zyl protons in the integration of the nmr spectrum indicated a composition of 0.49 g of **14**, 0.38 g of **16**, and 0.09 g of **15**. The overall yields therefore are 6.4 g (0.032 mol, 32%) of **14**, 6.0 g (0.030 mol, 30%) of **16**, and 1.4 g (0.0070 mol, 7%) of **15**, all based on **17**.

In a separate experiment, 0.30 g (0.0015 mol) of the initial distillate, 0.60 g of sodium acetate, 0.40 g (0.0036 mol) of semicarbazide HCl, 4 ml of water, and 7 ml of ethanol were combined. After standing for 7 days, 0.11 g (0.00043 mol, 28%) of 3-methyl-2-phenylcycloheptanone (**14**) was isolated from the mixture as its semicarbazone: mp 210.5–213°; nmr ($CDCl_3$) τ 6.74 (d, benzyl hydrogen). This represents a 20% yield based on **17**. Two recrystallizations from 42% aqueous ethanol yielded a solid, mp 218.5–219.5°.

Anal. Calcd for $C_{15}H_{21}N_3O$: C, 69.47; H, 8.16; N, 16.20. Found: C, 69.46; H, 7.96; N, 16.08.

Lastly, two 0.1-g aliquots of the initial mixture were combined with a fivefold excess of CF_3CO_2H and CF_3CO_2D, respectively. The samples were heated at 75° for 24 hr and cooled, and their nmr spectra were obtained: nmr (CF_3CO_2H) revealed that the only change in the spectrum[24] of this sample and the spectrum of the untreated initial mixture was a marked decrease in the intensity of the benzyl proton in **15**, τ 6.33, and a marked increase in the intensity of the benzyl proton in **16**, τ 6.55; nmr (CF_3CO_2D) revealed that the only change in the nmr spectrum of this sample and the spectrum of the untreated initial mixture was that signals attributed to the benzyl protons were almost absent. In a second and related experiment 1 g of the initial mixture was treated with 10 g of CF_3CO_2H for 24 hr at 75° and the product was isolated as described for **3**. The results were the same as above:[24] nmr τ 6.10 (br m, benzyl hydrogen of **15**, barely detectable), 6.36 (br q, benzyl hydrogen of **16**), and 6.78 (d, benzyl hydrogen of **14**).

Registry No.—**1**, 50986-74-8; **2**, 51016-54-7; **3**, 50986-99-7; **4**, 50987-00-3; **4** 2,4-DNP, 50987-01-4; **5**, 50986-75-9; **6**, 50986-76-0; **7**, 50986-77-1; **8**, 50986-78-2; **10**, 50987-02-5; **10** 2,4-DNP, 50987-03-6; **11**, 50987-04-7; **12**, 50986-79-3; **13**, 50986-80-6; **14**, 50987-05-8; **14** semicarbazone, 50987-06-9; **15**, 50987-07-0; **16**, 50987-08-1; **16** 2,4-DNP, 50987-09-2; **17**, 50986-81-7; **18**, 50986-82-8; camphor, 76-22-2; benzyl chloride, 100-44-7; 2-methylcyclopentanone, 1120-72-5; 2-methylcyclohexanone, 583-60-8; bicyclo[2.2.2]octanone-2, 2716-23-6; isopropyl bromide, 75-26-3.

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(1) (a) A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968); (b) *Tetrahedron Lett.*, 5327 (1967); (c) *J. Org. Chem.*, **33**, 3953 (1968); (d) *ibid.*, **35**, 2670 (1970); (e) A. J. Sisti and M. Meyers, *ibid.*, **38**, 4431 (1973).

(2) T. A. Geissman and R. I. Akawie, *J. Amer. Chem. Soc.*, **73**, 1993 (1951).

(3) All bromohydrins herein were used directly without purification, since they were relatively unstable.

(4) The product **3** was treated in two experiments with trifluoroacetic acid and trifluoroacetic acid-*d* and the isolated product in each case was identical with **3** from the ring-expansion reaction (eq 2) (except for deuterium exchange which resulted with CF_3CO_2D). Thus the thermodynamically more stable isomer for **3**, and presumably **4**, was isolated directly from the expansion reaction. The structural assignments depicted (eq 2) would appear to be the more stable ones for **3** and **4**.

(5) R. R. Sauers and R. J. Tucker, *J. Org. Chem.*, **28**, 876 (1963).

(6) J. Berson and P. Reynolds-Warnhoff, *J. Amer. Chem. Soc.*, **86**, 595 (1964); J. Berson and D. Willner, *ibid.*, **86**, 609 (1964).

(7) R. R. Sauers and J. A. Beisler, *J. Org. Chem.*, **29**, 210 (1964).

(8) The principle of least motion may be another factor promoting C-2–C-3 bond migration over C-1–C-2 bond migration; more of the carbon atoms in the molecule are in motion and with a greater degree when the C-1–C-2 bond migrates than when the C-2–C-3 bond migrates.

(9) E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 125.

(10) The nitrous acid deamination of 2-aminomethyl[2.2.2]bicyclooctane has been reported to yield primarily 2-hydroxy[3.2.2]bicyclononane (70%), resulting from C-2–C-3 bond migration, compatible with the observations herein; see K. Alder, H. Krieger, and H. Weiss, *Ber.*, **88**, 144 (1955).

(11) Arguments for the predominance of one of the diastereoisomeric bromohydrins (**2**, **12**) can be presented. From that isomer, conformational and steric considerations for the preferred migration of one bond over the other can be offered (assuming the migrations to be trans and coplanar). Such a detailed mechanistic argument would be too ambitious for the data presented. One, however, cannot overlook these considerations as possible additional factors affecting the product distribution.

(12) A. J. Sisti, G. M. Rusch, and H. K. Sukhon, *J. Org. Chem.*, **36**, 2030 (1971).

(13) It has been demonstrated experimentally with a representative number of ring-enlarged ketones[1b,d,4] that under the reaction conditions the more stable isomers are isolated. The structures assigned for **10** and **11** would appear to be the more stable.

(14) B. Tchoubar, *Bull. Soc. Chim. Fr.*, 160 (1949).

(15) It is assumed that the cis isomer **16** is more stable than the trans isomer **15**. Recent evidence (M. Hanack, "Conformational Theory," Academic Press, New York, N. Y., 1965, pp 151 and 163) indicates that cycloheptanone probably exists in a twist chair conformation and it would seem reasonable that the methyl group in the equatorial position might be more stable, as in 2-methylcyclohexanone; thus the cis isomer **16** (phenyl equatorial) should be the more stable.

(16) C. Gutsche and C. Chang, *J. Amer. Chem. Soc.*, **84**, 2263 (1962).

(17) All melting points are uncorrected. Infrared spectra, all of pure liquid films unless otherwise stated, were determined with a Perkin-Elmer Model 257 Grating Infrared. The nmr spectra, in CCl_4 solutions unless otherwise specified, were determined with a Varian A-60 instrument.

(18) Initially heat was applied to the condenser to prevent the unreacted camphor, which sublimed, from obstructing the condenser. During the distillation of **1** the condenser was cooled in the usual manner.

(19) A. I. Shavrygin, *Zh. Obshch. Khim.*, **21**, 749 (1951).

(20) J. Cook and C. Hewett, *J. Chem. Soc.*, 62 (1936).

(21) Prepared by the oxidation of bicyclo[2.2.2]octanol-2 according to the procedure of Walborsky [A. Youssef, M. Baum, and H. Walborsky, *J. Amer. Chem. Soc.*, **81**, 4709 (1959)]. The alcohol was prepared from bicyclo[2.2.2]oct-5-en-2-yl acetate [J. Hine, J. Brown, L. Zalkow, W. Garden, and M. Hine, *J. Amer. Chem. Soc.*, **77**, 594 (1955)] by conversion to the unsaturated alcohol [H. Goering, R. Greiner, and M. Sloan, *ibid.*, **83**, 1391 (1961)] followed by reduction [K. Mislow and J. Berger, *ibid.*, **84**, 1956 (1962)].

(22) The Grignard was standardized by the procedure of Gilman [H. Gilman, E. Zollner, and J. Dickey, *J. Amer. Chem. Soc.*, **51**, 1576 (1929)].

(23) R. Ireland and J. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

(24) The shift in τ values undoubtedly is due to a solvent effect (CCl_4 to CF_3CO_2H), and the values obtained for treated and untreated samples whose spectra were measured in CCl_4 were almost identical.

A New Synthesis of β,γ-Unsaturated Carbonyl Compounds[1]

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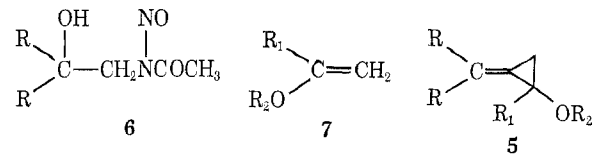
Treatment of 1-alkylidene-2-alkoxycyclopropanes with mercuric acetate in aqueous alcohol, followed by treatment of the vinylmercuric derivative thus produced with hydrogen sulfide, affords γ,γ-disubstituted β,γ-unsaturated carbonyl compounds, free from the corresponding α,β-unsaturated isomers, in high yields.

The ready availability of 1-alkylidene-2-alkoxycyclopropanes, **1**, from addition of alkylidene carbenes to vinyl ethers[3] made a study of the further reactions of this hitherto unavailable class of compounds of interest. In preliminary exploratory work, 1-cyclohexylidene-2-*tert*-butoxycyclopropane, **2**, was shown to yield the dimethyl acetal of 3-cyclohexylidenepropanal, **3**, on treatment with a cation-exchange resin in methanol, and 3-cyclohexylidenepropanal 2,4-dinitrophenylhydrazone, **4**, on treatment with 2,4-dinitrophenylhydrazine reagent.[4] All attempts to isolate 3-cyclohexylidenepropanal after acidic treatment of **2** failed. Because routes to β,γ-unsaturated carbonyl-con-

Table I
Synthesis of 1-Alkylidene-2-alkoxycyclopropanes[a]

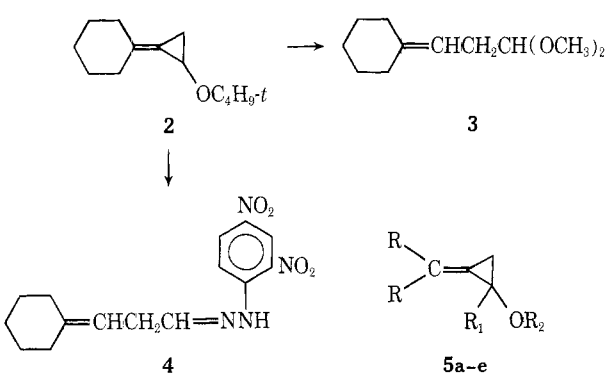


6 7 5

6	7	5[b]	Yield,[c] %
RR = $-(CH_2)_5-$, **6a** (37150-64-4)	$R_1 = R_2 = CH_3$ (116-11-0)	**5a** (51004-16-1)	64[d]
RR = $-(CH_2)_4-$, **6b** (51021-65-9)	$R_1 - R_2 = CH_3$	**5b** (51004-17-2)	66[e]
R = CH_3, **6c** (51021-66-0)	R_1 = Ph; $R_2 = CH_3$ (4747-13-1)	**5c** (51004-18-3)	35[e]
RR = $-(CH_2)_5-$, **6a**	$R_1 = OC_2H_5$; $R_2 = C_2H_5$ (2678-54-8)	**5d** (51004-19-4)	63[f]
RR = $-(CH_2)_5-$, **6a**	R_1 = H; $R_2 = C_2H_5$ (109-92-2)	**5e**[g] (37150-70-2)	80[d]

[a] Registry no. in parentheses under compound. [b] RR are same as R in **6**. [c] Isolated yields of pure material obtained after distillation based on acetylaminomethyl alcohol used—hence overall of 2 steps. See Generalizations in the Experimental Section. [d] Average of several runs. [e] One run. [f] Average of 2 runs. [g] Reference 3.

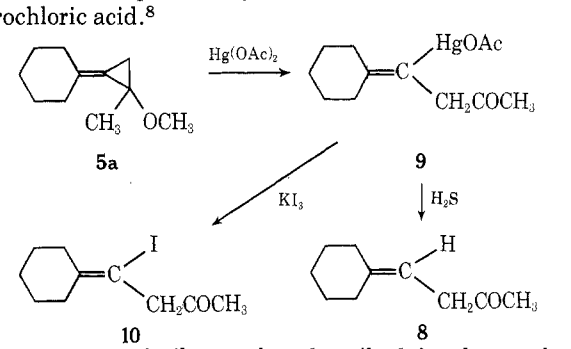
taining compounds free from the α,β-unsaturated isomers are rare, further work with compounds related to **2** seemed desirable. In this paper, the preparation and some reactions of 1-alkylidene 2-substituted 2-alkoxycyclopropanes, **5**, are described.



2 3 4 5a–e

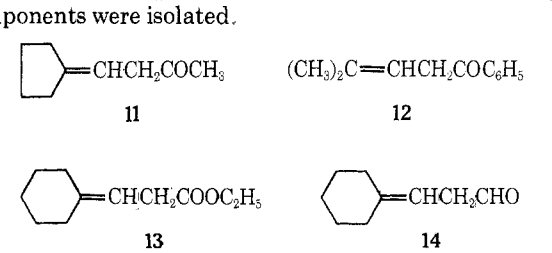
The cyclopropanes, **5**, of interest were prepared by reacting the *N*-nitrosoacetylaminomethyl alcohols, **6**, with excess enol ethers, **7**, by the method described.[3] The yields of **5** decrease as the excess of olefin used decreases. However, the excess olefin can be recovered (see Experimental Section). The compounds prepared and yields thereof are listed in Table I.

Attempts to find acidic conditions suitable for direct conversion of **5a** into 4-cyclohexylidene-2-butanone, **8**, were unsuccessful. However, treatment of **5a** with aqueous alcoholic mercuric acetate presumably afforded an organomercuric acetate, **9**, which was immediately converted into **8** (overall yield 86% based on **5a**) by treatment with hydrogen sulfide. In the case of **5d**, the intermediate mercury compound was also reduced to **13** with sodium borohydride, but there was no advantage over the hydrogen sulfide route. Because of the instability of **9**, evidence as to the structure was sought by treatment with potassium periodide, a reagent known to cause replacement of the mercury in arylmercury[5] and alkylmercury[6] compounds by iodine. The resulting iodo compound, 4-iodo-4-cyclohexylidene-2-butanone, **10**, was also so unstable that a pure sample for analysis could not be obtained. However, pmr, ir, and mass spectral data on crude **10** were sufficiently definitive to leave no doubt as to the structure of **10**. The replacement of vinyl mercury by iodine (to produce **10**) has been accomplished previously[7] and is apparently the first time vinyl mercury has been so replaced. The replacement of vinyl mercury by hydrogen has been accomplished by treatment with concentrated hydrochloric acid.[8]



5a 9 10 8

By treatment similar to that described for the synthesis of **8**, compounds **5b–d** were converted into 4-cyclopentylidene-2-butanone, **11** (94%), 3-isopropylidenepropiophenone, **12** (76%), and ethyl 3-cyclohexylidenepropionate, **13** (74%), respectively. However, all attempts to convert **5e**[3] into 3-cyclohexylidenepropanal, **14**, by this procedure yielded multicomponent mixtures from which no pure components were isolated.



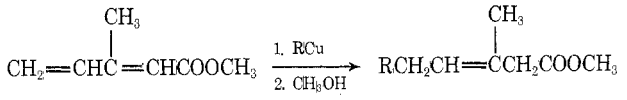
11 12 13 14

Compounds **11**, **12**, and **13** all proved to be entirely β,γ-unsaturated carbonyl-containing compounds. If any α,β-unsaturated isomers were present, they were undetected by glpc (probably ±1%), ir, and pmr (probably ±5%) determinations. Thus, since a new effective route to γ,γ-disubstituted β,γ-unsaturated ketones and esters is at hand, comparison with other methods is of interest.

The addition of trialkylboranes to ethyl 4-bromocrotonate in the presence of potassium 2,6-di-*tert*-butylphenoxide seems to be a general method for producing γ-substituted β,γ-unsaturated esters but has not been applied to the synthesis of β,γ-unsaturated ketones or γ,γ-disubstituted β,γ-unsaturated esters.[9]

$$R_3B + BrCH_2CH{=}CHCO_2C_2H_5 \longrightarrow RCH{=}CHCH_2CO_2C_2H_5$$

The conjugate 1,6 addition of an organocuprous reagent to a conjugated dienoate yields a β,γ-unsaturated ester. This reaction has not yet been extended to ketones.[10]



Other methods for producing β,γ-unsaturated carbonyl compounds contaminated with the corresponding α,β-unsaturated isomers have been recorded.[11-15]

Experimental Section

Generalizations. All melting and boiling points are uncorrected. Melting points were taken with a Thomas-Hoover melting point apparatus. Microanalyses were performed by the M-H-W Laboratories, Garden City, Mich.

Infrared absorption spectra were recorded on a Perkin-Elmer Infracord spectrophotometer. Proton magnetic resonance (pmr) spectra were recorded on a Varian A-60 nmr spectrophotometer, Varian Associates, Palo Alto, Calif.; all samples were dissolved in CCl_4 with tetramethylsilane (TMS) as an internal standard, chemical shifts are reported in δ values (TMS 0.0). All vapor phase chromatographic analyses were performed on a Wilkens Aerograph Model A-700; column (10 ft × ¼ in.): 30% SE-30 on 45/60 a/w Chromosorb A, flow rate 25 ml of helium/min. Vacuum distillations were carried out in a total-reflux partial-take-off column. The boiling points recorded represent the constant boiling material thus obtained. Additional amounts of product were undoubtedly present in lower and higher boiling fractions. The yields in general represent the average of two or more runs after experience with the product had been gained.

2-Methoxy-2-methylcyclohexylidenecyclopropane (5a). To a stirred solution of **6**, prepared as described[3] from 8.55 g (50 mmol) of 1-(*N*-acetylaminomethyl)cyclohexanol[3] and 2.5 g of Aliquat-336[16] in 100 ml of 2-methoxypropene[17] maintained at −10 to −5°, was added dropwise a solution of 2.5 g (60 mmol) of sodium hydroxide in 5 ml of water over 1 hr. The theoretical volume of nitrogen was collected. The reaction mixture was warmed to room temperature for 15 min, diluted with saturated sodium chloride solution, and extracted with ether. The organic layer was filtered through anhydrous sodium sulfate, and the solvent was fractionally distilled at atmospheric pressure with a 10 in. total reflux partial take-off column (hereinafter referred to as a conventional work-up). The residue was chromatographed over 50 g of neutral Woelm alumina with 250 ml of pentane to remove Aliquat-336. The eluate was concentrated by atmospheric fractional distillation as before, and the residue was distilled to afford 5.8 g (64%) of **5a**: bp 99° (13 mm); ir 5.62 μ (C=C); pmr 3.19 (s, 3, OCH_3), 2.2 (m, 4, allylic), 1.58 (m, 6, aliphatic), 1.45 (s, 3, CH_3), and 1.05 (m, 2, cyclopropyl); mass spectrum *m/e* 166.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.3; H, 10.9.

An experiment identical with that described above except that the solvent system consisted of 75 ml of pentane and 7.2 g (100 mmol) of 2-methoxypropene afforded 1.7 g (24%) of **5a**, identified by comparison with an authentic sample.

1-(*N*-Acetylaminomethyl)cyclopentanol (15). A mixture of 42.3 g (0.3 mol) of 1-oxa-3-azaspiro[4.4]nonan-2-one[18] and 150 ml of 50% potassium hydroxide was refluxed for 20 min. The cooled mixture was transferred under argon to a separatory funnel. The organic layer was separated, diluted with 200 ml of methanol, and treated dropwise with 30.6 of pure acetic anhydride. After 30 min at reflux the volatile materials were removed on a rotary evaporator, and the residue was recrystallized from benzene–petroleum ether (bp 60–110°) to yield 40.8 g (87%) of **15**: mp 119–120°; ir 2.85 (OH), 3.00 (NH), and 6.01 μ (C=O); pmr (acetone-d_6) 3.52 (m, 2, NH, OH, exchangeable with D_2O), 3.28 (d, 2, CH_2NH), 1.88 (s, 3, $COCH_3$), and 1.57 (broad s, 8, cyclopentyl); mass spectrum *m/e* 157.

Anal. Calcd for $C_8H_{15}NO_2$: C, 61.1; H, 9.6; N, 8.9. Found: C, 60.9; H, 9.8; N, 8.8.

1-(*N*-Nitrosoacetylaminomethyl)cyclopentanol (6b). The nitrosation is carried out exactly as described for **6**[3a] to yield a yellow oil with no NH and a strong carbonyl at 5.75 μ. No further analytical data were obtained on **6b** owing to its thermal instability; the compound must be used immediately or stored in methylene chloride solution for up to 1 week in the freezing compartment of a refrigerator.

2-Methoxy-2-methylcyclopentylidenecyclopropane (5b). In a similar way from 1-(*N*-nitrosoacetylaminomethyl)cyclopentanol prepared from 7.85 g (50 mmol) of **15** there was obtained 5.0 g (66%) of **5b**: bp 85° (13 mm); ir 5.54 μ (C=C); pmr 3.20 (s, 3, OCH_3), 2.32 (m, 4, allylic), 1.71 (m, 4, aliphatic), 1.38 (s, 3, CH_3), and 1.35–0.80 (m, 2, cyclopropyl); mass spectrum *m/e* 152.

Anal. Calcd for $C_{10}H_{16}O$: C, 79.0; H, 10.6. Found: C, 78.8; H, 10.3.

2-Methoxy-2-phenylisopropylidenecyclopropane (5c). In a similar way, from α-methoxystyrene[17] (100 ml) and 6.6 g (50 mmol) of 1-acetylaminomethyl-2-methyl-2-propanol[3a] there was obtained 3.3 g (35%) of **5c**: bp 132° (22 mm); ir 5.67 μ (C=C); pmr 6.97 (s, 3, aromatic), 3.13 (s, 3, OCH_3), 1.80 (s, 6, allylic CH_3), and 1.42 (m, 2, cyclopropyl); mass spectrum *m/e* 188.

Anal. Calcd for $C_{13}H_{15}O$: C, 83.0; H, 8.5. Found: C, 83.1; H, 8.7.

Cyclohexylidenecyclopropanone Diethyl Ketal (5d). Similarly, from **6** and ketene diethyl acetal,[19] there was obtained 6.62 g (63%) of **5d**: bp 88° (2 mm); ir 5.65 μ (C=C); pmr 3.65 (q, J = 7.0 Hz, 4, $-OCH_2CH_3$), 2.28 (m, 4, allylic), 1.58 (m, 6, aliphatic), 1.13 (t, J = 7.0 Hz, 6, $-OCH_2CH_3$), and shoulder on 1.13 (m, 2, cyclopropyl); mass spectrum *m/e* 210.

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.3; H, 10.5. Found: C, 74.4; H, 10.4.

4-Cyclohexylidene-2-butanone (8). To a stirred solution of 2.0 g of **5a** (12 mmol) in 25 ml of ethanol and 3 ml of water was added a solution of 3.84 g (12 mmol) of mercuric acetate in 20 ml of water. After 5 min, hydrogen sulfide was passed in for 5 min. The resulting black mixture was vacuum filtered through a bed of Celite to remove mercuric sulfide. The product was extracted with ether, and the organic layer was washed successively with water, saturated sodium chloride solution, and filtered through anhydrous sodium sulfate. The solvent was fractionally distilled with a 6 in. total reflux column and the residue distilled to afford 1.57 g (85%) of **8**: bp 120° (20 mm); ir 5.82 μ (C=O); pmr 5.23 (t, J = 7.0 Hz, 1, vinyl), 3.05 (d, 7.0 Hz, 2, $=CHCH_2COCH_3$), 2.10 (m, 4, allylic), 2.03 (s, 3, $COCH_3$), and 1.50 (m, 6, aliphatic); mass spectrum *m/e* 152; uv (C_6H_{12}) λ_{max} 223 nm (ϵ 589).[20] Ozonolysis of a methanolic solution followed by triphenylphosphine reduction[21] afforded cyclohexanone as the only glpc volatile material.

Anal. Calcd for $C_{10}H_{16}O$: C, 79.0; H, 10.5. Found: C, 78.6; H, 10.6.

4-Cyclopentylidene-2-butanone (11). Treatment of **5b** as described above yielded **11** (94%): bp 119° (35 mm); ir 5.82 μ (C=O); pmr 5.38 (t, J = 7.5 Hz, 1, vinyl), 3.0 (d, J = 7.5 Hz, 2, $-CHCH_2COCH_3$), 2.20 (m, 4, allylic), 2.05 (s, 3, $COCH_3$), and 1.62 (m, 4, aliphatic); mass spectrum *m/e* 138.

Anal. Calcd for $C_9H_{14}O$: C, 78.3; H, 10.2. Found: C, 78.5; H, 10.0.

3-Isopropylidenepropiophenone (12). Treatment of **5c** as described above yielded **12** (76%): bp 105° (1 mm); ir 5.91 μ (C=O); pmr 7.82 (m, 2, ortho H), 7.33 (m; 3, meta and para H), 5.35 (t, 1, vinyl), 3.52 (d, 2, $-CHCH_2COPh$), and 1.70 (d, 6, allylic CH_3); mass spectrum *m/e* 174.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.8; H, 8.1. Found: C, 82.6; H, 7.9.

Ethyl 3-Cyclohexylidenepropionate (13). Treatment of **5d** as described above yielded **13** (74%): bp 72° (0.4 mm); ir 5.75 μ (C=O); pmr 5.26 (t, J = 7.0 Hz, 1, vinyl), 4.10 (q, 2, $-OCH_2CH_3$), 2.95 (d, J = 7.0 Hz, 2, $-CHCH_2CO_2Et$), 2.12 (m, 4, allylic), 1.55 (m, 6, aliphatic), and 1.21 (t, 3, $-OCH_2CH_3$); mass spectrum *m/e* 182.

Anal. Calcd for $C_{11}H_{18}O$: C, 72.5; H, 9.9. Found: C, 72.4; H, 9.8.

4-Iodo-4-cyclohexylidene-2-butanone (10). To a solution of 1.0 g (6.0 mmol) of **5a**, 15 ml of methanol, and 2.0 ml of water maintained at 20° was added dropwise over a period of 10 min a solution of 1.92 g (6.0 mmol) of mercuric acetate in 10 ml of water. When the addition was complete, 10 ml of a potassium iodide–iodine solution (*e.g.*, 6 mmol of KI, 8 mmol of I_2) was added dropwise at about 20° over a 20-min period. The black color of the KI/I_2 solution disappeared immediately upon contact with the vinyl mercuric acetate solution. After the addition was complete, a pale orange oil separated. The reaction mixture was extracted thrice with ether. The combined organic portions were worked up in a conventional way, and the solvent was removed under reduced pressure at room temperature to afford 1.5 g (90% from **5a**)

of **10** as a pale orange oil: ir (neat) 5.80 μ sharp (C=O); pmr 3.80 (s, 2, $=ClCH_2COCH_3$), 2.35 (m, 4, allylic), 2.14 (s, 3, $COCH_3$), and 1.58 (m, 6, aliphatic); mass spectrum *m/e* 278, 151 (parent minus I). This oil turned black and became viscous when exposed to air for short periods of time or when heated to 40°. Because of this sensitivity no further analytical data were obtained.

Registry No.—**8**, 21527-61-7; **10**, 51004-20-7; **11**, 51004-21-8; **12**, 36597-09-8; **13**, 18559-89-2; **15**, 51004-22-9; 1-oxa-3-azaspiro[4,4]-nonan-2-one, 19684-59-4.

References and Notes

(1) This work was supported by Grant No. 12445 of the National Science Foundation.
(2) This work formed part of the Ph.D. thesis presented by M. C. V. Z., to The Ohio State University, 1973.
(3) (a) M. S. Newman and Z. ud Din, *Syn. Commun.*, **1**, 247 (1971); (b) *J. Org. Chem.*, **38**, 547 (1973).
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The Chemistry of Metalated Heterocycles. Dimerization of 2-Lithiomethyl-1,3-thiazoles, -1,3,4-thiadiazoles, and -1,3,4-oxadiazoles

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The carbanions derived from 2-methyl-1,3-thiazoles **2** are shown to retain their integrity at low temperatures by C-alkylation with alkyl halides. On the other hand, if these lithiated species are allowed to warm from −78° (their temperature of formation) to ambient temperatures, nucleophilic attack occurs with trace amounts of nonmetalated thiazole **1** producing the dimer **4**. Similar results were obtained when the 2-methyl-1,3,4-thiadiazole **5** (X = S) and the 2-methyl-1,3,4-oxadiazole **5** (X = O) were transformed into their lithio salts. These data tend to nullify the previously suggested mechanism for dimerization involving a ketenimine intermediate.

In a preliminary report[1] the behavior of thiazoles **1** and 1,3,4-thiadiazoles **5** after conversion to their respective lithio salts **2** and **6** was described. It was shown that alkylation of the lithio thiazole with methyl iodide at low temperature produced the expected 2-ethyl derivative whereas allowing **2** to warm to room temperature led to the dimer **4** in 75–90% yield. Similar behavior was noted for the lithio thiadiazole **6**, which produced, after low-temperature alkylation, the 2-ethyl derivative **7** or the dimer **8** upon warming in the absence of methyl iodide. Of further interest was the fact that the dimeric products **4** and **8** readily reversed upon heating (>150°) to the starting heterocycles. This facile dimerization of the lithiated heterocycles and their subsequent reversion to monomers has apparently escaped detection despite the extensive literature pertaining to metalation of heterocycles.[2] The purpose of the present paper is not only to report further details regarding the dimerization of lithio heterocycles but to offer a mechanism for this process.

In the case of the thiazole system **1**, the dimer **4** may be envisioned as forming through two different mechanisms (Schemes I and II). The lithio thiazole may rearrange upon warming from −78° to 25° to the thiolithio ketenimine **9**, which is attacked as it is formed by unrearranged lithio thiazole, leading to the adduct **10**. Quenching of the solution would produce the thiol imine **11**, resulting in cyclization to the observed dimer **4**. This pathway, originally suggested for the dimer formation,[1] is based upon the analogous dimerization of oxazine and oxazoline carbanions **14** to their respective dimers **16**,[3a] Proof of the intermediacy of the ketenimine **15** was presented by isolation and characterization of the entrapped O-trimethylsilyl de-