3079, 2970, 2878, 2219, 1595, 1551, 1480; MS m/z 355 (EI), 356 (CI); MS exact mass calcd for $C_{20}H_{18}ClNO_3$ 355.0975, found 355.0984.

9-Butyl-3-chloro-1-cyano-2-ethoxy-4-hydroxyphenanthrene (21f). In a manner similar to the above using 0.49 g (1.49 mmol) of **20** and 0.61 g (7.48 mmol) of 1-hexyne, 0.05 g (10%) of **21f** was isolated as a white crystalline solid: mp 145-146 °C; ^{1}H NMR ($CDCl_3$) δ 9.57-9.61 (m, 1 H), 8.12-8.16 (m, 1 H), 7.87 (s, 1 H), 7.66-7.72 (m, 2 H), 7.22 (s, 1 H), 4.44 (t, J = 7 Hz, 2 H), 3.13 (t, J = 7 Hz, 2 H), 1.72-1.85 (m, 2 H), 1.46-1.59 (m, 5 H), 1.00 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.30, 154.62, 142.56, 133.58, 131.27, 129.77, 128.34, 127.39, 126.97, 124.40, 122.08, 116.01, 115.48, 111.98, 96.13, 71.87, 33.65, 32.44, 23.12, 15.85, 14.12; IR (KBr) 3300, 2971, 2950, 2881, 2240, 1573, 1418; MS m/z 353 (EI), 354 (CI); MS exact mass calcd for $C_{21}H_{20}ClNO_2$ 353.1182, found 353.1176.

Acknowledgment. We wish to thank the National Institutes of Health (GM-36312 and CA-11890) for financial support of this work. We are also grateful to Catherine A. Moore for technical support in obtaining mass spectral data and to Professor Robert Doedens for the single-crystal X-ray analysis of **17**.

Supplementary Material Available: ^{13}C NMR spectra for **4a-c** and an ORTEP drawing and single-crystal X-ray data for **17** (10 pages). Ordering information is given on any current masthead page.

Synthesis and Reactions of α-Chloro-β,γ-unsaturated Esters. 1†

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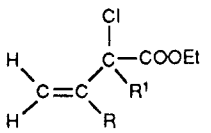
Received November 27, 1989

Four new α-chloro-β,γ-unsaturated esters were prepared in good yield by the reaction of hypochlorous acid with substituted ethyl 2-butenoates. Reaction of these substituted allylic chlorides with several nucleophiles has been investigated. Thiophenol in the presence of aqueous sodium hydroxide react with ethyl 2-chloro-3-methyl-3-butenoate (**2**) to give **6**, whereas ethyl 2-chloro-2,3-dimethyl-3-butenoate (**1**) is unreactive. Tertiary allylic chlorides **1**, **3**, and **4** react with secondary amines to give exclusive abnormal S_N2 reaction products. With benzylamine abnormal S_N2 substitution is followed by cyclization to give 1-benzyl-3-pyrrolin-2-ones. While ethyl lithioacetate reacts with **1** to give acylation product **18**, sodium diphenylmethide in liquid ammonia undergoes alkylation on the tertiary carbon possibly by an electron-transfer reaction pathway. Lithio-1,3-dithiane reacts with **1** to give 2,3-dimethyl-6,10-dithiaspiro[4.5]dec-2-en-1-one (**20**) via a two-step process, viz., acylation followed by a novel variation of the intramolecular abnormal S_N2 reaction. Raney nickel desulfurization of **20** gave 2,3-dimethyl-2-cyclopenten-1-one. Synthetic and mechanistic implications of these results are discussed.

In connection with one of our ongoing projects, we required the use of certain highly substituted allylic halides, in particular, α-chloro-β,γ-unsaturated esters of the general structure



1: R = CH_3, R^1 = CH_3
2: R = CH_3, R^1 = H
3: R = Ph, R^1 = H
4: R = Ph, R^1 = CH_3

A literature survey revealed that there was no general and efficient synthesis for this type of compound. The synthesis of 2-bromo-3-butenoic acid from acrolein cyanohydrin proceeds in too poor a yield to be of synthetic utility.[1] Furthermore, this procedure has not been extended to other substituted 2-halo-3-butenoic acids. The other known described example is the synthesis of ethyl 2-bromo-3-phenyl-3-butenoate by kinetic deconjugation[2] of ethyl 2-bromo-3-methylcinnamate with LDA/THF. The Darzens condensation of ethyl 2-bromopropionate with acetone followed by the lithium salt catalyzed rearrangement of the glycidic ester to give ethyl 2-hydroxy-2,3-dimethyl-3-butenoate has also been reported.[3,4] Although this route will eventually lead to a synthesis of our desired allylic halides, we sought a simpler synthetic route.

Wolinsky[5] and co-workers have shown that by a judicious choice of reaction conditions, hypochlorous acid can convert highly substituted α,β-unsaturated ketones into α-chloro-β,γ-unsaturated ketones. Recently Buynak[6] has extended this reaction to alkylidene β-lactams.

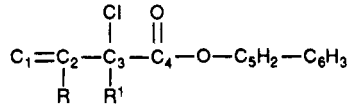
The ready availability of alkyl/aryl-substituted acrylic esters by the Horner[7] modification of the Wittig reaction prompted us to explore the Wolinksy[8] reaction on sub-

† This work was completed at Petrolite Corporation and is covered by two Pending U.S. patents assigned to Petrolite Corporation, St. Louis, MO.

(1) (a) Glattfield, J. W. E.; Hoen, R. E. *J. Am. Chem. Soc.* **1935**, *57*, 1405. (b) Baldwin, J. E.; Haber, S. B.; Hoskins, C.; Kruse, L. I. *J. Org. Chem.* **1977**, *42*, 1239.
(2) Chari, R. V. J.; Wemple, J. *Tetrahedron Lett.* **1979**, *2*, 111.
(3) Hartman, B. C.; Rickborn, B. *J. Org. Chem.* **1972**, *37*, 943.
(4) Gordon-Gray, C. G.; Whiteley, C. G. *J. Chem. Soc. Perkin Trans. 1* **1977**, 2040.
(5) (a) Hedge, S. G.; Wolinsky, J. *Tetrahedron Lett.* **1981**, *22*, 5019. (b) Hedge, S. G.; Yogel, M. K.; Saddler, J.; Rockwell, N.; Haynes, R.; Oliver, M.; Wolinsky, J. *Tetrahedron Lett.* **1980**, 441.
(6) Buynak, J. D.; Mathew, J.; Rao, M. N.; Haley, E.; George, C.; Shriwardhane, U. *J. Chem. Soc., Chem. Commun.* **1987**, 735.
(7) (a) Gallagher, G.; Webb, R. L. *Synthesis* **1974**, 122. (b) Shahak, I.; Almong, J.; Bergmann, E. D. *Israel J. Chem.* **1969**, *7*, 585.
(8) The term Wolinsky reaction is used to imply the deconjugative chlorination of unsaturatd carbonyl compounds in its original scope.

0022-3263/90/1955-3880$02.50/0

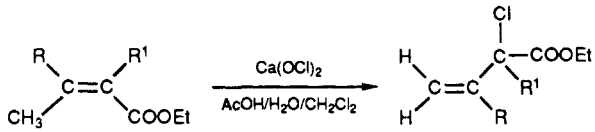
Table I. Reaction Products of Hypochlorous Acid with α,β-Unsaturated Esters



ester	product	yield, %	^{1}H NMR chemical shifts[a]	^{13}C NMR assignments[a]
R = CH_3, R^1 = CH_3	1	80[b]	5.25 (s, 1 H), 5.05 (q, 1 H, J = 1.5 Hz), 4.20 (q, 2 H, J = 7 Hz), 1.90 (s, 3 H), 1.85 (d, 3 H, J = 1.4 Hz), 1.3 (t, 3 H, J = 7 Hz)	113.8 (C_1), 143.6 (C2), 68.4 (C_3, 169.1 (C4), 62.7 (C5), 13.9 (C_6), 19.3 (CH_3), 27.9 (CH_3)
R = CH_3, R^1 = H	2	66[b]	5.20 (s, 1 H), 5.10 (br s, 1 H), 4.80 (s, 1 H), 4.20 (q, 2 H, J = 7 Hz), 1.90 (s, 3 H), 1.2 (t, 3 H, J = 7 Hz)	117.3 (C1), 139.6 (C2), 59.3 (C3), 168.8 (C4), 61.9 (C5), 14.0 (C6), 18.1 (CH_3)
R = Ph[c], R^1 = H	3	52[b,d]	7.30 (m, 5 H), 5.60 (s, 1 H), 5.55 (s, 1 H), 5.30 (2, 1 H), 4.15 (q, 2 H, J = 7 Hz), 1.20 (t, 3 H, J = 7 Hz)	118.5 (C1), 148.5 (C2), 59.3 (C3), 168.5 (C4), 62.2 (C5), 13.8 (C6), 128.4 and 126.7 (Ph)
R = Ph[e], R^1 = CH_3	4	74[b]	7.35 (m, 5 H), 5.75 (s, 1 H)8 5.40 (s, 1 H), 4.20 (q, 2 H, J = 7 Hz), 2.00 (s, 3 H), 1.20 (t, 3 H, J = 7 Hz)	117.7 (C1), 148.7 (C2), 70.1 (C3), 169.4 (C4), 62.2 (C5), 13.8 (C6), 128.2 and 127.1 (Ph)

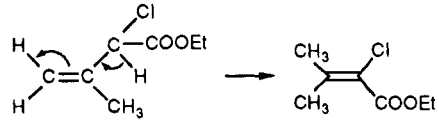
[a] Shift in ppm from TMS in $CDCl_3$. [b] Isolated after flash column chromatography on silica gel. [c] Prepared by the condensation of triethyl phosphonoacetate with acetophenone using NaH in DMF. [d] The conjugated isomer ethyl 2-chloro-3-phenyl-2-butenoate was isolated in 24% yield. [e] Prepared by the condensation of triethyl phosphonopropionate with acetophenone using NaH/DMF.

stituted acrylic esters. The reaction is best effected in a two-phase system of methylene chloride/water. We found that the combination of calcium hypochlorite/acetic acid[9] to generate the hypochlorous acid is more convenient than the dry ice method originally employed by Wolinsky. The reaction has been successfully performed with ethyl 2,3-dimethyl-2-butenoate, ethyl 3-methyl-2-butenoate, (*E*)-ethyl 3-phenyl-2-butenoate, and (*E*)-ethyl 2-methyl-3-phenyl-2-butenoate:



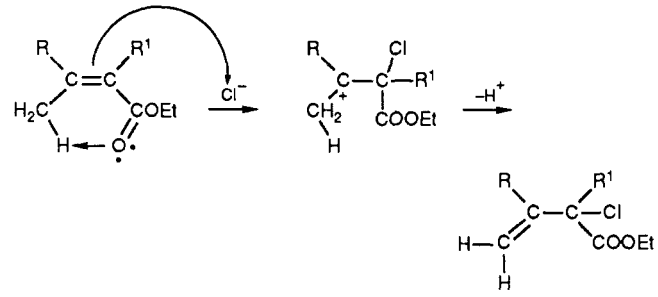
The results together with the analytical data are given in Table I.

The lower yields of allylic chlorides obtained with **2** and **3** are due to the presence of a labile hydrogen α to the ester moiety. Part of the product isomerizes to the thermodynamically stable 2-chloro-3-substituted-2-butenoate, a route not available to the trisubstituted acrylates



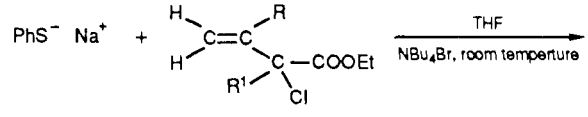
5

The isomeric chlorides can be separated by careful flash column chromatography on silica gel. Ethyl 2-butenoate and ethyl 2-methyl-2-butenoate did not yield any of the desired allylic chlorides. With these compounds, a mixture of products including chlorohydrins was formed as indicated by proton NMR and TLC of the crude reaction. Complete substitution at the β carbon of the acrylate is therefore essential for the formation of these allylic chlorides. A polar two-step mechanism is proposed for this transformation wherein an initial addition of the chloronium ion on the double bond to generate a carbocation at the β carbon of the acrylate is followed by a rapid loss of the proton on the methyl group at this carbon. It is likely that the rapid collapse of the carbocation disfavors the normal chlorohydrin formation[10]

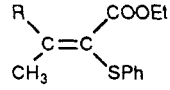


Reaction of Allylic Chlorides with Nucleophiles

We first studied the reaction of thiophenol with these allylic chlorides in the presence of base under phase-transfer reaction conditions. The reaction of sodium thiophenolate with 2 gave ethyl 2-(phenylthio)-3-methyl-2-butenoate (**6**), in good yield. In a similar fashion ethyl 2-(phenylthio)-3-phenyl-2-butenoate (*E* and *Z*), **7**, was produced from **3**. No reaction was observed when **1** or **4** were reacted under the same conditions. The reaction can



1: R = CH_3, R^1 = CH_3
2: R = CH_3, R^1 = H
3: R = Ph, R^1 = H
4: R = Ph, R^1 = CH_3



6: R = CH_3 84% yield
7: R = Ph 58% yield (*E* and *Z*)

be interpreted as proceeding by an S_N2-type mechanism. Alkylation of the thio anion on the secondary carbon

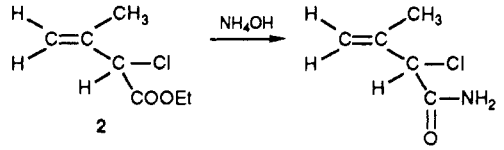
(9) The use of glacial acetic acid for this process originated in the laboratory of Prof. Buynak. See ref 6.

(10) Hopwood, J. A.; Williams, D. L. H. *J. Chem. Soc. B* **1968**, 718.

bearing the chlorine atom takes place followed by base-induced isomerization to the more stable conjugated system. However one cannot rule out the alternate carbene mechanism, which would also explain the observed result. The failure of **1** and **4** to react with these thio anions may be explained either on the basis of the steric hindrance involved in the transition state for S_N2-type alkylation or the nonavailability of carbene pathway.

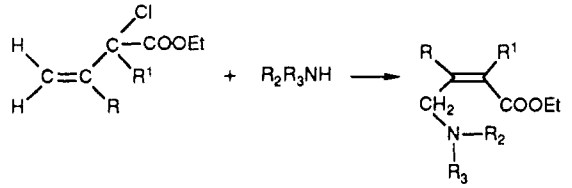
Compound **6** has previously been synthesized by either condensation of α-(phenylthio)acetate carbanions[11] with acetone or the Pummerer[12,13] style dehydration of sulfoxides. The new method is not only superior to the previous methods in terms of product yield and ready availability of starting materials but represents a general route for introducing a sulfur nucleophile at the 2-position of substituted acrylates.[4]

The reaction of the allylic chlorides with amines was also studied. Aqueous ammonia reacted with 2-chloro-3-methyl-3-butenoate (**2**) to yield the simple amide.



2

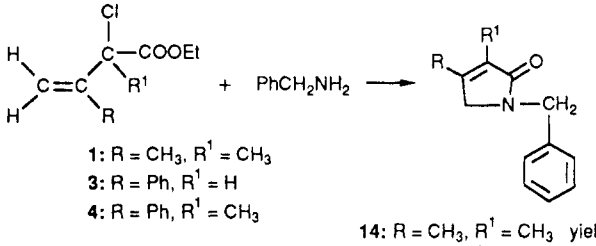
No reaction was observed with **1** and aqueous ammonia. When the allylic chlorides **1**, **3**, or **4** were reacted with diethylamine or piperidine, allylamines were isolated.



1: R = CH_3, R^1 = CH_3	**8**: R = CH_3, R^1 = CH_3, R_2 = R_3 = CH_2CH_3	yield 32%
	9: R = CH_3, R^1 = CH_3, R_2 + R_3 = $(CH_2)_5$	yield 82%
3: R = Ph, R^1 = H	**10**: R = Ph, R^1 = H, R_2 = R_3 = CH_2CH_3	yield 68%
	11: R = Ph, R^1 = H, R_2 + R_3 = $(CH_2)_5$	yield 86%
4: R = Ph, R^1 = CH_3	**12**: R = Ph, R^1 = CH_3, R_2 + R_3 = CH_2CH_3	yield 71%
	13: R = Ph, R^1 = CH_3, R_2 + R_3 = $(CH_2)_5$	yield 92%

The formation of the allylic amine products from **1**, **3**, and **4** is the result of an abnormal S_N2 reaction.[15-18] It is to be noted that in these reactions regiospecificity (exclusive abnormal S_N2) is accompanied by the formation of only one geometric isomer. Compounds **8**–**13** were assigned the *Z* stereochemistry on the basis of comparison of NMR chemical shifts of allylic protons in similar systems.[19] It is plausible that the preferential formation of the *Z* isomer may reflect the thermodynamic stability of the product.

The reaction of benzylamine with **1**, **3**, and **4** proceeds in a similar fashion except that an intramolecular cyclization of the allylamine to 3-pyrrolin-2-one takes place.

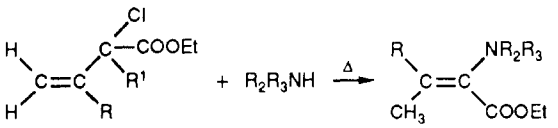


1: R = CH_3, R^1 = CH_3
3: R = Ph, R^1 = H
4: R = Ph, R^1 = CH_3

14: R = CH_3, R^1 = CH_3	yield 76%
15: R = Ph, R^1 = H	yield 68%
16: R = Ph, R^1 = CH_3	yield 74%

This reaction presents an efficient synthesis of the unsaturated lactams **14**–**16**. The parent 3-pyrrolidin-2-one ring system is present in a number of physiologically active compounds and has been the target of several synthetic studies.[20] For example, a synthesis of 1-benzyl-3-pyrrolin-2-one was reported by Syntex workers as early as 1977.[21] However, the synthesis involves four steps starting from 1-benzylpyrrolin-2-one.

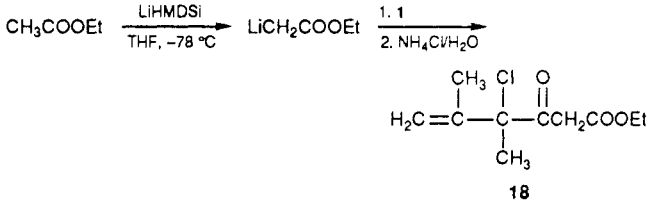
Reaction of **2** with piperidine yielded ethyl 2-piperidino-3-methyl-2-butenoate (**17**) by the attack of the amine on the secondary allylic carbon, while the reaction of **2** with diethylamine resulted in the formation of ethyl 2-chloro-3-methyl-2-butenoate (**5**). The reason for this is not clear at the present time.



2: R = CH_3, R^1 = H

17: R = CH_3, R_2 + R_3 = $(CH_2)_5$ yield 70%

The reaction of **1** with a relatively strong carbanion was next examined. Thus ethyllithio acetate[22] was generated at −78 °C from ethyl acetate and lithium bis(trimethylsilyl)amide in THF. Addition of **1** to the ester enolate at −78 °C followed by warming to 0 °C and aqueous workup gave the acylation product **18** in 69% isolated yield.

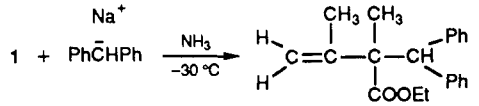


18

The reaction of **1** with the strong nucleophile sodium diphenylmethide (pK_a of diphenylmethane[23] = 35) was

(11) Takaki, K.; Okamura, A.; Oshiro, Y.; Agawa, T. *J. Org. Chem.* **1978**, *43*, 402.
(12) Hagiware, H.; Nakayama, K.; Uda, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3679.
(13) Durman, J.; Hunt, P. G.; Warren, S. *Tetrahedron Lett.* **1983**, *24*, 2113 and references therein.
(14) The reaction of ethyl 2-bromo-3-methyl-2-butenoate with 2 equiv of benzenethiol in a K_2CO_3/acetone system has been shown to proceed by a AdNSNE mechanism to yield ethyl 2-(phenylthio)-3-methyl-2-butenoate. See: Rosnati, V.; Salimbeni, S.; Vettori, U.; Saba, A. *Gazz. Chim. Ital.* **1981**, *111*, 249.
(15) Although we have not established that the reaction is truly second order, it is nevertheless a valid assumption since SN1′ pathway is prohibitive due to the destabilization of carbocations adjacent to an electron-withdrawing carbethoxy group.
(16) For abnormal SN2 reactions of amines with allylic halides activated by a keto group, see: Maury, G.; Wu, E. M.; Cromwell, N. H. *J. Org. Chem.* **1968**, *33*, 1900.
(17) (a) Young, W. G., Webb, I. D.; Goering, H. L. *J. Am. Chem. Soc.* **1951**, *73*, 1076. (b) Fukui, K.; Fujimoto, H. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2116.
(18) Catchpole, A. G.; Hughes, E. O.; Ingold, C. K. *J. Chem. Soc.* **1948**, 8.
(19) Stereochemistry of the amine adducts was assigned *Z* based on the chemical shifts of methylene protons and protons on the double bond. See: (a) Klein, J.; Aminadau, N. *J. Chem. Soc.* **1970**, 1380. (b) Silverman, R. B.; Invergo, B. J.; Levy, M. A.; Andrews, C. R. *J. Biol. Chem.* **1987**, *262*, 3192.
(20) (a) Kochhar, K. S.; Carson, H. J.; Clouser, K. A.; Elling, J. W.; Gramer, L. A.; Sherman, H. L.; Pinnick, H. W. *Tetrahedron Lett.* **1984**, *25*, 1871. (b) Jones, R. C. F.; Bates, A. D. *Tetrahedron Lett.* **1986**, *27*, 5825.
(21) (a) Guzman, A.; Muchowski, J. M.; Saldena, J. *Chem. Ind.* **1977**, *9*, 357. (b) For synthesis of other N-substituted-3-pyrrolin-2-ones, see: Chalchat, J. C.; Garry, R. P.; Michet, A. C. R. *Seances Acad. Sci., Ser. 2* **1982**, *295* (10), 871.
(22) (a) Rathke, M. W.; Deitch, J. *Tetrahedron Lett.* **1971**, 2953. (b) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 531.
(23) McEwen, W. K. *J. Am. Chem. Soc.* **1936**, *58*, 1124.

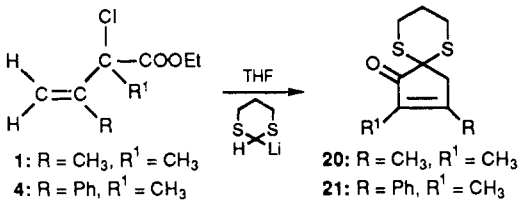
investigated. Addition of 1 equiv of **1** to a freshly prepared solution of sodium diphenylmethide in liquid ammonia followed by workup yielded after flash column chromatography 76% of **19**, the product resulting from alkylation at the tertiary carbon.



19

A normal S_N2 type of reaction is highly unlikely due to the steric crowding in the transition state. Sodium diphenylmethide is a powerful nucleophile capable of electron-transfer reactions.[24,25] A mechanism involving electron transfer to the allylic chloride **1** resulting in a radical anion which eliminates chloride ion and then couples with diphenylmethide is proposed here. It should be noted that the radical-coupled product tetraphenylethane was isolated in 12% yield, which is further support for this mechanism. There is growing evidence from a number of recent findings that in the reaction of nucleophiles with sterically hindered alkyl halides the electron-transfer pathway is preferred over the polar S_N2 type of mechanism.[26-28] Furthermore, reaction of **1** with weaker nucleophiles such as sodium diethylmalonate or sodium methoxide gave only recovered starting material under a variety of conditions.

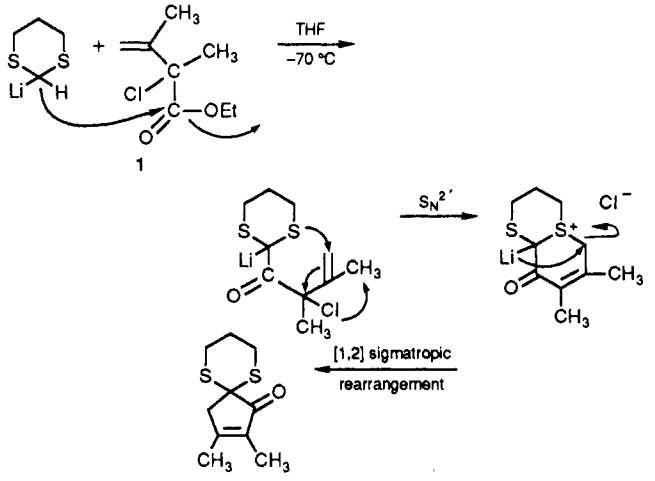
The reaction of the sulfur-stabilized carbanion, lithio-1,3-dithiane, with the tertiary allylic chlorides was also investigated. Lithio-1,3-dithiane is known to undergo alkylation,[29] acylation,[30] and conjugate addition[31] at low temperature. The reaction of this carbanion with **1** or **4** yielded 2,3-dimethyl-6,10-dithiaspiro[4.5]dec-2-en-1-one[32] (**20**) and 2-methyl-3-phenyl-6,10-dithiaspiro[4.5]dec-2-en-1-one (**21**), respectively.



1: R = CH_3, R^1 = CH_3
4: R = Ph, R^1 = CH_3

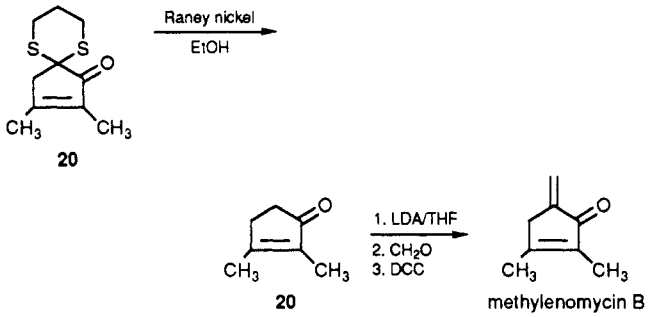
20: R = CH_3, R^1 = CH_3
21: R = Ph, R^1 = CH_3

The first step of the reaction is an acylation of **1** by lithio-1,3-dithiane to give an intermediate keto–dithiane enolate followed by a novel variation of the intramolecular abnormal S_N2 reaction. It is proposed that the final step is an intramolecular attack by sulfur on the allylic carbon to give a stable sulfonium ylide followed by a [1,2] sigmatropic[33] rearrangement to give the observed product.



The [1,2] sigmatropic shift is usually a very facile process and may well be concerted.[34] A significant experimental observation that lends support to the proposed mechanism is that the cyclopentenone formation is complete at −70 °C within a few minutes after mixing the reagents. That this is a sulfur-assisted S_N2' reaction can be attested by the fact that in the absence of sulfur similar systems undergo this cyclization only at higher temperature under forcing conditions. The details of this will be presented in a forthcoming paper. Furthermore, ylide formation during alkylation of selenium- and sulfur-substituted enolates has been well documented.[35] Ylide formation and subsequent [2,3] sigmatropic shift have been observed in the alkylation of allylic halides with 2-lithio-2-formyl-1,3-dithiane,[36] where the initial step involves a normal S_N2 attack by the sulfur atom.

The synthetic implications of this transformation are appealing since it opens up a new and easy route to substituted cyclopentenones. For example we have converted **20** through a Raney nickel desulfurization to yield 2,3-dimethyl-2-cyclopenten-1-one. This cyclopentenone can be, by the known procedure, converted to the antibiotic methylenomycin B[37] and therefore constitutes a formal total synthesis of this antibiotic.



Since a number of natural products such as prostanoids,[37b] jasmonoids, and pentanomycins incorporate the cyclopentenone unit, the general utility of this novel transformation deserves further studies. We have currently extended this methodology to the synthesis of di-

(24) (a) Recent work has shown that electrochemical oxidation of lithium diphenylmethide leads to tetraphenylethane. See: Bank, S.; Gernon M. *J. Org. Chem.* **1987**, *52*, 5105. (b) Bank, S.; Schepartz, A.; Giammater, P.; Zubieta, J. *J. Org. Chem.* **1983**, *48*, 3458.

(25) The possibility of electron-transfer mechanism in the conjugate addition of sodium diphenylmethide with acrylic esters has been suggested. See: Kofron, W. G.; Mathew, J. *J. Org. Chem.* **1976**, *41*, 114.

(26) Bordwell, F. G.; Wilson, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 5470.

(27) Everson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(28) For an indepth review on single electron transfer reactions, see: Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

(29) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231.

(30) Cameron, A. G.; Hewson, A. T. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2979.

(31) Vedejs, E.; Nader, B. *J. Org. Chem.* **1982**, *47*, 3193.

(32) (a) Kawamoto, I.; Muramatsu, S.; Yura, Y. *Tetrahedron Lett.* **1974**, *48*, 4223. (b) For a recent synthesis of a similar system, see ref 30.

(33) (a) Mithcell, R. H.; Boekelheide, Y. *J. Am. Chem. Soc.* **1974**, *96*, 1547. (b) For examples of [1,2] sigmatropic shift of stabilized sulfonium ylides, see: Block, E. *Reactions of organosulfur compounds*; Academic Press, Inc.: New York, 1978; p 118.

(34) Dewar, M. J. S.; Ramsden, C. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1839.

(35) Reichs, H. J.; Cohen, M. L. *J. Am. Chem. Soc.* **1979**, *101*, 1307.

(36) Wilson, S. R.; Mathew, J. *Synthesis* **1980**, 625.

(37) For other synthetic approaches to methylenomycin B, see: (a) Newton, R. F.; Reynolds, D. P. *Synth. Commun.* **1981**, *11*, 527. (b) Mikolajczyk, M.; Grazejszczak, S.; Kyzwa, P. *Tetrahedron Lett.* **1982**, *23*, 2237. (c) Jernow, J.; Tautz, W.; Rosen, P.; Williams, T. H. *J. Org. Chem.* **1979**, *44*, 4212. (d) Welch, S. C.; Assereg, J. H.; Loh, T. P.; Glase, S. A. *J. Org. Chem.* **1987**, *52*, 1440.

hydrojasmone and *cis*-jasmone. The results of these studies as well as the reaction of other heteroatom-stabilized carbanions with these allylic halides will be reported shortly.

Conclusions

We have shown that α-chloro-β,γ-unsaturated esters are viable intermediates for the efficient synthesis of several classes of compounds. The allylic chlorides are easily prepared from readily available unsaturated esters. These allylic halides undergo S_N2' reactions with neutral nucleophiles. In this study, abnormal S_N2 reaction products were not observed with thio anions or carbanions. A new route to functionalized cyclopentenones has been discovered, which most likely involves a [1,2] sigmatropic rearrangement of a stable sulfonium ylide.

Experimental Section

Melting points were determined in open capillaries with a Mel-Temp Laboratory Devices apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Petrolite Corporation, Analytical Section. The ^{13}C NMR spectra were obtained on a JOEL FX-60 spectrometer opeating at 15.04 MHz. Proton NMR spectra were obtained on a Perkin-Elmer R-32 90-MHz spectrometer. The chemical shifts (+) are downfield from tetramethylsilane. IR spectra were obtained on a Beckman AccuLab 8 spectrometer. Mass spectra were obtained on DuPont instruments DP-1 mass spectrometer system. GC analysis was performed on a Perkin-Elmer Sigma-2B gas chromatography using a DB-Wax column available from J and W Scientific. Flash column chromatography[38] was performed with silica gel 60 (230–440 mesh) purchased from Merck. All commercial chemicals were used as received. THF was either distilled from $LiAlH_4$ or Gold Label anhydrous THF supplied by Aldrich Chemical Company. Reagent grade $CHCl_3$, CH_2Cl_2, EtOAc, hexane, and ether were used. All reactions were done under N_2 unless specified.

Ethyl 2-Chloro-2,3-dimethyl-3-butenoate (1). To a stirred suspension of calcium hypochlorite (11 g, 70 mmol) in methylene chloride (20 mL) was added ethyl trimethylacrylate (14 g, 0.1 mol) all at once. The mixture was cooled to 0 °C and water (50 mL) was added followed by dropwise addition of glacial acetic acid (8 mL, 0.14 mol). The cloudy two-phase system was stirred at ice-bath temperature for 15 min and then warmed to room temperature. Water (100 mL) and methylene chloride (200 mL) were added. The organic layer was separated and washed with dilute sodium bicarbonate (2 × 40 mL) and water (40 mL) and then dried over anhydrous magnesium sulfate. Evaporation gave 15 g of crude colorless oil. GC and GC/MS analysis of this crude product indicated that 90% of the desired allylic chloride was present in the mixture. (Retention time, 4.3; *m/e* 176, injection port temperature was 220 °C). Flash column chromatography on silica gel (5% EtOAc/hexane) gave the allylic chloride **1** as a colorless oil (14 g, 80%), bp 54 °C/0.5 mmHg. IR (neat): 1750, 1600, 1500, and 1470 cm^{-1}. Mass spectrum: *m/e* 176 (M^+), 140 (base peak). Anal. Calcd for $C_8H_{13}O_2Cl$: C, 53.49; H, 7.36;, Cl, 20.11. Found: C, 53.92; H, 7.63; Cl, 20.27.

Ethyl 2-Chloro-3-methyl-3-butenoate (2). The above general procedure was followed. Thus, from ethyl 3,3-dimethylacrylate (1.30 g, 10 mmol), calcium hypochlorite (1.0 g, 7 mmol), acetic acid (0.8 mL, 11 mmol), and water (6 mL) was obtained a crude yellow oil. Flash column chromatography gave pure **2** (1.1 g, 66%) as a colorless oil, bp 50 °C/0.5 mmHg. IR (neat): 1750, 1600, and 1500 cm^{-1}, Mass spectrum: *m/e* 162 (M^+), 126 (base peak). Anal. Calcd for $C_7H_{11}O_2Cl$: C, 51.69; H, 6.76; Cl, 21.84. Found: C, 51.27; H, 6.74; Cl, 21.28.

Ethyl 2-Chloro-3-phenyl-3-butenoate (3). From ethyl 3-phenyl-2-butenoate (5.0 g, 22 mmol) and calcium hypochlorite (2.7 g, 19 mmol) was obtained a mixture of isomers (4.2 g, 83%) that was 70% of the desired ethyl 2-chloro-3-phenyl-3-butenoate and 30% of the conjugated ethyl-2-chloro-3-phenyl-2-butenoate by flash column chromatography on silica gel (5% EtOAc–hexane). These two regioisomers can be separated by flash column chromatography using 2% EtOAc/hexane as the eluting solvent. Mass spectrum: *m/e* 224 (M^+), 189 (base peak). Anal. Calcd for $C_{12}H_{13}ClO_2$: C, 64.14; H, 5.79. Found: C, 64.37; H, 5.92. IR (neat): 1750, 1600, 1500, and 1470 cm^{-1}.

Ethyl 2-Chloro-2-methyl-3-phenyl-3-butenoate (4). The *E* isomer of ethyl 2,3-dimethylcinnamate (8 g, 40 mmol) gave under the above general reaction conditions and after flash column chromatography, the desired allylic chloride **4** as a colorless oil (5 g, 64%). IR (neat) 1750, 1600, 1510, and 1480 cm^{-1}. Mass spectrum: *m/e* 238 (M^+), 203 (base peak). Anal. Calcd for $C_{13}H_{15}ClO_2$: C, 65.40; H, 6.28; Cl, 14.88. Found: C, 65.08; H, 6.31; C, 14.62.

Ethyl 2-(Phenylthio)-3-methyl-2-butenoate (6). A mixture of thiophenol (0.7 g, 6.36 mmol), **2** (1.05 g, 6.5 mmol), THF (2 mL), and tetrabutylammonium bromide (50 mg, cat.) was stirred at room temperature while 4 N NaOH (1.5 mL, 1 equiv) was added rapidly. The resulting mixture was diluted with water (50 mL) and extracted with ether (2 × 20 mL). Evaporation of solvent left a crude yellow oil (1.4 g). This was subjected to flash column chromatography. The vinyl sulfide **6** was obtained as a pale yellow oil (0.95, 81%). ^1H NMR ($CDCl_3$): 7.25 (m, 5 H), 4.10 (q, 2 H), 2.20 (s, 3 H), 2.18 (s, 3 H), and 1.10 (t, 3 H). ^{13}C NMR ($CDCl_3$): 164.54, 151.93, 133.62, 128.69, 128.30, 125.96, 60.90, 23.76, 23.37, and 13.89. Mass spectrum: *m/e* 236 (M^+), 201 (base peak). IR (neat): 1710, 1600, 1500, and 1470 cm^{-1}.

Ethyl 2-(Phenylthio)-3-phenyl-2-butenoate (7). Following the general procedure for phase-transfer alkylation, flash column chromatography of the crude yellow oil gave the vinyl sulfide **7** as an inseparable mixture of isomers (58%). ^1H NMR: 7.30 (m, 10 H), 4.05 (q, 2 H), 3.80 (q, 2 H), 2.40 (s, 3 H), 2.35 (s, 3 H), 1.10 (t, 3 H), and 0.75 (t, 3 H). ^{13}C NMR: 167.45, 149.82, 142.26, 129.83, 128.71, 60.77, 23.37, and 13.38. Mass spectrum: *m/e* 298 (M^+), 253, 115 (base peak). IR (neat): 1725, 1500, 1460, and 1250 cm^{-1}. Anal. Calcd for $C_{18}H_{18}SO_2$: C, 72.48; H, 6.04; S, 1074. Found: C, 72.01; H, 6.26; S, 10.87.

(*Z*)-Ethyl 2,3-Dimethyl-4-piperidino-2-butenoate (9). To a solution of **1** (0.75 g, 4.2 mmol) in toluene (0.5 mL) was added piperidine (1.1 mL, 2.8 equiv), and the solution was heated at 70 °C for 2 h. The yellow cake was cooled to room temperature, diluted with ether (50 mL), and filtered. The yellow filtrate washed with water (2 × 10 mL) and extracted with 1 N HCl (2 × 20 mL). The aqueous acidic extract adjusted to pH 9 with ammonium hydroxide and extracted with ether (2 × 20 mL). The organic extracts were washed with brine (10 mL) and dried over anhydrous K_2CO_3. Evaporation of solvents under vacuum gave amine[39] **9** as a viscous oil (0.85 g, 82%). ^1H NMR: 4.25 (g, 2 H), 3.10 (s, 2 H), 2.30 (t, 4 H), 1.90 (s, 3 H), 1.80 (s, 3 H), 1.50 (m, 6 H), and 1.30 (t, 3 H). IR (neat): 2980, 1725, 1500, 1250, and 1140 cm^{-1}. ^{13}C NMR: 170.11, 139.90, 125.70, 62.33, 59.86, 54.43, 26.10, 24.21, 17.66, 15.97, and 14.28. Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.33; H, 10.22; N, 6.22. Found: C, 69.11; H, 10.14; N, 5.97.

Ethyl 2,3-Dimethyl-4-(diethylamino)-2-butenoate (8). From diethylamine (1.0 g, 13 mmol) and allylic chloride **1** (0.8 g, 4.4 mmol) in benzene (1 mL) by the standard procedure and workup was obtained the pure amine adduct **8** as a yellow viscous oil (0.3 g, 32%). IR (neat): 1730, 1500, 1180 cm^{-1}. ^1H NMR: 4.20 (q, J = 7 Hz, 2 H), 3.20 (s, 2 H), 2.45 (q, 4 H), 1.90 (s, 3 H), 1.80 (s, 3 H), 1.30 (t, 3 H), and 1.00 (t, 6 H). ^{13}C NMR: 170.34, 138.98, 125.54, 60.11, 56.87, 46.87, 15.75, 14.23, and 11.81. Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.60; H, 10.79; N, 6.57. Found: C, 67.21; H, 10.45; N, 6.26.

(*Z*)-Ethyl 3-Phenyl-4-(diethylamino)-2-butenoate (10). To a solution of **3** (1.0 g, 4.42 mmol) in toluene (0.5 mL) was added diethylamine (1.45 mL, 3 equiv). A white precipitate developed in 5 min. The solution was warmed to 50 °C and kept at this temperature for 1 h. The thick yellow cake was diluted with ether (100 mL) and filtered. The yellow filtrate was evaporated under vacuum to give a viscous oil (1.4 g). This crude oil was subjected to the general treatment as described earlier to give the amine adduct **10** as a pale yellow oil (0.95 g, 78%). ^1H NMR ($CDCl_3$): δ 7.40 (m, 5 H), 6.10 (s, 1 H), 4.25 (q, 2 H), 4.0 (s, 2 H), 2.55 (q,

(38) Still, W. C.; Kahn, H.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(39) Owen, L. N.; Sultanbawa, M. U. S. *J. Chem. Soc.* **1949**, 3089.

4 H), 1.30 (t, 3 H), and 0.95 (t, 6 H). IR (neat): 2980, 1730, 1630, 1500, 1450, and 1170 cm^{-1}. Mass spectrum: m/e 261 (M^+). ^{13}C NMR: 166.35, 157.52, 140.96, 128.43, 127.91, 127.13, 120.25, 59.96, 50.90, 46.87, 14.28, and 11.26. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.56; H, 8.81; N, 5.36. Found: C, 73.15; H, 8.50; N, 5.06.

(*Z*)-Ethyl 3-Phenyl-4-piperidino-2-butenoate (11). The above procedure was repeated on **3** (0.8 g, 3.6 mmol) and piperidine (1 mL, 3 equiv) to give after work up and general treatment the pure amine adduct **11** as a pale yellow viscous oil (0.9 g, 88%). Mass spectrum: m/e 273 (M^+), 259 (base peak). IR (neat): 2940, 1720, 1500, 1450, and 1160 cm^{-1}. ^1H NMR: 7.75 (m, 2 H), 7.50 (m, 3 H), 6.20 (s, 1 H), 4.30 (q, 2 H), 3.95 (s, 2 H), 2.65 (m, 4 H), 1.65 (m, 6 H), and 1.45 (t, 3 H). ^{13}C NMR: 170.11, 141.80, 128.04, 127.40, 125.96, 120.38, 62.30, 60.25, 54.15, 25.84, 24.15, and 14.28. Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.72; H, 8.42; N, 5.09. Found: C, 74.44; H, 8.12, N, 4.96.

Ethyl 2-Methyl-3-phenyl-4-(diethylamino)-2-butenoate (12). From diethylamine (1.0 g, 13 mmol) and allyl chloride **4** (1.0 g, 4.2 mmol) was obtained by the standard procedure and workup the pure amine as a yellow viscous oil (0.75 g, 71%). IR (neat): 3020, 1725, 1500, and 1450 cm^{-1}. ^{13}C NMR: 170.21, 148.89, 141.32, 128.67, 127.91, 126.76, 60.46, 56.74, 46.98, 17.66, 14.43, and 11.29. ^1H NMR: 7.35 (m, 5 H), 4.25 (q, 2 H), 3.45 (s, 2 H), 2.45 (q, 4 H), 1.80 (t, 3 H), and 1.00 (t, 6 H). Mass spectrum: m/e 275 (M^+), 247 (base peak). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.18; H, 9.09; N, 5.09. Found: C, 74.04; H, 8.67; H, 5.38.

Ethyl 2-Methyl-3-phenyl-4-piperidino-2-butenoate (13). From piperidine (0.9 g, 5 mmol) and allyl chloride **4** (0.8 g, 1.68 mmol) was obtained by the standard procedure a viscous oil of the amine adduct **13** (0.84 g, 92%). IR (neat): 1725, 1600, and 1500. ^1H NMR: 7.40 (m, 5 H), 4.30 (q, 2 H), 3.25 (s, 2 H), 2.40 (4 H, m), 1.80 (s, 3 H), 1.50 (m, 6 H), and 1.30 (t, 3 H). ^{13}C NMR: 171.21, 148.09, 141.04, 128.65, 127.91, 62.46, 60.25, 54.15, 25.84, 24.28, 17.46, and 14.15. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.26; H, 8.71; N, 4.87. Found: C, 75.70; H, 8.64; N, 5.21.

1,5-Dihydro-1-benzyl-3,4-dimethyl-2*H*-pyrrol-2-one (14). To a solution of **1** (0.80 g, 4.4 mmol) in toluene (1 mL) was added benzylamine (1.1 g, 3 equiv). The cloudy solution was stirred at room temperature for 1 h and then heated to 70 °C for 2 h. The yellow cake was diluted with ether (20 mL) and filtered. The yellow filtrate was evaporated to give a yellow viscous oil (1.1 g). Flash column chromatography gave the unsaturated lactam **14** (5% EtOAc/CH_2Cl_2) as a yellow viscous oil (0.75 g, 76%). IR (neat): 2750, 1680, 1500, and 1450 cm^{-1}. ^1H NMR: 7.30 (s, 5 H), 4.60 (s, 2 H), 3.60 (s, 2 H), 1.90 (s, 3 H), and 1.80 (s, 3 H). ^{13}C NMR: 177.45, 145.70, 137.62, 128.62, 127.71, 53.63, 45.97, 12.85, and 8.80. Mass spectrum: m/e 102 (M^+), 186, 91 (base peak). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.61; H, 7.46; N, 6.76. Found: C, 77.33; H, 7.54; N, 7.45.

1,5-Dihydro-1-benzyl-4-phenyl-2*H*-pyrrol-2-one (15). To a solution of **3** (0.8 g, 3.6 mmol) in benzene (0.5 mL) was added benzylamine (1 mL, 3 equiv). The cloudy solution was heated at 70 °C for 2 h. The resulting yellow cake was diluted with ether (20 mL) and filtered, and the yellow filtrate was evaporated to give viscous paste. Flash column chromatography on silica gel gave the desired unsaturated lactam **15** eluting in 20% EtOAc/CH_2Cl_2 as a white powder. (0.85 g, 68%), mp 162–163 °C. IR (KBR): 3050, 1670, 1500, 1450, 1220, and 1070 cm^{-1}. Mass spectrum: m/e 249 (M^+), 220 (base peak). ^{13}C NMR: 154.90, 137.26, 130.21, 128.69, 127.78, 125.70, 119.73, 51.81, and 45.71. ^1H NMR: 7.50 (m, 10 H), 6.60 (s, 1 H), 4.80 (s, 2 H), and 4.30 (s, 2 H). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.92; H, 6.02; N, 5.62. Found: C, 81.81; H, 5.88; N, 5.65.

1,5-Dihydro-1-benzyl-3-methyl-4-phenyl-2*H*-pyrrol-2-one (16). By the above procedure **4** (1 g, 4.2 mmol) was reacted with benzylamine to give after flash column chromatography the lactam **16** as a yellow viscous oil (0.8 g, 74%). IR (neat): 3050, 2950, 1680, 1500, and 1450 cm^{-1}. ^1H NMR: 7.40 (m, 10 H), 4.70 (s, 2 H), 4.05 (s, 2 H), and 2.15 (s, 3 H). ^{13}C NMR: 176.82, 145.76, 139.56, 128.69, 128.04, 51.55, 46.23, and 10.77. Mass spectrum: m/e 263 (M^+), 158 (base peak). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.18; H, 6.46; N, 5.32. Found: C, 82.38; H, 6.41; N, 5.57.

Ethyl 2-Piperidino-3-methyl-2-butenoate (17). A mixture of **2** (0.6 g, 3.6 mmol), toluene (0.5 mL), and piperidine (1 g, 3 equiv) was heated at 65 °C for 2 h and the resulting yellow cake diluted with ether (20 mL) and filtered. The yellow filtrate was evaporated under vacuum to give a viscous oil from which the pure amine was isolated in high purity by the standard method to give **17**: bp 80 °C/1 mm (0.6 g, 78%). ^1H NMR: 4.30 (q, 2 H), 2.45 (m, 4 H), 2.30 (s, 3 H), 2.15 (s, 3 H), 1.60 (m, 6 H), and 1.40 (t, 3 H). IR (neat): 2980, 1720, 1600, and 1500 cm^{-1}. Mass spectrum: m/e 211 (M^+), 196 (base peak).

Ethyl 3-Oxo-4-chloro-4,5-dimethyl-5-hexenoate (18). To a stirred solution of hexamethyldisilazane (1 mL, 4.2 mmol) in THF (5 mL) at 70 °C under nitrogen was added 2.5 M *n*-BuLi (1.7 mL, 2.05 equiv) dropwise via syringe. After 15 min, a solution of ethyl acetate (0.4 mL, 3.9 mmol) in THF (2 mL) was added dropwise via syringe. The resulting deep yellow solution was stirred for 45 min. A solution of ester **1** (0.37 g, 2.1 mmol) in THF (2 mL) was added rapidly. The pale yellow orange solution was stirred at −70 °C for 30 min and then warmed to 0 °C. 1 N HCl (20 mL) was added and then extracted with ether (2 × 20 mL). The ether extracts were washed with saturated brine (2 × 10 mL) and dried over magnesium sulfate. Evaporation gave a yellow oil (1.05 g). Flash column chromatography on silica gel gave ethyl 3-oxo-4-chloro-4,5-dimethyl-5-hexenoate (**18**) as a pale yellow oil (0.35 g, 71%), eluting in 20% EtOAc–$CHCl_3$. ^1H NMR: 5.35 (s, 1 H), 5.15 (q, J = 1 Hz, 1 H), 4.15 (q, 2 H), 3.70 (s, 2 H), 1.85 (d, J = 1 Hz, 3 H), 1.75 (s, 3 H), and 1.30 (t, 3 H). ^{13}C NMR: 202.8, 170.60, 145.4, 115.70, 62.33, 61.29, 46.63, 25.71, 19.34, and 14.02. IR (neat): 2980, 1760, 1720, 1650, 1450, and 1300 cm^{-1}. Mass spectrum: m/e 218 (M^+), 182 (base peak). Anal. Calcd for $C_{10}H_{15}O_3Cl$: C, 54.91; H, 6.86; Cl, 16.24. Found: C, 54.79; H, 6.7; Cl, 15.97.

Ethyl 2-Methyl-2-(diphenylmethyl)-3-methyl-3-butenoate (19). Anhydrous liquid ammonia (50 mL) was condensed into a three-neck flask fitted with a dry ice condenser, dropping funnel, and inlet tube. A crystal of anhydrous ferric chloride was added followed by a tiny piece of sodium. When the deep blue color of the solution faded to grey, more sodium was added until a total of 0.23 g (10 mmol) was consumed. To the grey suspension was added a solution of diphenylmethane (1.68 g, 10 mmol) in ether (5 mL) via the dropping funnel. The orange red solution was stirred for 15 min and then a solution of ester **1** (1.76 g, 10 mmol) in ether (2 mL) was added rapidly. A colorless solution with some white precipitate resulted instantly. Ammonium chloride (2 g, excess) was added and then the ammonia was allowed to evaporate while ether (100 mL) was added. The ether suspension was washed with 0.5 N HCl (50 mL) and the ether extract was again washed with brine (2 × 10 mL) and dried over magnesium sulfate. Evaporation of solvent gave a yellow viscous oil (3 g). Flash column chromatography on silica gel gave unreacted diphenylmethane (0.3 g, 12%), tetraphenylethane (0.5 g, 10%), and the adduct **19** (2.25 g, 76%) as a viscous oil, which solidified to white fluffy crystals. This was dried under vacuum, mp 48 °C. ^1H NMR: 7.30 (10 H, m), 5.05 (3 H, m), 4.10 (2 H, q), 1.80 (3 H, s), 1.55 (3 H, s), and 1.15 (3 H, t). ^{13}C NMR: 174.24, 143.36, 141.67, 130.41, 127.80, 126.09, 114.79, 60.79, 55.06, 56.81, 21.03, 19.02, and 13.89. IR (neat): 3050, 2970, 1740, 1600, 1500, 1450, and 1210 cm^{-1}. Mass spectrum: m/e 308 (M^+). Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.94; H, 7.80. Found: C, 81.81; H, 7.79.

2,3-Dimethyl-6,10-dithiaspiro[4.5]dec-2-en-1-one (20). To a solution of dithiane (1.2 g, 10 mmol) in THF (15 mL) at −70 °C was added dropwise with stirring 2.5 M *n*-BuLi (4 mL, 1 equiv). The pale yellow solution was stirred at this temperature for 45 min. A solution of the allylic chloride **1** (1.0 g, 5.7 mmol) in THF (2 mL) was added rapidly in 30 s. The resulting solution was slowly allowed to warm to room temperature in 1 h. The yellow solution changed to a deep orange brown at room temperature. The reaction mixture was poured into a solution of ether (20 mL) and saturated NH_4Cl (5 mL). The organic extract was washed with brine (5 mL) and dried. Evaporation of solvent gave a yellow viscous oil. Flash column chromatography gave an intensely UV-active lower R_f fraction (5% EtOAc/hexane). The pooled fractions were evaporated to give colorless solid **20** (0.9 g, 74%), mp 62 °C. IR (KBr): 2970, 1700, 1650, 1430, and 1050 cm^{-1}. Mass spectrum: m/e 214 (M^+), 81 (base peak). ^{13}C NMR: 204.01, 162.32, 131.28, 48.43, 45.18, 26.12, 24.54, 16.49, and 8.18. ^1H NMR: 3.95 (2 H, dt, 7- and 9-axial H's), 2.62 (2 H, dd, 4-CH_2), 2.20–2.55 (2 H, m, 7- and 9-equatorial H's), 2.05 (3 H, s), 1.80 (2 H, m, 8-CH_2), and 1.70 (3 H, s). Anal. Calcd for $C_{10}H_{14}S_2O$: C, 56.07; H, 6.54; S, 29.90. Found: c, 56.12; H, 6.59; S, 30.13.

2-Methyl-3-phenyl-6,10-dithiaspiro[4.5]dec-2-en-1-one (21). The above general procedure was followed on dithiane (0.6 g, 5 mmol) and allylic chloride **4** (0.7 g, 3.2 mmol) to give after flash column chromatography the desired cyclopentenone **21** as a yellow viscous oil (0.4 g, 45%). IR (neat): 1700, 1650, 1600, and 1500 cm^{-1}. Mass spectrum: *m/e* 276 (M^+), 243 (base peak). ^{13}C NMR: 204.06, 159.34, 134.92, 129.86, 128.56, 127.65, 128.17, 46.48, 45.32, 26.36, 24.14, and 10.25. ^1H NMR: 7.50 (s, 5 H, Ar H), 3.95 (2 H, dt, J = 14, 2.5 Hz, 7- and 9-axial H's), 2.95 (2 H, d, J = 2.5 Hz, 4-CH_2), 2.60 (2 H, dm, J = 14 Hz, 7- and 9-equatorial H's), 2.10 (2 H, m, 8-CH_2's), and 1.95 (3 H, s). Anal. Calcd for $C_{15}H_{16}S_2O$: C, 65.21; H, 5.79; S, 23.18. Found: C, 65.02; H, 5.94; S, 22.96.

2,3-Dimethyl-2-cyclopenten-1-one (22). A solution of **20** (0.84 g, 4 mmol) in ethanol (25 mL) was treated carefully with a slurry of Raney nickel[40] (1.2 mL) and refluxed for 1 h. The mixture was then cooled, filtered through Celite, and concentrated. Flash column chromatography of the resulting oil gave the cyclopentenone **22** (0.3 g, 70%) eluting in 50% EtOAc/hexane as a colorless oil. IR (neat): 1700, 1650 cm^{-1}. ^1H NMR: 2.38 (m, 4 H), 2.10 (s, 3 H), and 1.68 (s, 3 H). Mass spectrum: *m/e* 110 (M^+), 67 (base peak). ^{13}C NMR: 209.15, 169.30, 135.80, 33.50, 30.96, 16.10, and 7.20.

Acknowledgment. We thank Dr. Derek Redmore for proofreading the entire manuscript. Prof. Barry Trost (Standford University) and Prof. Frederick Bordwell (Northwestern University) are acknowledged for some helpful information.

(40) Obtained from Aldrich Chemical Company.

Micellar Catalysis of Organic Reactions. 27.† Micellar Bound Meisenheimer Complexes

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Received October 17, 1989

Reactions of nitro activated aryl halides with base in the presence of dihydroxy micelles of cetyl(2,3-dihydroxypropyl)dimethylammonium bromide (CDHPDAB) give rise to spiro Meisenheimer complexes that are covalently bound to the micelles. From the large fluorine/chlorine rate ratios observed for these reactions, we conclude that the initial attack on the aryl halide by the micellar hydroxyl group is the rate-determining step for the formation of the Meisenheimer complex. For the subsequent decomposition of the complex the rate of reaction is dependent on hydroxide concentration if the complex contains only one ortho substituent. This indicates that the breakdown of the aryl micellar ether formed in the first step of the decomposition is the rate-determining step. However, for complexes containing two ortho substituents, the rate of decomposition is almost independent of the hydroxide concentration, indicating for these complexes that the rate-determining step is the initial unimolecular breakdown of the Meisenheimer complex to form the micellar ether. It is proposed that this change is caused by the built-in solvation effect of Bunnett et al. in which the positive charge on the side chain of the complex is stabilized by an electrostatic interaction with either the negatively charged carboxylate group or the dipolar nitro group.

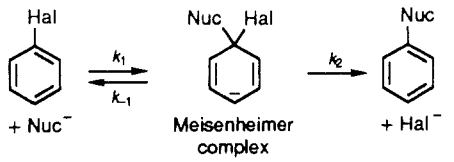
Introduction

The currently accepted mechanism for the nucleophilic aromatic substitution of activated aromatic substrates (see Scheme I) is a two-step process in which carbon–nucleophile bond formation precedes carbon–nucleofuge bond breakage.[1-4] An anionic intermediate termed a Meisenheimer complex[5-7] is formed during this reaction. In most reactions the formation of this complex is rate determining since the presence of a good nucleofuge makes the breakdown of the complex fast. This conclusion is supported by the large fluorine/chlorine rate ratios observed.

For the formation of the complex the polarization of the carbon–halogen bond is important in determining the reactivity (electrophilicity) of the aromatic carbon atom under attack. The greater electronegativity of fluorine than that of chlorine[8a] thus results in the observed F/Cl rate ratios. On the other hand, the decomposition of the complex involves carbon–halogen bond breakage, and in this case the mobility of the halogens should depend on the carbon–halogen bond strength as is the case for both S_N1 and S_N2 reactions.[8b]

Attempts to isolate the Meisenheimer complexes formed in these S_NAr reactions failed because the decomposition

Scheme I



of the complex (k_2 or k_{-1} in Scheme I) was too fast.

To overcome this problem it has become common to study the reactions of activated aryl ethers with alkoxide ions for which decomposition of the complex is slow because alkoxide ions are poor nucleofuges. In suitably stabilized compounds, e.g., 1-ethoxy-2,4,6-trinitrobenzene, the Meisenheimer complex formed by reaction with methoxide ions has been isolated. In less stabilized systems, e.g., the 2,4-dinitrobenzene and the mononitrobenzene derivatives, the corresponding intermediate has

† Part 26: Broxton, T. J.; Christie, J. R.; Chung, R. P.-T. *Aust. J. Chem.* **1989**, *42*, 855.

(1) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273.
(2) Bunnett, J. F. *Q. Rev. Chem. Soc.* **1958**, *12*, 1.
(3) Bunnett, J. F.; Garbisch, E. N.; Pruitt, K. M. *J. Am. Chem. Soc.* **1957**, *79*, 385.
(4) Bunnett, J. F.; Garst, R. H. *J. Am. Chem. Soc.* **1965**, *87*, 3879.
(5) Meisenheimer, J. *Ann. Chim.* **1902**, *323*, 205.
(6) Foster, R.; Fyfe, C. A. *Rev. Pure Appl. Chem.* **1966**, *16*, 61.
(7) Pollitt, R. J.; Saunders, B. C. *J. Chem. Soc.* **1964**, 1132.
(8) McMurry, J. *Organic Chemistry*, 2nd ed.; Brooks Cole Publishing Co.: Pacific Grove, CA 1984; (a) p 40, (b) p 353, (c) p 101.

0022-3263/90/1955-3886$02.50/0