(5) With 1,3- or 1,4-dihalides or sulfonates the intermediates are the corresponding cyclic five- or six-membered ring disulfides, respectively. In fact, the method provides a convenient synthesis of such compounds; see, R. M. Dodson and V. C. Nelson, *J. Org. Chem.*, **33**, 3966 (1968). For other cases where cyclization cannot readily occur, oligodisulfides or oligotrisulfides presumably result.
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A New Conversion of 3,5-Disubstituted Isoxazoles to α,β-Unsaturated Ketones

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It is well known that 3,5-disubstituted isoxazoles are very stable compounds to acids, bases, hydrides, and oxidative reagents. Previously, we reported that 3,5-dimethylisoxazole, easily obtainable from 2,4-pentanedione and hydroxylamine, reacted regiospecifically at the methyl group in the 5 position with alkyl halides in the presence of an alkali amide in liquid ammonia.[1] Other electrophiles such as aldehydes, ketones, esters,[2] nitriles, and ketimines[3] react to give the corresponding alcohols, ketones, and amines. Recently, Büchi and his coworkers reported[4] that isoxazoles, prepared from α,β-unsaturated ketones, could be converted into α,β-unsaturated ketones (**11**) by reduction with sodium and *tert*-butyl alcohol in liquid ammonia.

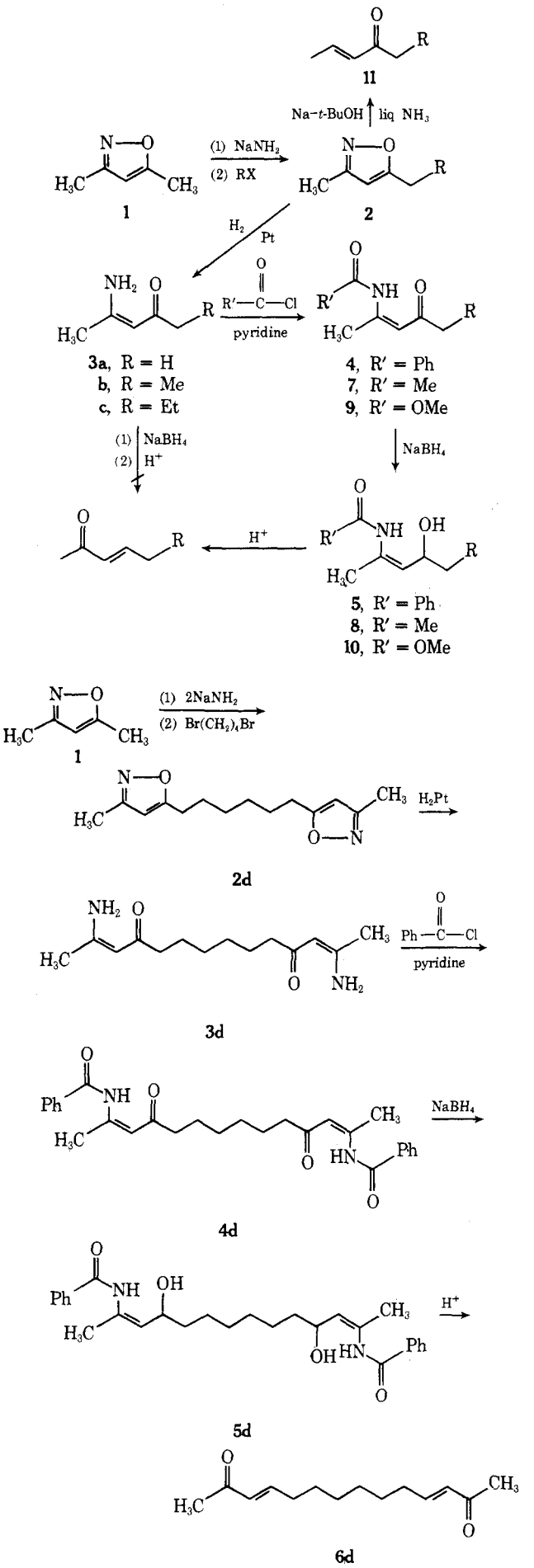
In this paper, we describe how isoxazoles can be converted regiospecifically into α,β-unsaturated ketones (**6**), which are isomeric with **11**. As a typical example, 5-ethyl-3-methylisoxazole (**2b**), prepared from 3,5-dimethylisoxazole (**1**) and methyl iodide, was hydrogenated over a platinum catalyst to afford 2-amino-2-hexen-4-one (**3b**). The reduction of **3b** with sodium borohydride was attempted, but the expected reaction did not occur and the starting material was recovered. At this point the superdelocalizability for nucleophilic reagents (Sr^N) at C-4 of **3b** was calculated by the HMO method, to give the result shown in Table I.[5] The

Table I

Compd	Sr^N Values at C-4	Sr^N Values at C-2
3	1.9388	1.6494
4	2.0432	1.7400
7	2.0422	1.7423
9	2.0214	1.7259

corresponding Sr^N value of the *N*-benzoyl derivative (**4b**) was also calculated and shown to be higher. Thus reduction of the carbonyl group of **4b** with sodium borohydride is expected to be easier and, indeed, on treatment with sodium borohydride, **4b** gave 2-benzamide-2-hexen-4-ol (**5b**). This

Scheme I



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