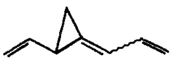
Communications

Synthesis and Thermolysis of 1-Allylidene-2-vinylcyclopropane and 1-(1-Buta-1,3-dienyl)-2-methylenecyclopropane

Summary: The syn and anti isomers of 1-allylidene-2-vinylcyclopropane (**1**) undergo thermal isomerization to 3-methylene-1,4-cycloheptadiene (**5**) and 4-vinyl-3-methylenecyclopentene (**6**). 1-(1-Buta-1,3-dienyl)-2-methylenecyclopropane (**2**) rearranges to 5-vinyl-3-methylenecyclopentene (**7**).

Sir: Current interest in the thermally induced vinylmethylenecyclopropane → 3-methylenecyclopentene rearrangement[1] prompts us to report on the synthesis and thermolysis of the interestingly related hydrocarbons, 1-allylidene-2-vinylcyclopropane (**1**) and 1-(1-buta-1,3-dienyl)-2-methylenecyclopropane (**2**).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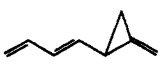
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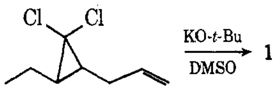
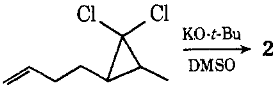
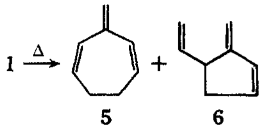
Addition of 1-allyl-2,2-dichloro-3-ethylcyclopropane (**3**)[2] to a solution of KO-*t*-Bu (2.1 equiv) in dimethyl sulfoxide at ~18° gives **1** (~40% yield) as a mixture of syn and anti isomers (eq 1). The mixture is separable by gas chromatography (10% UCON 50 HB on Chromosorb P column operated at 30°), but structural assignments have not been made.[3] Similarly, compound **2**[4] is prepared in 30% yield from 1-(1-but-1-ene)-2,2-dichloro-3-methylcyclopropane (**4**)[5] (eq 2).


3 (1)

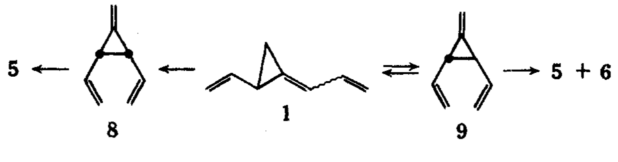

4 (2)

Thermolysis studies of **1** were carried out on the pure syn and anti isomers. Both isomers disappear in cyclohexane solution by a first-order rate law to give 3-methylene-1,4-cycloheptadiene (**5**)[6] and 4-vinyl-3-methylenecyclopentene (**6**).[7] One isomer (**1a**)[3] rearranged more readily and gave 80% **5** and 20% **6** (73% conversion). The slower isomer (**1b**)[3] gave 86% **5** and 13% **6** (eq 3).

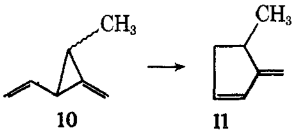

5 6 (3)

Some preliminary kinetic results on the rearrangements of **1a** and **1b** are shown in Table I. The activation parameters do not allow an unequivocal choice of mechanism, although the results are satisfactorily explained by invoking a series of consecutive reactions whereby **1a** and **1b** are converted into **8** and **9** by a methylenecyclopropane rearrangement[8] (Scheme I). This is consistent with the high positional selectivity imparted by the vinyl group in the degenerate methylenecyclopropane rearrangement observed for vinylmethylenecyclopropane.[1g] A Cope rearrangement of **8** would give **5**, whereas **9** might be expected to give both **5** and **6**. Attempts to detect **9** during rearrangement of **1a** (the fast isomer) have been unsuccessful.

Scheme I



A regiospecific conversion ([3,5]-sigmatropic process) of *syn*-**1** → **5** seems unreasonable since both *syn*- and *anti*-**1** give mainly **5**. Similarly, a concerted [3,3]-sigmatropic process involving the conversion 1 → **6** or **9** → **6** seems unlikely in view of recent studies involving related systems.[1e,g] More likely, **6** results from a concerted [1,3]-sigmatropic process or its structural equivalent in the form of a biradical. Kende and Riecke[1e] and Gilbert and Higley[2g] have proposed the intervention of orthogonal biradicals for similar rearrangements, although more recent studies favor a concerted [1,3]-sigmatropic process for the conversion **10** → **11** (eq 4).[9] At this time we are not able to differentiate between these mechanisms for the system under study here, although efforts directed toward the synthesis of **9** are underway.


10 11 (4)

Hydrocarbon **2** rearranges cleanly by a first-order process (Table I) to give **7** (eq 5). Again, this conversion is probably best described mechanistically as involving a concerted [1,3]-sigmatropic shift or its structural equivalent in the form of a biradical.

Table I
Kinetic Data[a] and Activation Parameters for 1a and 1b

Reactant	T, °C	$k \times 10^6$, sec^{-1}	E_a, kcal/mol	Log A
1a	47.0	11.3 ± 1.3	22.8 ± 1.1	11.3 ± 0.70
	54.2	25.1 ± 1.1		
	61.5	52.2 ± 2.0		
	64.2	67.5 ± 0.90		
1b	42.0	2.54 ± 0.01	25.1 ± 0.70	12.4 ± 0.46
	49.5	6.43 ± 0.31		
	59.5	24.0 ± 1.8		
	66.5	47.3 ± 0.91		
	74.0	103 ± 3.5		
2	30.0	4.38 ± 0.31	19.4 ± 1.05	9.6 ± 0.70
	34.5	6.41 ± 2.05		
	49.0	29.1 ± 1.4		
	56.5	58.2 ± 5.1		

[a] Kinetic runs were carried out in sealed capillary tubes using cyclohexane solvent with gas chromatographic analysis.

7 (5)

Comparison of the activation energy reported for the vinylmethylenecyclopropane → 3-methylenecyclopentene rearrangement (25.8 kcal)[9] with that found for 2 → 7 is interesting. If rupture of the cyclopropane bond is the rate-determining step in both cases, then the difference in activation energies ($\sim$8.4 kcal) may reflect the difference in stabilization energies of the pentadienyl and allyl radicals, only slightly lower than the value of 9 kcal for another system involving cleavage of a cyclopropane bond.[10]

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation (Grant C-490) and The Research Corporation for support of this work.

References and Notes

(1) (a) T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, **90**, 4749 (1968); (b) T. C. Shields and W. E. Billups, *Chem. Ind. (London)*, 619 (1969); (c) W. R. Roth and Th. Schmidt, *Tetrahedron Lett.*, 3639 (1971); (d) W. E. Billups, K. H. Leavell, W. Y. Chow, and E. S. Lewis, *J. Amer. Chem. Soc.*, **94**, 1770 (1972); (e) A. S. Kende and E. E. Riecke, *J. Amer. Chem. Soc.*, **94**, 1397 (1972); (f) M. F. Semmelhack and R. J. DeFranco, *J. Amer. Chem. Soc.*, **94**, 8838 (1972); (g) J. C. Gilbert and D. P. Higley, *Tetrahedron Lett.*, 2075 (1973).

(2) Prepared from 1,4-heptadiene and dichlorocarbene ($CHCl_3$, KO-*t*-Bu) in *n*-pentane at 0°.

(3) The isomer with the shorter retention time (**1a**) showed the following spectral properties: nmr (CCl_4) δ 1.07 (m, 1 H), 1.53 (m, 1 H), 2.11 (m, 1 H), 4.7–5.6 (m, 5 H), 6.42 (m, 2 H); ir (neat) 755 (m), 895 (s), 995 (s), 1614 (s), 1634 (s) cm^{-1}; uv λ_{max} (C_6H_{12}) 230 nm (ϵ 25,000). The remaining isomer (**1b**) showed nmr (CCl_4) δ 1.07 (m, 1 H), 1.52 (m, 1 H), 2.18 (m), 1 H), 4.7–5.7 (m, 5 H), 6.42 (m, 2 H); ir (neat) 897 (s), 995 (s), 1614 (s), 1634 (s) cm^{-1}; uv λ_{max} (C_6H_{12}) 232 nm (ϵ 19,000).

(4) Spectral properties: nmr (CCl_4) δ 1.01 (m, 1 H), 1.45 (m, 1 H), 2.17 (m, 1 HO), 4.60–5.48 (m, 5 H), 5.98 (m, 2 H); ir (neat) 882 (s), 990 (s), 1200 (m), 1428 (m), 1640 (s), 2960 (s) cm^{-1}; uv λ_{max} (C_6H_{12}) 237 nm (ϵ 38,000).

(5) Prepared from 1,5-heptadiene and dichlorocarbene ($CHCl_3$, KO-*t*-Bu) in *n*-pentane at 0°.

(6) Spectral properties: nmr (CCl_4) δ 2.32 (t, J = 2.5 Hz, 4 H), 5.1 (s, 2 H), 5.50–6.20 (m, 4 H) (irradiation at δ 2.32 reduces the δ 5.50–6.20 multiplet to an AB quartet with $J_{AB} \simeq$ 11 Hz); ir (neat) 785 (s), 880 (s), 1435 (m), 1445 (m), 1570 (m), 1786 (s), cm^{-1}; uv λ_{max} (C_6H_{12}) 246 mm (ϵ 15,000), 255 (13,000). The spectral data reported here for **5** differ substantially from those reported by earlier workers. See D. S. Matteson, J. J. Drysdale and W. H. Sharkey, *J. Amer. Chem. Soc.*, **82**, 2853 (1960); W. von E. Doering and D. W. Wiley, Tetrahedron, **11**, 183 (1960).

(7) Spectral properties: nmr (CCl_4) δ 1.98–2.87 (m, 2 H), 3.0–3.6 (m, 1 H), 4.60–5.90 (m, 5 H), 5.90–6.40 (m, 2 H); ir (neat) 760 (s), 864 (m), 908 (m) 988 (m), 1071 (m), 1432 (m), 1732 (s) cm^{-1}; uv λ_{max} (C_6H_{12}) 235 nm (ϵ 14,000).

(8) For a relevant discussion see W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

(9) W. E. Billups, K. H. Leavell, E. S. Lewis, and S. Vanderpool, *J. Amer. Chem. Soc.*, **95**, 8096 (1973).

(10) J. A. Pettus and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

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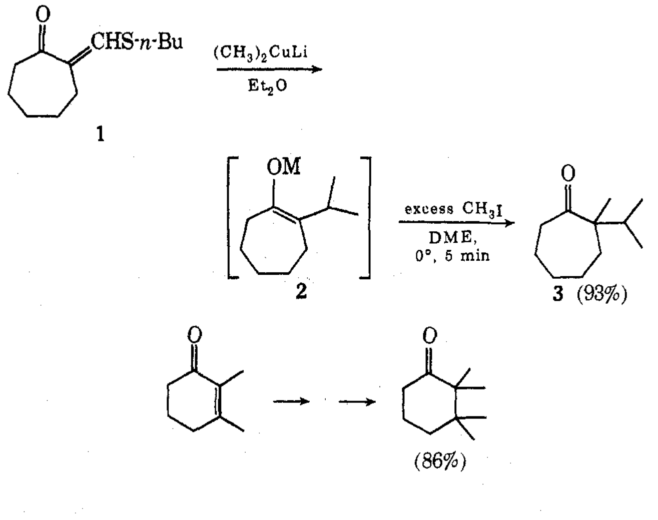
Conjugate-Addition Alkylation of α,β-Unsaturated Ketones

Summary: The copper–lithium enolates formed in the conjugate addition of organocopper lithium reagents to α,β-unsaturated ketones may be alkylated with generally high regioselectivity and efficiency in 1,2-dimethoxyethane as solvent.

Sir: The combination of dissolving metal reduction of α,β-unsaturated ketones (and analogous functions) with direct alkylation of the enolate anion so formed provides a simple and efficient method for regioselective alkylation.[1] Although it would clearly be a useful extension of this method to couple similarly the conjugate addition of organocopper reagents to α,β-unsaturated ketones[2] with alkylation,[3] attempts to alkylate the copper–lithium enolate intermediates have been either unsuccessful[4] or unsatisfactorily slow.[5,6] The ostensible unreactivity of these enolates was presumed to be the consequence of increased covalency of the copper–oxygen, as opposed to the lithium–oxygen, bond.[4]

We have discovered that the copper–lithium enolates formed in the conjugate addition of organo- (methyl- and vinyl-) copper lithium reagents to α,β-unsaturated ketones, while quite unreactive in ether (normally the solvent of choice for maximum yield of 1,4 addition),[2,7] become receptive to alkylation in 1,2-dimethoxyethane (DME). Thus, the half-life for methylation of the enolate produced in the double conjugate addition[4] to 2-*n*-butylthiomethylene ketone 1 is reduced from $\sim$5 hr at room temperature in ether to $\ll$30 sec at 0° in DME, a reactivity difference of $\sim 10^5$.[8,9]



It is interesting that neither DME or tetramethylethylenediamine[10] in ether in stoichiometric proportions (3 equiv/1 equiv of Cu) nor 1:1 DME–ether was nearly so effective as pure DME in enhancing the rate of methylation of **2**, although *all* reactions were considerably faster than in pure ether. Accordingly, it seems to be necessary to remove essentially all of the ether prior to the addition of DME. Both tetrahydrofuran and hexamethylphosphoramide had a rate-accelerating effect comparable to, but apparently slightly less than, DME. The results of a survey upon the scope of this procedure for conjugate-addition alkylation are collected in Table I.

Some enolate ⇄ ketone equilibration is obviously occurring in certain cases (particularly the slower alkylation reactions) with concomitant formation of unalkylated, isomeric, and dialkylated products. However, we judge the yields of the desired conjugate-addition alkylation product to be comparable to those expected in the alkylation of the corresponding pure lithium enolate, considering the relatively hindered environment of the reaction site.[1b] It is noteworthy that the methylation of the lithium enolate 2