structure was supported by ir and nmr spectra. Without purification, **5b** was hydrolyzed with dilute sulfuric acid at room temperature. From the ir and nmr spectra, the product was found to be 3-hexen-2-one (**6b**), which had identical spectral data and retention time on vpc with an authentic sample. In addition, the semicarbazone of **6b** showed no melting point depression on admixture with an authentic sample.

Since the Sr^N values at C-4 of N-acetylated (**7b**] and *N*-carbomethoxylated derivatives (**9b**) were also calculated to be higher than that of **3b**, the reduction of **7b** and **9b** with sodium borohydride was investigated. After treatment with dilute sulfuric acid, the products from both **7b** and **9b** were identical with authentic **6b.** Similarly, 3-hepten-2-one (**6c**) and 3,11-tetradecadiene-2,13-dione (**6d**) were obtained from 3-methyl-5-*n*-propylisoxazole (**2c**) and 1,6-bis(3-methyl-5-isoxazolyl)hexane (**2d**), respectively.

In conclusion, this report, in conjunction with Büchi's report, provides a selective method for (1) isomerization of an α,β-unsaturated ketone, (2) protection and regeneration of an α,β-unsaturated ketone, or (3) conversion of a 1,3-diketone regiospecifically into an α,β-unsaturated ketone.

Experimental Section

***N*-Acylation of 3.** To a solution of **3**[1,6] (0.005 mol) in anhydrous pyridine (10 ml) was added 1 g of acyl chloride with stirring in an ice bath. Stirring was continued for another 3 hr at room temperature. The mixture was poured onto ice and extracted with methylene chloride. The extract was washed with dilute hydrochloric acid and water, dried with magnesium sulfate, and concentrated under reduced pressure. The residue was purified by recrystallization from an *n*-hexane–benzene mixture.

2-Benzamido-2-hexen-4-one (4b) was obtained from **3b** and benzoyl chloride: yield 96%; mp 33.0–34.0°; ir (KBr) 3440, 1695, 1650, 1600, and 700 cm^{-1}; nmr ($CDCl_3$) δ 5.43 (s, 1 H), 7.5 (m, 3 H), 8.02 (m, 2 H), and 13.38 (broad s, 1 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 72.11; H, 6.97; N, 6.26.

2-Benzamido-2-hepten-4-one (4c) was obtained from **3c** and benzoyl chloride: yield 90%; mp 44.0–45.0°; ir (KBr) 3410, 1690, 1640, 1595, 850, and 695 cm^{-1}; nmr ($CDCl_3$) δ 5.32 (s, 1 H), 7.5 (m, 3 H), 8.0 (m, 2 H), and 13.45 (broad s, 1 H).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.47; H, 7.34; N, 6.17.

2,13-Bis(benzamido)tetradeca-2,12-diene-4,11-dione (4d) was obtained from **3d** and benzoyl chloride: yield 90%; mp 159.0–160.0°; ir (KBr) 3450, 1690, 1600, and 705 cm^{-1}; nmr ($CDCl_3$) δ 5.30 (s, 2 H), 7.5 (m, 6 H), 8.0 (m, 4 H), and 13.4 (broad s, 2 H).

Anal. Calcd for $C_{28}H_{32}N_2O_4$: C, 73.02; H, 7.00; N, 6.08. Found: C, 73.27; H, 7.04; N, 6.20.

2-Acetamido-2-hexen-4-one (7b) was obtained from **3b** and acetyl chloride: yield 80%; bp 210–212° (760 mm); ir (liquid film) 3425, 1720, 1645, 1600, and 890 cm^{-1}; nmr ($CDCl_3$) δ 2.13 (s, 3 H), 5.3 (s, 1 H), and 12.3 (broad s, 1 H).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.80; H, 8.44; N, 8.92.

2-Carbomethoxyamino-2-hexen-4-one (9b) was obtained from **3b** and methyl chloroformate: yield 50%; mp 63.5–65.0°; ir (KBr) 3475, 1760, 1655, 1600, and 870 cm^{-1}; nmr ($CDCl_3$) δ 3.71 (s, 3 H), 5.32 (s, 1 H), and 11.95 (broad s, 1 H).

Anal. Calcd for $C_8H_{13}NO_3$: C, 56.12; H, 7.65; N, 8.18. Found: C, 55.96; H, 7.64; N, 8.08.

Sodium Borohydride Reduction of 4, 7, and 9. A solution of **4**, **7**, or **9** (4 mmol) in methanol (20 ml) was reduced with an excess sodium borohydride (5 mmol). After 10 hr, the mixture was poured onto water and extracted with methylene chloride. The extract was dried and evaporated. It was difficult to purify the residue by chromatography or distillation, because of its instability.

2-Benzamido-2-hexen-4-ol (5b) was obtained from **4b:** yield 80%; ir (liquid film) 3320, 1655, 1515, 1025, and 700 cm^{-1}; nmr ($CDCl_3$) δ 1.55 (m, 2 H), 2.95 (broad s, 1 H), 4.35 (m, 1 H), 4.88 (d, 1 H), and 9.05 (broad s, 1 H).

2-Benzamido-2-hepten-4-ol (5c) was obtained from **4c:** yield 67%; ir (liquid film) 3325, 1655, 1515, 1025, and 700 cm^{-1}.

2,13-Bis(benzamido)tetradeca-2,12-diene-4,11-diol (5d) was obtained from **4d:** yield 96%; ir (liquid film) 3350, 1730, 1650, 1520, 1030, and 700 cm^{-1}; nmr ($CDCl_3$) δ 1.35 (m, 12 H), 4.3 (m, 2 H), 4.8 (d, 2 H), and 9.57 (s, 2 H).

2-Acetamido-2-hexen-4-ol (8b) was obtained from **7b:** yield 30%; ir (liquid film) 3300, 1665, 1620, 1525, and 880 cm^{-1}; nmr ($CDCl_3$) δ 0.9–1.6 (m, 5 H), 2.05 (s, 6 H), 3.43 (s, 1 H), 4.12 (q, 1 H), 4.9 (d, 1 H), and 8.03 (broad s, 1 H).

2-Carbomethoxyamino-2-hexen-4-ol (10b) was obtained from **9b:** yield 95%; ir (liquid film) 3325, 1745, 1720, 1680, and 1180 cm^{-1}; nmr ($CDCl_3$) δ 1.5 (m, 2 H), 2.07 (s, 1 H), 2.75 (broad s, 1 H), 3.67 (s, 1 H), and 8.03 (broad s, 1 H).

Hydrolysis of 5, 8, and 10. To a solution of crude **5**, **8**, or **10** in dichloromethane was added dilute sulfuric acid and the mixture was stirred for 10 hr at room temperature. This suspension was washed with water and extracted with methylene chloride. The extract was dried over magnesium sulfate and evaporated. The resulting products were purified by fractional distillation and/or silica gel column chromatography.

3-Hexen-2-one (6b) was purified by fractional distillation: yield 60% (from **5b**), 67% (from **8b**), 76% (from **10b**); bp 130–140°. The semicarbazone of **6b** was recrystallized from aqueous ethanol: mp 196° (lit.[7] 198°).

3-Hepten-2-one (6c) was purified by fractional distillation: yield 30% (from **5c**); bp 163–165°. The 2,4-dinitrophenylhydrazone of **6c** was recrystallized from aqueous ethanol: mp 122–123° (lit.[8] 125–126°).

3,11-Tetradecadiene-2,13-dione (6d) was purified by silica gel column chromatography eluting with benzene–ethyl acetate mixture: yield 42%; ir (liquid film) 1660, and 1620 cm^{-1}; nmr ($CDCl_3$) δ 1.4 (m, 8 H), 2.2 (m, 4 H), 2.25 (s, 6 H), 6.02 (d, 2 H), and 6.82 (d–t, 2 H). The bis-2,4-dinitrophenylhydrazone of **6d** was recrystallized from aqueous ethanol: mp 130° dec; ir (KBr) 3400, 1620, 1590, and 1325 cm^{-1}.

Anal. Calcd for $C_{26}H_{30}N_8O_8$: C, 53.60; H, 5.19; N, 19.24. Found: C, 53.36; H, 5.40; N, 19.54.

Registry No.—3b, 33663-57-9; **3c,** 33663-59-1; **3d,** 41027-52-5; **4b,** 53535-13-0; **4c,** 53535-14-1; **4d,** 53535-15-2; **5b,** 53535-16-3; **5c,** 53535-17-4; **5d,** 53535-18-5; **6b,** 763-93-9; **6c,** 1119-44-4; **6d,** 53535-19-6; **6d** bis (2,4-DNPH), 53535-20-9; **7b,** 53535-21-0; **8b,** 53535-22-1; **9b,** 53535-23-2; **10b,** 53535-24-3; benzoyl chloride, 98-88-4; acetyl chloride, 75-36-5; methyl chloroformate, 79-22-1.

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Pyrolyses of Cyclopropylketene Dimer and Ethyl Cyclopropaneacetate

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Photolysis of certain cyclopropyl ketones generates cyclopropylketenes[1] which have been cited as thermal precursors of the 2-cyclopentenones also formed.[1a–d,2]

We have investigated the rearrangement of cyclopropylketene (**1**) generated *in situ* by pyrolysis of its dimer (**2**) and have found, in addition to cyclopentenone (**3**), allene **4** and spirodiene **5**. Results are summarized in Table I.

There is ample evidence that ketene dimers crack thermally to the parent ketenes[4] or to allenes[5] (and carbon dioxide). Thus, we suggest that alternative cracking patterns a and b, as shown, account for the products observed. That the allene was the precursor of the spirodiene was

Table I
Pyrolysis of Dimer 2[a]

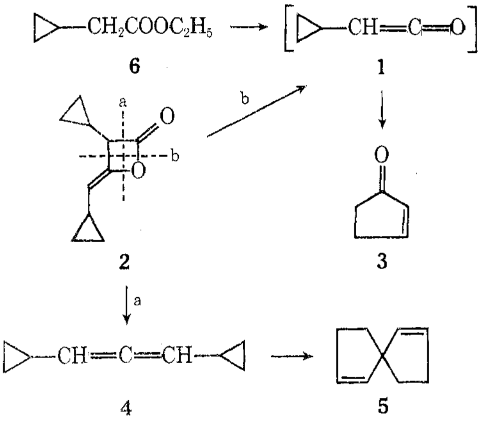
Run	T,[b] °C	Packing	% yield[c] 3	4	5
1	560	Glass wool	31	0.2	14
2	540	Glass wool	17	0	9
3	555	6-mm helices	15	20	3

[a] The pyrolysis procedure has been described previously.[3] Dimer (1-3 g) was introduced as vapor (0.2-1.8 mm) at 0.8-2.1 g/hr. [b] Temperature at the center of the hot tube, ±10°. [c] Yields are based upon glpc analysis. A 5 or 10 ft × 0.25 in. column packed with Chromosorb W coated with 20% by weight of Apiezon L was used, with ethyl benzoate or 4-methylcyclohexanone as internal standard. Identification of 3 was done by comparing glpc retention times and ir spectra with those of an authentic sample. For identification of 4 and 5, see Experimental Section.

Table II
Pyrolysis of Ethyl Cyclopropaneacetate 6[a]

Run	T,[b] °C	% 3 produced[c]	% 6 recovered
4	585	39	42
5	610	34	30
6	625	27	20

[a] The pyrolysis procedure has been described previously.[3] Ester entered the glass wool packed hot tube as vapor (0.25-2.0 mm) at *ca.* 1 g/hr. [b] Temperature at the center of the hot tube, ±10°. [c] Yields are based upon glpc analysis as described above. Yields of 3 produced are based on unrecovered 6.



suggested by the increased yield of allene at the expense of spirodiene (run 3 *vs.* run 2) with a smaller packing surface at the same rate of distillation.

Pyrolysis of ethyl cyclopropaneacetate (6)[6] also gave cyclopentenone. Results are summarized in Table II.

Acyl oxygen cleavage of esters affording ketenes is less well known than the more usual alkyl oxygen cleavage giving alkenes.[7] Phenyl esters, in particular, are prone to acyl oxygen cleavage, as are certain other esters.[8] There is some evidence that β-keto esters afford acylketenes pyrolytically in the presence of a glass surface.[3,9] Consequently we suggest that cyclopropylketene (1) may be the primary product of pyrolysis of ester 6 (although a vinylcyclopropane rearrangement of the enol form is certainly not excluded).

Experimental Section

Melting points were determined on a Mel-Temp apparatus (uncorrected). Microanalyses were performed by Spang Analytical Laboratory, Ann Arbor, Mich. Glpc results were obtained with a Varian-Aerograph Model A90-P3 thermal conductivity machine. Infrared spectra were taken on a Perkin-Elmer Model 237B or Beckman IR-20 grating spectrophotometer; ultraviolet spectra, with a Cary 14; nmr spectra, with a Varian A-60A; mass spectra, with a Varian/MAT CH-7 (at 70 eV). Pyrolyses were performed as described previously[3a] with a Hevi-Duty Electric Co. Type 77-T (600 W, "Multi-Unit") oven using a 37 × 2.5 cm Vycor tube packed as described above.

Dimer 2 (3-Cyclopropyl-4-cyclopropylmethylidene-2-oxetanone). The dimer 2 was prepared by Sauer's procedure[10] from *the corresponding acid chloride*[11] *and triethylamine in* 41% *yield:* bp 79–80° (0.20 mm); ir (CCl_4) 3.23, 5.32, 5.80 μ; nmr (CCl_4) δ 0.12–1.92 (m, 10, cyclopropyl CH), 3.88 (d, d, J_1 = 1.3 Hz, J_2 = 6.2 Hz, CHC*H*C=CH), 4.35 (d, d, J_1 = 1.3 Hz, J_2 = 9.1 Hz, CHC*H*=CCH); uv (EtOH) λ_{max} 210 nm (ε 2400); mass spectrum order of intensity *m/e* 82 > 54 > 39 > 164 = 41, parent ion *m/e* 164.[12] Compound 2 was converted to *N*-*p*-bromophenyl-2,4-dicyclopropyl-3-oxobutyramide, by treatment with *p*-bromoaniline, in 78% yield: mp 130–131° (ethanol–water); ir (CCl_4) 3.05, 5.95, 6.60 μ; nmr ($CDCl_3$) δ 0.35–1.67 (m, 10, cyclopropyl CH), 2.60 (d, 2, J = 6.5 Hz, $CHCH_2$), 2.83 (d, 1, J = 10 Hz, $CHCH(CO\text{–})_2$), 7.45 (s, 4, Ar H).[12]

No cyclopentenone was observed (glpc) in the reaction mixture during preparation of the dimer.

Allene 4 (1,3-Dicyclopropyl-1,2-propadiene). The allene was trapped from the glpc effluent of the dimer pyrolysate: ir (CCl_4) 3.23, 5.11 μ; nmr (CCl_4) δ 0.10–1.43 (m, 10, cyclopropyl CH), 5.00 (d, d, 2, J_1 = 3.2 Hz, J_2 = 5.0 Hz, CHC*H*=C); uv (EtOH) λ_{max} 213 nm (ε 1490); mass spectrum order of intensity *m/e* 91 > 39 > 77 > 105 > 65 = 51 = 41 > 120, parent ion *m/e* 120.[12]

Spirodiene 5 (Spiro[4.4]nonadiene-1,6). The spirodiene[13,14] was also trapped from the glpc effluent of the dimer pyrolysate: ir (CCl_4) 3.28, 6.22 μ; nmr (CCl_4) δ 1.63–1.97 (m, 4, $CH_2CH_2CH{=}C$), 2.17–2.53 (m, 4, $CH_2CH_2CH{=}C$), 5.83–5.72 (m, 4, $CH_2CH{=}CH$–); mass spectrum order of intensity *m/e* 105 > 120 > 91 > 90 > 79 > 77 > 78 > 65 > 64, parent ion *m/e* 120, consistent with the literature values.[14a,12]

Pyrolysis of the dimer also gave 25–30% of nonvolatile material. Hydrolysis of this with hot 10% aqueous sodium hydroxide afforded small amounts of 2-pentenoic acid, cyclopropaneacetic acid, and 1,3-dicyclopropylacetone,[15] totaling about 60% of the nonvolatile fraction and presumably derived from dimer or oligomers of cyclopropylketene.

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Registry No.—**2,** 53432-85-2; **3,** 930-30-3; **4,** 53432-86-3; **5,** 6569-94-4; **6,** 53432-87-4; *N*-*p*-bromophenyl-2,4-dicyclopropyl-3-oxobutyramide, 53432-88-5; *p*-bromoaniline, 106-40-1.

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