponding carbonyl compounds, and on this basis a number of extensive studies have been carried out.[2] In the same category, our attention has been focused on 2-substituted acrylonitriles (1-cyano-1-alkenyl esters, 1) whose general reactions can



(1)

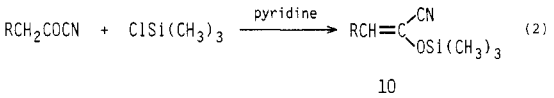
be summarized in terms of the synthetic equivalent of ketene. Not only 2-chloroacrylonitriles[3] but also 2-(acyloxy)acrylonitriles (1) are excellent dienophiles in the Diels–Alder reaction and are utilized for the introduction of a two-carbon oxoethano unit in 6- and 5-membered rings through the reactions not only with cyclic dienes[4] but also with dienones.[5]

The present study has investigated the general utilization of 2-acetoxyacrylonitrile (**1a**) and 2-((trimethylsilyl)oxy)acrylonitrile (**10**) as a two-carbon unit in the construction of cyclopropanone skeletons through the reaction with diazoalkanes. Turro and Hammond reported[6] the first synthesis of cyclopropanone by the reaction of ketene with diazomethane, and thereafter a series of analogous syntheses appeared.[7] Ketene, however, is a too labile compound to be handled at ambient temperatures in laboratories. In contrast, acrylonitriles **1** and **10** are stable synthetic equivalents of ketene and the addition of carbenes to these olefins will produce the corresponding cyclopropanone cyanohydrin derivatives **8** which may act as the precursors of cyclopropanones.

In addition to the carbene addition, diazoalkanes are expected to undergo the 1,3-dipolar cycloaddition reaction with these acrylonitriles (**1**, **10**) and, through the formation of pyrrazoline intermediate, finally give the cyanohydrins **8**.

Results and Discussion

Preparation of 2-Substituted Acrylonitriles. 2-Acetoxyacrylonitrile (**1**) was synthesized according to our reported method.[8] 2-((Trimethylsilyl)oxy)acrylonitrile (**10**) was reported by Hunig[9] to be obtainable from ketene

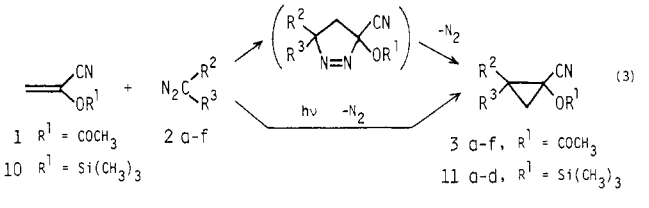


(2)

and cyanotrimethylsilane. To obtain this useful ketene equivalent **10** we newly developed a convenient synthetic method which involves the reaction of acetyl cyanide with chlorotrimethylsilane in the presence of pyridine in ether (see Experimental Section).

Addition of Carbenes to 1. In general, it has been held that the substitution of a withdrawing group reduces the olefin reactivity toward carbenes.[10] Interestingly, it has been reported that the substitution of both donating and withdrawing groups on the same olefin carbon enhances the free radical addition reactions.[11] Our attempt was first based upon the working hypothesis that acrylonitriles **1** and **10** have a capto-dative type substitution[12] and will be reactive toward carbene addition.

Carbenes were generated from diazoalkanes under photolysis conditions and the results of the addition reactions are summarized in Table I. The trans:cis isomer ratio in the adduct obtained from the addition of phenylcarbene was determined to be 1.38 by the ^{1}H NMR structural assignment of isomers as follows. The two isomers showed their acetyl methyl protons at δ 1.74 and 2.09. Since **3a** and **3e** show their methyl protons at δ 1.67



(3)

(1) 2-Substituted Acrylonitriles 9. For part 7, see ref 5.

(2) For a review, see Greene, T. W. "Protective Groups in Organic Synthesis"; Wiley: New York, 1981; pp 141–2.

(3) For example: (a) Evans, D. A.; Scott, W. L.; Truesdale, K. *Tetrahedron Lett.* **1972**, 121. (b) Corey, E. J.; Ravindranathan, T.; Terashima, S. *J. Am. Chem. Soc.* **1971**, *93*, 4326.

(4) For example: (a) Bartlett, P. D.; Tate, B. T. *J. Am. Chem. Soc.* **1956**, *78*, 2473. (b) Birch, A. J.; Hutchinson, E. G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1757. (c) Gompper, R.; Etzbach, K. H. *Angew. Chem.* **1978**, *90*, 630. (d) Oku, A.; Nozaki, Y.; Hasegawa, H.; Harada, T. *J. Org. Chem.*, in press.

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(8) (a) Oku, A.; Arita, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3337. (b) Oku, A.; Nakaoji, S.; Kadono, T.; Imai, H. *Ibid.* **1979**, *52*, 2966.

(9) Hertenstein, V.; Hunig, S. *Angew. Chem.* **1975**, *87*, 195.

(10) Moss, R. A. "Carbenes"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1973; Vol. 1, p 153.

(11) Arita, S. Master's Thesis, Kyoto Institute of Technology, **1979**, 077302.

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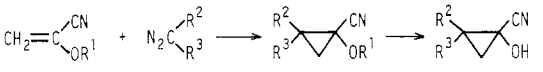
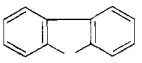
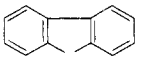
Table I. Reaction of 2-Substituted Acrylonitriles with Diazoalkanes



1, 10 2 3, 11 8

no.	substituent R¹	R²	R³	reaction conditions: method	temp, °C	time, h	product yield, %[a] (cis:trans isomer ratio) 3	11	8[c]
1	$COCH_3$	Ph	Ph	$h\nu$	25	8	70		
2	$COCH_3$	Ph	H	$h\nu$	0	2	48 (1.38)		
3	$COCH_3$			$h\nu$	25	4	24		
4	$COCH_3$	H	H	$h\nu$	25	11	42		
5	$COCH_3$	H	$COOC_2H_5$	$CuSO_4$	80	1	5		
6	$COCH_3$	Ph	Ph	dark	25	24	62		
7	$COCH_3$	Ph	H	dark	0-25	22	42 (1.35)		
8	$COCH_3$			dark	15-35	54	71		
9	$COCH_3$	Ph	CH_3	dark	16	15	81[b]		
10	$Si(CH_3)_3$	Ph	Ph	$h\nu$	15	5		63	67
11	$Si(CH_3)_3$	Ph	H	$h\nu$	15	10		40 (1.55)	49 (1.68)
12	$Si(CH_3)_3$	Ph	Ph	dark	35	56			51
13	$Si(CH_3)_3$	Ph	H	dark	18	24			42 (2.14)
14	$Si(CH_3)_3$	Ph	CH_3	dark	16	15			24[b]

[a] Unless otherwise noted, isolated yields after recrystallization or distillation are listed. [b] Mixture of cis and trans isomers. [c] Isolated yields after silica gel chromatography. The reaction mixture was hydrolyzed in aqueous 90% methanol without isolating the primary product 11.

and 2.07, respectively, the methyl group positioned cis to the phenyl is suffering a shielding effect while the trans one is not. Therefore, the higher chemical shift (δ 1.74) can be assigned to the cis and the lower one (δ 2.09) to the trans isomer of **3b**. 1-Acetoxy-1-cyanocyclopropanes **3**, thus formed, may be formed by either (1) the addition of carbene or (2) the 1,3-dipolar cycloaddition of diazoalkane. However, the second mechanism cannot be the major reaction channel for the reason described in the following section; therefore, the carbene mechanism seems to be the most predominant one.

1,3-Dipolar Addition of Diazoalkanes to 1. The construction of cyclopropane rings by the 1,3-dipolar cycloaddition of diazoalkanes to olefins, followed by the pyrolytic or photolytic elimination of a nitrogen molecule, has been well-known.[13] Since **1** acts as an effective dienophile, it can also be expected to act as a good dipolarophile in [3 + 2] cycloaddition reactions.

The mixing of phenyldiazomethane (**2b**) with **1** in ether at 0 °C under dark conditions caused the disappearance of the red color of **2b** in 4 h and the evolution of 25% of the theoretical amount of nitrogen. The decoloration as well as the nitrogen evolution proceeded at a distinctively slower rate under nonphotolytic conditions than under photolytic conditions where those behaviors were completed within 1 h. Additional stirring increased the amount of nitrogen evolved (Figure 1). After 22 h, 1-acetoxy-1-cyano-2-phenylcyclopropane (**3b**, 42%) was obtained.

Although the pyrrazoline intermediates were not isolated, it is evident that the reaction proceeded via the 1,3-dipolar addition because the nitrogen evolution took place after the disappearance of the diazo color, and the following photolysis of the reaction mixture forced the nitrogen evolution (86% of the theoretical amount) to be completed within 1 h as shown in Figure 1. These observations apparently mean that, under photolysis conditions, the generation of carbenes from diazoalkanes

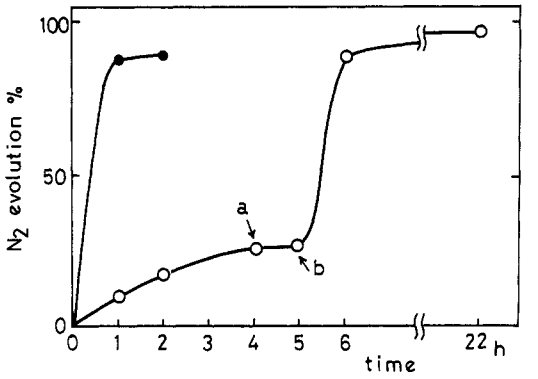
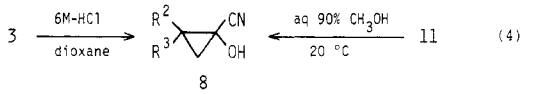


Figure 1. Amount of N_2 gas evolved in the reaction of $PhCHN_2$ (**2b**) with 2-acetoxyacrylonitrile (**1**) at 0 °C: (●) photolysis; (○) dark conditions; (a) red color disappeared; (b) temperature allowed to rise to 20 °C.

proceeds predominantly over the 1,3-addition reactions. Other diazoalkanes behaved similarly and the results are shown in Table I.

Hydrolysis of 1-Acetoxy-1-cyanocyclopropanes (3). Preparation of Cyclopropanone Cyanohydrins (8). The acid (HCl) hydrolysis of **3** yielded the corresponding



8

cyanohydrins **8** efficiently, and in some cases quantitatively. Results are shown in Table II. The independent treatment of each of the separated cis and trans isomers of **3b** with aqueous 6 M HCl in dioxane yielded the corresponding isomer of cyanohydrin **8b** quantitatively, and therefore, the initial stereochemistry of acetate **3b** was retained.

The synthesis of the parent cyclopropanone cyanohydrin was first reported by Tilborg[14] who adopted the reaction

(13) Huisgen, R.; Grashey, R.; Sauer, J. "The Chemistry of Alkanes"; Patai, S., Ed.; Interscience: New York, 1964; p 806.

(14) Tilborg, W. J. M. Van; Schaafsma, S. E.; Steinberg, H.; DeBoer, Th. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 419.

Table II. Acid Hydrolysis of 1-Acetoxy-1-cyanocyclopropanes 3 in Aqueous 6 M HCl-Dioxane

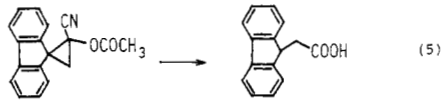
compd	R^2	R^3	reaction conditions: temp, °C	time, h	product yield, %[a]	
3a	Ph	Ph	90	1.5	8a	92
3b	Ph	H[b]	60	1.0	8b	96
3d	Ph	CH_3[b]	80	1.5	8d	88
3e	H	H[c]	63	0.5	8e	62

[a] The value refers to the isolated yield. [b] A mixture of cis and trans isomers. [c] Methanol was used as solvent.

of ketene with diazomethane followed by the treatment with HCN at low temperatures. Our method seems better than his because the reagents are stable and handled easily. In fact, the parent cyanohydrin **8e** was obtained successfully from the hydrolysis of **3e**, and its structure was confirmed by the reacetylation to give **3e**.

Cyclopropanols are known to be easily cleaved by acids.[15] For example, DePuy and co-workers reported[16] that the ring cleavage of 1-methyl-2-phenylcyclopropanol by DCl in dioxane gave methyl 2-deuterio-2-phenethyl ketone, and they explained the result in terms of the edge protonation which resulted in the formation of a carbocation on the hydroxy-substituted carbon atom. In contrast, cyclopropanone cyanohydrins (**8**) shown in Table II are extraordinarily stable under acidic conditions. Consequently, the protonation of the cyclopropane ring or to the hydroxyl group of **8** is evidently disfavored by the cyano group.[17]

As exceptions, 2-acetoxy-2-cyanospiro[cyclopropane-1,9′-fluorene] (**3c**) underwent a facile acid-catalyzed ring-opening to give 2-(9-fluorenyl)acetic acid (**9**) quantitatively,



3c 9 (5)

and ethyl 2-acetoxy-2-cyanocyclopropanecarboxylate (**3f**) gave methyl ethyl succinate. The high reactivity of **3c** can be explained in terms of the edge protonation on the ring that is assisted by the bisected configuration between 3-membered ring and aromatic rings as well as by the strained bicyclic spiro structure.

Addition of Carbenes to 2-((Trimethylsilyl)oxy)-acrylonitrile (10). Since the electron-donating nature of the (trimethylsilyl)oxy group is greater than that of acetoxyl group, it can be expected that the former group will enhance the olefin reactivity toward carbenes. In fact, similar to the reaction between **1** and diazoalkanes, 2-((trimethylsilyl)oxy)acrylonitrile (**10**) reacted with diazoalkanes to give cyclopropanation product **11** in respectable yields (see Table I and eq 3 where R = $Si(CH_3)_3$). Adduct **11b** was obtained as a mixture of cis and trans isomers (cis:trans = 1.55). The stereochemical assignment was made on the basis of ^1H NMR analysis; the trimethylsilyl protons appearing at higher field (δ 0.07) were assigned to the isomer with the trimethylsilyl group oriented cis to the phenyl group, whereas those protons appearing at δ 0.33 were assigned to the trans isomer.

Of interest to us was the quantitative transformation of adducts **11** to the corresponding cyclopropanone cyanohydrins **8** when a methanolic solution of the adduct was chromatographed through a silica gel column.[18] Therefore, we treated the addition reaction mixture directly with aqueous 90% methanolic solution at an ambient temperature with the result of obtaining **8** (see eq 4). Results are shown in Table I. Thus, this procedure starting from **10** is evidently a shorter one than that starting from **1** for the synthesis of cyclopropanone cyanohydrins **8** and hence seems to be synthetically useful.

1,3-Dipolar Addition of Diazoalkanes to 10. With regard to the substituent effect of the (trimethylsilyl)oxy group, the 1,3-dipolar cycloaddition of diazoalkanes to **10** should be examined and compared with the reaction of **1**.

The reaction was carried out in the dark analogously to the procedure described above for **1**, and the product mixture, without isolation, was treated with aqueous methanol to give the corresponding cyanohydrins (**8**). The results are shown in Table I.

The comparison of the reactivity of **1** with that of **10** is interesting. First of all, a significant depression in the product yield was observed for the reaction of **10** with diazofluorene or 1-phenyldiazoethane. Second, the time required for the completion of the 1,3-dipolar addition of phenyldiazoethane is different between **1** and **10** as can be monitored by the decoloration of the diazo compound; i.e., the color disappeared within 1 h in the reaction with **1** but did not decolorize with **10**. Thus, the donating nature of the (trimethylsilyl)oxy group apparently lowered the dipolarophilic nature of the double bond more than that of the acetoxyl group.

Conclusion

In this study, a number of cyclopropanone cyanohydrins and their derivatives were prepared by the reaction of diazoalkanes with 2-acetoxyacrylonitrile (**1**) and 2-((trimethylsilyl)oxy)acrylonitrile (**10**). This method can be registered as a novel synthetic method for cyclopropanone cyanohydrins. First, the cyclopropanation process consists of either carbene addition under photolytic conditions or 1,3-dipolar addition under dark conditions. Second, for the hydrolysis process, we can choose either the acid hydrolysis of adducts **3** or the aqueous methanolic treatment of adducts **11**.

Cyclopropanone cyanohydrins (**8**), thus formed, can be regarded as substituted cyclopropanols. The O–H bond of cyclopropanol has been known to be susceptible to a homolytic bond-cleavage reaction,[15] and further investigations on the air oxidation of cyclopropanone cyanohydrins will be reported separately.

Experimental Section

General. Chemical shifts of nuclear magnetic resonance spectra (^1H NMR) are given in δ units in $CDCl_3$ solutions. Infrared spectra (IR) were taken on a JASCO IRA-1 grating spectrometer, and mass spectra were taken on a Hitachi RMU-6L. Combustion analyses were performed by a Microanalytical Laboratory of Kyoto University. For photolysis, a Ushio UM-452 medium-pressure mercury lamp equipped with a Pyrex filter was used.

Reagents. 2-Acetoxyacrylonitrile (**1**) was prepared according to our reported method.[8] The preparation of 2-((trimethylsilyl)oxy)acrylonitrile (**10**) is described below. Solvents were dried and distilled before use.

2-((Trimethylsilyl)oxy)acrylonitrile (10). To an ice-cooled solution of pyridine (18.1 g, 0.23 mol) in ether (100 mL) was added a mixed ether solution (20 mL) of acetyl cyanide (13.45 g, 0.195 mol) and chlorotrimethylsilane (25.3 g, 0.23 mol) over 30 min. After stirring for 24 h at 15 °C, the mixture was distilled two times to give **10** (56%), bp 57–61 °C (50 torr). The workup with water

(15) Gibson, D. H.; DePuy, C. H. *Chem. Rev.* **1974**, *74*, 605.
(16) DePuy, C. H.; Breitbeil, F. W.; DeBruin, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 3347.
(17) Stork, G., Depezay, J. C.; d'Angelo, J. *Tetrahedron Lett.* **1975**, 389.
(18) Reference 2, p 296.

to remove pyridine hydrochloride is not recommended.

1-Acetoxy-1-cyano-2,2-diphenylcyclopropane (3a). A diethyl ether solution (15 mL) of **1** (3.33 g, 30 mmol) and diphenyldiazomethane (**2a**, 1.90 g, 10 mmol) was irradiated by a medium-pressure mercury lamp for 8 h under ice-water cooling. The amount of nitrogen evolved was 260 mL (10 mmol). After the ether and unreacted **1** were removed in vacuum, ethanol was added to precipitate **3a** (1.9 g, 70%): mp 68–71 °C, crystallized from cyclohexane–petroleum ether; ^{1}H NMR 1.67 (3 H, s), 2.02 (1 H, d, J = 6.8 Hz), 2.22 (1 H, d, J = 6.8 Hz), 7.0–7.9 (10 H, m); IR (KBr pellet) 2250 (m), 1770 (s) cm^{-1}; mass spectrum (relative intensity) 277 (M$^+$, 0.7), 234 (77), 217 (86), 180 (96), 165 (94), 43 (100). Anal. Found: C, 77.80; H, 5.57. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45.

1-Acetoxy-1-cyano-2-phenylcyclopropane (3b). An ethereal solution of **1** (18 mmol) and phenyldiazomethane (**2b**, 6 mmol)[19] was irradiated for 3 h (N_2 evolved 5.8 mmol) similarly to that described above. After workup followed by a column chromatography (silica gel, cyclohexane), a mixture of cis and trans **3b** was obtained (48%). The trans:cis isomer ratio was 1.38, and isomers were separated by a column (silica gel, cyclohexane).

trans-**3b**: mp 45 °C; ^{1}H NMR 1.76 (1 H, dd, J = 7.2, 10.6 Hz), 1.88 (1 H, dd, J = 7.2, 8.4 Hz), 2.09 (3 H, s), 2.70 (1 H, dd, J = 10.6, 8.4 Hz), 7.2–7.5 (5 H, m); IR (liquid) 2250 (m), 1775 (s), 1200 (s) cm^{-1}; mass spectrum 201 (M$^+$, 2), 173 (3), 104 (18), 103 (5), 43 (100). Anal. Found: C, 71.60; H, 5.53; N, 6.97. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96.

cis-**3b**: mp 71–72 °C; ^{1}H NMR 1.74 (3 H, s), 1.80 (1 H, dd, J = 7.2, 9.7 Hz), 1.90 (1 H, dd, J = 7.2, 9.7 Hz), 2.95 (1 H, dd, J = 9.7, 9.7 Hz), 7.2–7.4 (5 H, m); IR (liquid) 2250 (m), 1775 (s), 1200 (s) cm^{-1}; mass spectrum 201 (M$^+$, 2), 173 (4), 104 (17), 103 (6), 43 (100). Anal. Found: C, 71.48; H, 5.66; N, 6.88.

2-Acetoxy-2-cyanospiro[cyclopropane-1,9′-fluorene] (3c). Recrystallization of the photolysis reaction product from **1** and diazofluorene[20] in cyclohexane gave **3c** (24%): mp 178–181 °C; ^{1}H NMR 2.00 (3 H, s), 2.41 (2 H, dd, J = 7.5 Hz), 6.9–7.9 (8 H, m); IR (KBr) 2250 (m), 1770 (s), 1200 (s) cm^{-1}; mass spectrum 275 (M$^+$, 4), 232 (13), 178 (46), 138 (100). Anal. Found: C, 78.35; H, 4.65; N, 4.86. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09.

1-Acetoxy-1-cyanocyclopropane (3e). An ethereal solution (144 mL) of diazomethane (50 mmol) was mixed with **1** (7 g, 153 mmol) and the mixture was irradiated for 10 h. A fractional distillation afforded **3e** (42%): bp 45–60 °C (0.45–0.7 torr); ^{1}H NMR, 1.38 (4 H, m), 2.07 (3 H, s); mass spectrum, 125 (M$^+$), 54, 43, 28. Anal. Found: C, 57.42; H, 5.68; N, 11.10. Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.20.

Ethyl 2-Acetoxy-2-cyanocyclopropanecarboxylate (3f). A mixture of **1** (3.83 g, 35 mmol) and $CuSO_4$ (0.35 g) in cyclohexane (10 mL) was warmed to 80 °C, to which was added a cyclohexane solution (40 mL) of ethyl diazoacetate (5.0 g, 44 mmol) over 1 h. Nitrogen gas was evolved quantitatively. After fractional distillation followed by a VPC separation, **3f** was obtained as a mixture of cis and trans isomers (5%): bp 105–110 °C (0.35 torr). ^{1}H NMR of isomer I: 1.28 (3 H, t, J = 7.0 Hz), 1.83 (1 H, d, J = 8.0 Hz), 1.97 (1 H, d, J = 10.6 Hz), 2.07 (3 H, s), 2.57 (1 H, dd, J = 10.6, 8.0 Hz), 4.17 (2 H, q, J = 7.0 Hz). ^{1}H NMR of isomer II: 1.33 (3 H, t, J = 7.0 Hz), 1.70 (2 H, 2 × dd, J = 9.8, 7.8, 6.4 Hz), 2.12 (3 H, s), 2.53 (1 H, dd, J = 9.8, 7.8 Hz), 4.30 (2 H, q, J = 7.0 Hz); mass spectrum 197 (M$^+$). Isomer ratio I/II was 0.7, but the structural assignment was not performed.

1,3-Dipolar Addition of 2a to 1. A mixture of **1** (3.33 g, 300 mmol) and **2a** (1.86 g, 9.7 mmol) in ether (15 mL) was stirred at 20 °C for 24 h. The amount of nitrogen evolved was 190 mL (8 mmol). After the solvent and **1** were removed, the residue was chromatographed (silica gel, benzene) to yield **3a** (62%).

1,3-Dipolar Addition of 2b to 1. A similar reaction of **1** and **2b** yielded **3b** (42%) as a mixture of cis and trans isomer. The cis:trans isomer ratio was 1.35.

1,3-Dipolar Addition of 2c to 1. The reaction of **1** with **2c**, which was carried out at 20 °C for 46 h and then under solvent reflux for 8 h and which evolved 9.5 mmol of nitrogen gas, yielded **3c** (71%).

1-Acetoxy-1-cyano-2-methyl-2-phenylcyclopropane (3d) by the 1,3-Dipolar Addition of 1-Phenyldiazoethane (2d) to 1. To an ethereal solution (30 mL) of **2d** (13 mmol)[21] was added **1** (4.3 g, 39 mmol) and the mixture was stirred at 20 °C. After 1 h the solution turned colorless (the amount of N_2 evolved was 6.3 mmol after 1 h, 13 mmol after 15 h). After the solvent was removed, the residue was chromatographed to give a mixture of cis and trans isomers of **3d** in 81%. This cis/trans isomer ratio was 1.6. Anal. Found: C, 72.52; H, 5.94; N, 6.66. Calcd for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.09; N, 6.51.

After repeated chromatography, the cis isomer was separated: mp 82–83 °C; ^{1}H NMR 1.42 (3 H, s), 1.45 (1 H, d, J = 7.2 Hz), 1.93 (1 H, d, J = 7.2 Hz), 2.18 (3 H, s), 7.2–7.6 (5 H, m); IR (KBr) 2245 (m), 1770 (s), 1200 (s) cm^{-1}; mass spectrum 215 (M$^+$, 0.3) 172 (18), 155 (31), 118 (98), 117 (78), 43 (100).

trans-**3d**: ^{1}H NMR 1.61 (1 H, d, J = 7.2 Hz), 1.73 (1 H, d, J = 7.2 Hz), 1.64 (3 H, s), 1.79 (3 H, s), 7.2–7.6 (5 H, m); VPC–mass spectrum 215 (M$^+$, 0.6), 172 (17), 155 (31), 118 (96), 117 (76), 43 (100).

1-Cyano-2,2-diphenyl-1-((trimethylsilyl)oxy)cyclopropane (11a). An ethereal solution (15 mL) of **10** (4.24 g, 30 mmol) and **2a** (1.92 g, 10 mmol) was irradiated by means of a medium-pressure mercury lamp for 5 h under ice cooling. A 8.4 mmol of N_2 was evolved. Distillation of the reaction mixture gave **11a** in 63% yield: bp 150 °C (0.015 torr); half-solid; ^{1}H NMR 0.09 (9 H, s), 1.93 (1 H, d, J = 6.6 Hz), 2.09 (1 H, d, J = 6.6 Hz), 7.0–7.4 (10 H, m); IR (KBr) 2238 (m), 1242 (s), 1240 (s) cm^{-1}.

11a was also obtained by the 1,3-dipolar addition of **2a** to **10** but the product mixture was hydrolyzed without purification to give cyanohydrin **8a** (vide infra).

1-Cyano-2-phenyl-1-((trimethylsilyl)oxy)cyclopropane (11b). A mixture of **10** (30 mmol) and **2b** (6.6 mmol) in ether (20 mL) was irradiated for 10 h (N_2 evolved was 6.0 mmol). After distillation a mixture of cis and trans isomers of **11b** was obtained in 40% yield: bp 100 °C (0.4 torr); cis/trans isomer ratio was 1.55; viscous oil. Isomers were not separated but their ^{1}H NMR were assigned as follows. Cis isomer: 0.07 (3 H, s), 1.4–2.0 (2 H, m), 2.5–2.8 (1 H, m), 7.2–7.7 (5 H, m). Trans isomer: 0.33 (3 H, s), 1.4–2.0 (2 H, m), 2.5–2.8 (1 H, m), 7.2–7.7 (5 H, m). IR (mixture, liquid) 2240 (m), 1242 (s), 1240 (s) cm^{-1}. Mass spectrum of cis isomer 231 (M$^+$, 100), 216 (100), 189 (22), 104 (67), 45 (79); trans isomer 231 (100), 216 (100), 189 (29), 104 (58), 45 (82).

11b was also obtained by the 1,3-dipolar addition of **2b** to **10**, and the cis/trans isomer ratio was 2.14 determined after the hydrolysis to cyanohydrin **8b** (vide infra).

2,2-Diphenylcyclopropanone Cyanohydrin (8a). Water (8 mL) and 35% HCl (8 mL) were added to a dioxane solution (20 mL) of **3a** and the mixture was heated at 90 °C for 1.5 h. After the solvent was removed, the residue was dissolved in ether, washed with water, dried ($MgSO_4$), and chromatographed (benzene/AcOEt = 9/1) to give **8a** (92%): mp 99–104 °C; ^{1}H NMR 1.96 (1 H, d, J = 6.6 Hz), 2.10 (1 H, d, J = 6.6 Hz), 3.16 (1 H, br s), 7.1–7.2 (10 H, m); IR (KBr) 3340 (s), 2260 (m), 1220 (s) cm^{-1}; mass spectrum 235 (M$^+$, 4), 196 (22), 105 (100), 94 (98), 77 (82). Anal. Found: C, 81.64; H, 5.60; N, 5.78. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95.

8a by the Hydrolysis of 11a. The product mixture obtained from the reaction of **10** with **2a** (vide supra) was dissolved in aqueous 90% methanol and stirred at an ambient temperature for 24 h. After column chromatography (benzene/AcOEt = 8/1) **8a** was isolated in 67% (based upon **2a**).

2-Phenylcyclopropanone Cyanohydrin (8b). A hydrolysis of **3b** (mixture of isomers) similar to that described above for **3a**, but at 60 °C for 1 h, yielded a mixture of cis and trans isomers of **8b** (96%). From the pure cis isomer of **3b**, cis **8b** was obtained in 94% yield: mp 98–104 °C (cyclohexane); ^{1}H NMR 1.64 (1 H, d, J = 10.0 Hz), 1.66 (1 H, d, J = 8.2 Hz), 2.64 (1 H, dd, J = 8.2, 10.0 Hz), 3.70 (1 H, br s), 7.1–7.5 (5 H, m); IR (liquid) 3400 (s), 2220 (m), 1220 (s) cm^{-1}; mass spectrum 159 (M$^+$, 50), 130 (82), 91 (100), 78 (53), 77 (53), 51 (52). From the pure trans isomer of **3b**, trans **8b** was obtained in 90% yield: viscous oil; ^{1}H NMR 1.64 (1 H, dd, J = 6.4, 9.6 Hz), 1.75 (1 H, dd, J = 6.4, 9.6 Hz), 2.72 (1 H, t, J = 9.6 Hz), 7.2–7.5 (5 H, m); IR (liquid) 3380 (s),

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2220 (m), 1220 (s) cm^{-1}; mass spectrum 159 (M^+, 44), 130 (74), 91 (100), 78 (47), 77 (48), 51 (47).

8b by the Hydrolysis of 11b. A hydrolysis of **11b**, which was obtained from the reaction of **10** with phenylcarbene, in aqueous methanol as described above for **11a** gave a mixture of cis and trans isomers of **8b** in 49% (based upon **2b**) yield. The cis/trans isomer ratio was 1.68, slightly larger than the ratio 1.55 before hydrolysis.

2-Methyl-2-phenylcyclopropanone Cyanohydrin (8d). Acid hydrolysis of **3d** (mixture of isomers, 3.4 mmol) in dioxane (15 mL) with 18% HCl (10 mL) at 80 °C for 1.5 h gave **8d** (88%, isomeric mixture). After repeated chromatography two isomers were separated. *trans*-**8d**: viscous liquid; ^1H NMR 1.43 (1 H, d, J = 6.6 Hz), 1.65 (1 H, d, J = 6.6 Hz), 1.59 (3 H, s), 3.24 (1 H, br s), 7.2–7.5 (5 H, m); IR (liquid) 3380 (s), 2240 (m), 1220 (s) cm^{-1}. *cis*-**8d**: viscous liquid; ^1H NMR 1.25 (1 H, d, J = 6.2 Hz), 1.50 (3 H, s), 1.78 (1 H, d, J = 6.2 Hz), 4.26 (1 H, br s), 7.2–7.6 (5 H, m); IR (liquid) 3380 (s), 2245 (m), 1225 (s) cm^{-1}.

8d by the Hydrolysis of 1-Cyano-2-methyl-2-phenyl-1-((trimethylsilyl)oxy)cyclopropane (11d). An ethereal solution (20 mL) of **10** (30 mmol) and **2d** (13 mmol) was stirred at an ambient temperature for 15 h (11 mmol of N_2 was evolved). The product mixture, without purification, was treated with aqueous 90% methanol and chromatographed to give a mixture of cis and trans **8d** in 24% yield.

2-(9-Fluorenyl)acetic Acid (9). Acid hydrolysis of **3c** (2.4 mmol) in dioxane (15 mL) with 18% HCl (12 mL) at 80 °C for 1.5 h gave **9** (99%): mp 131 °C; ^1H NMR 2.84 (2 H, d, J = 7.2 Hz), 6.59 (1 H, t, J = 7.2 Hz), 7.2–7.9 (8 H, m), 11.37 (1 H, s); IR (KBr) 3000 (m), 1700 (s), 750 (m) cm^{-1}.

9 from the Reaction of 10 with 2c. The photolysis of an ethereal mixture of **10** (30 mmol) and **2c** (9.6 mmol) for 10 h evolved N_2 gas (8.3 mmol), and the total product mixture was treated with 90% methanol to give **9** (10%) and fluorenone azine (31%). From the 1,3-dipolar addition reaction, **9** was also obtained in 8% yield.

Cyclopropanone Cyanohydrin (8e). A solution of **3e** (1.6 mmol) and 35% HCl (0.3 mL) in methanol (4 mL) was warmed under solvent reflux for 0.5 h. After solvent was removed at 25 °C (40 torr), the residue was extracted with 1 mL of ether ten times and dried ($MgSO_4$) for 1 h. The removal of ether yielded the parent cyanohydrin **8e** in 62% yield: ^1H NMR 1.23 (s). The hydrolysis product (1 mmol) and acetic anhydride (1 mmol) were mixed in ether (2 mL) to which was added pyridine (3 mg) at 15 °C. After 2 h **8e** disappeared and a bulb-to-bulb distillation yielded **3e** (63%).

Methanolysis of 3f. A mixture of **3f** (0.51 mmol), 35% HCl (0.1 mL) and methanol (3 mL) was warmed at 60 °C for 0.75 h. The VPC analysis of the product mixture, using authentic samples, proved that ethyl methyl succinate (65%) and dimethyl succinate (15%) were formed.

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Registry No. **1**, 3061-65-2; **2a**, 883-40-9; **2b**, 766-91-6; **2c**, 832-80-4; **2d**, 22293-10-3; **2e**, 334-88-3; **2f**, 623-73-4; **3a**, 87656-16-4; *cis*-**3b**, 87656-17-5; *trans*-**3b**, 87656-18-6; **3c**, 87656-19-7; *cis*-**3d**, 87656-20-0; *trans*-**3d**, 87656-21-1; **3e**, 87656-22-2; *cis*-**3f**, 87681-15-0; *trans*-**3f**, 87681-16-1; **8a**, 87656-23-3; *cis*-**8b**, 87656-24-4; *trans*-**8b**, 87656-25-5; *cis*-**8d**, 87656-26-6; *trans*-**8d**, 87656-27-7; **8e**, 14743-56-7; **9**, 6284-80-6; **10**, 54276-53-8; **11a**, 87656-28-8; *cis*-**11b**, 87656-29-9; *trans*-**11b**, 87656-30-2; H_3CCOCN, 631-57-2; $ClSi(CH_3)_3$, 75-77-4; fluorenone azine, 2071-44-5; ethyl methyl succinate, 627-73-6; dimethyl succinate, 106-65-0.

(4 + 2) Cycloaddition of Ketenes and β-Methoxy α,β-Unsaturated Ketones: 2-Pyranones

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The cycloaddition of diphenyl- and various chloroketenes to β-methoxy α,β-unsaturated ketones afforded (4 + 2) cycloaddition products. The cycloadducts resulting from the choroketenes were converted to 2-pyranones on treatment with zinc in moist acetic acid. The cycloaddition products from chloroketenes and β-(methoxymethylene)-α-tetralone were readily converted to substituted benzocoumarins.

Extensive studies in ketene chemistry indicate the reaction bias of ketenes with 4-π-electron compounds toward (2 + 2) cycloaddition reactions of these heterocumulenes to yield four-membered-ring compounds.[1] While the primary synthetic usefulness of the reactions of ketenes remains the formation of four-membered-ring compounds, there are an increasing number of reports in the literature that deal with the (4 + 2) cycloaddition reactions of ketenes.[2-9] This report decribes an investigation of the reaction of ketenes with β-methoxy α,β-unsaturated ketones to give (4 + 2) cycloaddition products which undergo conversion to 2-pyranones on treatment with zinc in moist acetic acid. We have further described the application of the synthetic methodology described here to the synthesis of 3- and 4-substituted benzocoumarins.

Dichloro- and phenylchloroketenes were generated in situ in the presence of commercially available 4-methoxy-3-buten-2-one (**1a**) by the dehydrochlorination of the corresponding chloro acid chlorides by the use of tri-

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