Tetrahedron Vol 49, No. 29, pp 6473-6482, 1993
Printed in Great Britain

0040-4020/93 $6 00+.00

1-Lithio-2,2-Diphenoxy-1-(Phenylsulfonyl)cyclopropane as β-Lithio Acrylate and Cyclopropanone Acetal Anion Synthons.

Manat Pohmakotr* and Jantima Ratchataphusit[1]

Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Rd, Bangkok 10400, THAILAND.

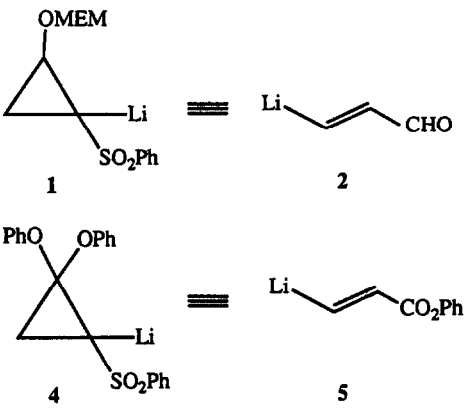
(*Received in UK* 6 *May* 1993)

Abstract: 1-Lithio-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (4) reacted with alkyl halides to give the alkylated cyclopropyl sulfones 6, which were subjected to hydrolysis with $TiCl_4$ in CH_2Cl_2 followed by elimination of the phenylsulfonyl group with DBU to afford α,β-unsaturated esters 8 and small amount of β,γ- unsaturated esters 9. Furthermore, reductive removal of the phenylsulfonyl group of compound 6 by using 6% Na-Hg furnished 2-alkyl substituted cyclopropanone acetals 12 in good yields.

INTRODUCTION

The chemistry of cyclopropanes have been extensively studied both in the theoretical point of view and in organic synthesis as three-carbon building blocks. The cleavage of cyclopropanes due to strain release offers the possibilities of making new carbon-carbon bonds and manipulating of some interesting synthetic conversions. This permits the development of synthetic strategies to many types of complex molecules[2]. Cyclopropanes possessing functional groups such as electron withdrawing and/or hetero-atom substituents[3a,b,c] are of special interest, because of their abilities to produce the corresponding cyclopropyl carbanions, which lead to some useful synthetic transformations.

Recently, development of new synthetic methods for the bond connection β to carbonyl group constitutes one of the most exciting area in the modern synthesis. Functionalised cyclopropanes such as siloxycyclopropanes have been shown to be very useful for serving such objectives.[3c,4] Our interest concerning the utility of the functionalised cyclopropanes as three-carbon building blocks has led us to investigate new other possibilities. In connection with our recent report concerning the synthetic utilities of 1-[(2-methoxyethoxy)methoxy)]-2-(phenylsulfonyl)cyclopropane (1) as a β-lithio acrolein synthon 2[5] prompted us to report herein that the anion 4 derived from 2,2-diphenoxy-1-(phenysulfonyl)cyclopropane (3)[6] could serve as a new β-lithio acrylate synthon 5.[7]

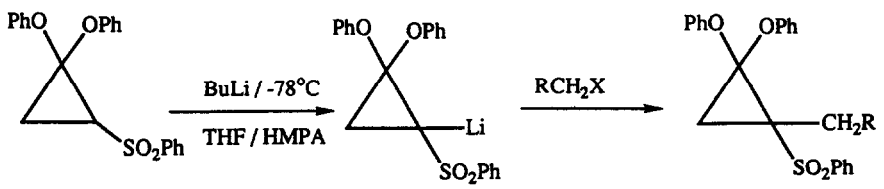


1 2

4 5

RESULTS AND DISCUSSION

Lithiation of the readily available cyclopropyl sulfone **3** could be achieved by employing butyllithium (1-1.2 equiv) in tetrahydrofuran (THF) at -78 °C for 1 h. The resulting THF solution of the anion **4** was reacted with benzyl bromide at - 78 °C followed by slowly warming up to room temperature (18 h) to provide the expected product **6a** in 41 %. Under similar reaction conditions, the anion **4** reacted with allyl bromide and butyl bromide to give the alkylated products **6b** and **6c** in 29% and 24% yields, respectively. From these experiments, we observed that not only the expected products **6** could be isolated, but also the starting sulfone **3** (20-24 %) along with the unidentified products. The anion **4** seemed to be partly decomposed during the reaction period. We therefore decided to use hexamethylphosphoramide (HMPA) as a cosolvent, hoping that it would facilitate both metalation and alkylation steps. As expected, lithiation of the cyclopropyl sulfone **3** with BuLi in THF in the presence of HMPA at -78 °C for 1 h followed by quenching with benzyl bromide (-78 °C to rt, 18 h) afforded the desired product **6a** in 69% after chromatographic purification. Moderate yields of **6b** (66%) and **6c** (56%) were obtained under the same conditions. A better yield of **6c** (87%) was obtained when butyl iodide was employed instead of butyl bromide. The results with other alkylating agents are summarized in **Table 1**. To study the scope and limitation of the reactivity of the anion **4**, it was further reacted with carbonyl compounds. It was found that the reaction of the anion with pivalaldehyde or acetone at -78 °C (2 h) or at -78 °C to room temperature (overnight) in the presence or absence of HMPA did not result the expected hydroxyalkylated adduct. From ^{1}H-NMR and TLC analyses of the crude products obtained, it was found that they contained mainly the starting cyclopropyl sulfone **3**.



3 4 6

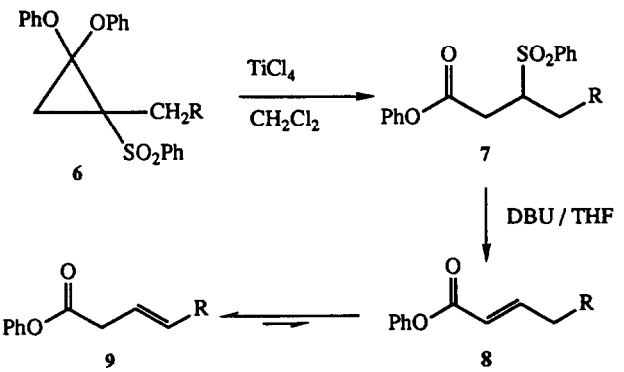
Table 1. Preparation of 1-Alkyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (**6**).

Alkylating Agents	Products 6	Yields (%)[a]
$PhCH_2Br$	**6a**, R = Ph-	69
$CH_2=CHCH_2Br$	**6b**, R = CH_2=CH-	66
$CH_3(CH_2)_3Br$	**6c**, R = $CH_3(CH_2)_2$-	56
$CH_3(CH_2)_3I$	**6c**, R = $CH_3(CH_2)_2$-	87
CH_3I	**6d**, R = H-	87
CH_3CH_2I	**6e**, R = CH_3-	72
$CH_3(CH_2)_4Br$	**6f**, R = $CH_3(CH_2)_3$-	75
$CH_3(CH_2)_5Br$	**6g**, R = $CH_3(CH_2)_4$-	80
$CH_3(CH_2)_6Br$	**6h**, R = $CH_3(CH_2)_5$-	70
$CH_3(CH_2)_7Br$	**6i**, R = $CH_3(CH_2)_6$-	81

[a] = Isolated products by flash column chromatography (SiO_2).

Hydrolysis of the Alkylated Cyclopropylsulfones 6.

Cyclopropanes containing both donor and acceptor substituents in the 1,2-position undergo ring cleavage under acidic conditions as extensively studied by many groups.[8] It was therefore expected that the cyclopropyl sulfones **6** could be transformed into β-sulfonyl esters of type **7** upon hydrolysis, which would be able to convert to the desired α,β-unsaturated esters **8** after treatment with base.



Initially, attempts were made to hydrolyse the cyclopropyl sulfone **6c** by employing various conditions e.g. conc. H_2SO_4/MeOH/reflux (3 h), 47% HBr/reflux (12 h), Me_3SiI/CH_3CN/reflux (18 h) and

AlI_3/CH_3CN/reflux (5 h).[9] The reactions, however, were unsuccessful, only the starting cyclopropyl sulfone **6c** was recovered in nearly quantitative yield. We turned our attention to use $TiCl_4$[10] for the hydrolysis of the cyclopropyl sulfone **6**. As expected, treatment of the cyclopropyl sulfone **6c** with 2-5 equiv. of $TiCl_4$ in dry dichloromethane at 0 °C to room temperature for 20 h afforded mainly the expected β-phenylsulfonyl substituted ester of **7** [R = $CH_3(CH_2)_2$-] and small amount of the unsaturated esters **8d** and **9d** as revealed by ^{1}H-NMR spectrum of the crude product obtained. Since the reaction gave a mixture of the desired products **7** [R = $CH_3(CH_2)_2$-], **8d** and **9d**, it was therefore tried to carry out the reaction starting from the cyclopropyl sulfone **6** to the unsaturated esters **8** and **9** without separation of the ring-opened product of type **7**. Thus, the reaction of the cyclopropyl sulfone **6c** with 5 equiv of $TiCl_4$ in CH_2Cl_2 followed by treatment of the resulting crude product obtained with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in THF at room temperature furnished a mixture of the expected products **8d** and **9d** in 43% (86:14) after chromatography. The results for the hydrolysis of other cyclopropyl sulfones **6** are listed in **Table 2**. The only case that did not give the expected unsaturated ester was the cyclopropyl sulfone **6a**, since the reaction provided a complex mixture. A mechanism for the hydrolytic ring opening of the cyclopropyl sulfone **6** was proposed to involve intermediates **10** and **11** leading to β-phenylsulfonyl ester **7** after aqueous workup.

The results demonstrated that the cyclopropyl anion **4** derived from the cyclopropanes possessing both donor and acceptor substituents such as compound **3** could serve as a β-lithio acrylate synthon **5**.

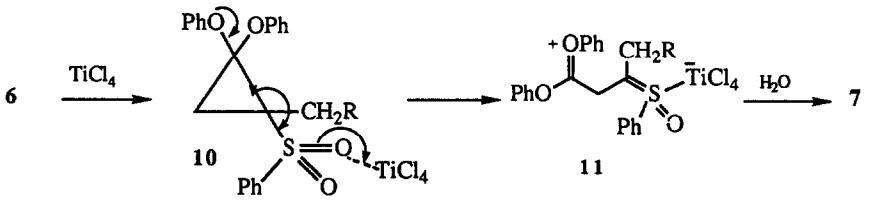


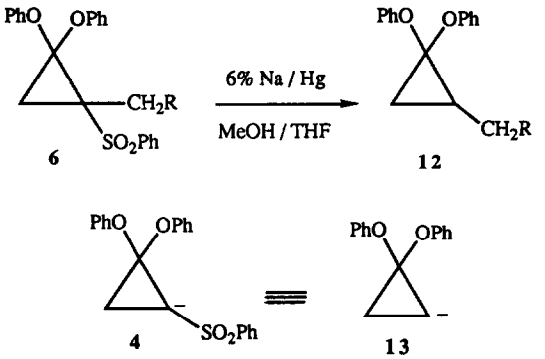
Table 2. Preparation of the Unsaturated esters **8** and **9** from the Cyclopropyl Sulfones **6**.

Sulfones **6**	Products **8** and **9**		Yields[a] (%)	Ratio[b] of 8:9
6d, R = H-	**8a**, R = H-	**9a**, ---	41	100:0
6e, R = CH_3-	**8b**, R = CH_3-	**9b**, R = CH_3-	38	85:15
6b, R = CH_2=CH-	**8c**, $CH_3(CH{=}CH)_2CO_2Ph$	**9c**, ---	31	100:0
6c, R = $CH_3(CH_2)_2$-	**8d**, R = $CH_3(CH_2)_2$-	**9d**, R = $CH_3(CH_2)_2$-	43	86:14
6f, R = $CH_3(CH_2)_3$-	**8e**, R = $CH_3(CH_2)_3$-	**9e**, R = $CH_3(CH_2)_3$-	45	85:15
6g, R = $CH_3(CH_2)_4$-	**8f**, R = $CH_3(CH_2)_4$-	**9f**, R = $CH_3(CH_2)_4$-	49	82:12
6h, R = $CH_3(CH_2)_5$-	**8g**, R = $CH_3(CH_2)_5$-	**9g**, R = $CH_3(CH_2)_5$-	43	86:14
6i, R = $CH_3(CH_2)_6$-	**8h**, R = $CH_3(CH_2)_6$-	**9h**, R = $CH_3(CH_2)_6$-	39	82:18

[a] = Isolated yields as a mixture of **8** and **9**.
[b] = Determined by ^{1}H-NMR spectroscopy.

Preparation of 2-Alkyl Cyclopropanone Acetals 12 by Reduction of the Cyclopropyl Sulfones 6.

Having succeeded in preparing the α,β-unsaturated esters **8** from cyclopropyl sulfones **6**, it was tried to further present the synthetic utilities of the products of type **6**. If the phenylsulfonyl group of compound **6** could be removed, 2-alkyl substituted cyclopropanone acetals of type **12**[12], would be achieved. This conversion should provide an easy entry to substituted cyclopropanone acetals, which may be useful as intermediates in organic synthesis. The anion **4** will therefore be the synthetic equivalent of the cyclopropanone acetal anion **13**,[11,12] which can not be directly generated.



The conversion of the cyclopropyl sulfone **6** to the desired 2-alkyl substituted cyclopropanone **12** could be accomplished by using excess 6% Na-Hg[13] in a mixture of methanol and THF at room temperature. Good yields of the products **12** were obtained and the results are summarized in **Table 3**.

Table 3. Preparation of 2-Alkyl substituted Cyclopropanone Acetals **12.**

Cyclopropanes	Results	Yields[a] (%)
6d	**12a**, R = H-	91
6e	**12b**, R = CH_3-	79
6b	**12c**, R = CH_2=CH-	86
6c	**12d**, R = $CH_3(CH_2)_2$-	93
6f	**12e**, R = $CH_3(CH_2)_3$-	77
6g	**12f**, R = $CH_3(CH_2)_4$-	83
6h	**12g**, R = $CH_3(CH_2)_5$-	88
6i	**12h**, R = $CH_3(CH_2)_6$-	86
6a	**12i**, R = Ph-	91

[a] = Isolated yields.

CONCLUSION

Our above results clearly demonstrated that the sulfonyl carbanion **4** derived from the donor-acceptor substituted sulfonylcyclopropane **3** could serve as β-acrylate anion **5** and cyclopropanone acetal anion synthon **13**. The reaction provided an easy entry for the synthesis of α,β-unsaturated esters and 2-alkyl substituted cyclopropanone acetals,[11,12] which are useful precursors in organic synthesis.

EXPERIMENTAL SECTION

Melting points were determined by a Buechi 510 Melting Point Apparatus and are uncorrected. ^{1}H-NMR spectra were measured at 60 MHz with a Varian EM-360L spectrometer using Me_4Si as internal reference; J-values are given in Hz. IR spectra were recorded on a Jasco A-302 Spectrophotometer. Mass spectra were obtained on an INCOS 50 Mass Spectrometer at 70 eV. Elemental analyses were performed by using a Perkin Elmer Elemental Analyzer 2400 CHN. 2,2-Diphenoxy-1-(phenylsulfonyl)cyclopropane (**3**) was prepared according to the literature procedure[6].

Preparation of 1-Alkyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropanes 6a-i.

General Procedure:

To a cooled (-78 °C) THF (9 ml) solution of 2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (**3**) (0.73 g, 2 mmol) in the presence of HMPA (1 ml) was added dropwise ^{n}BuLi (1.4 M solution in hexane, 1.8 ml, 2.5 mmol). After stirring under argon at -78 °C for 1 h, alkyl halide (2.5 mmol) was added. The resulting mixture was stirred and slowly warmed up from -78 °C to room temperature overnight (18 h). Water (30 ml) was added and the product was extracted with ethyl acetate (3x30 ml). The combined extracts were washed with H_2O (5x10 ml), brine (10 ml) and dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography (silica gel, 10-15 % EtOAc in hexane) to afford a solid product of **6**.which could be recrystallized from a mixture of ethyl acetate and hexane.

1-Benzyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (6a): 69%; m.p. 142-143 °C; IR($CHCl_3$): ν_{max} 3020, 1600 1500, 1450, 1420, 1320, 1310, 1180, 1150, 1090, 1080, 1030, 980, 870, 690 cm^{-1}; NMR($CDCl_3$): δ 1.43 and 2.36 (each d, J = 8 Hz, 2H *-CH_2- parts of cyclopropane*), 2.73 and 3.76 (each d, J = 16 Hz, 2H, *benzylic protons*), 6.4-7.5 (m, 10H, Ar-*H*), 7.6-8.0(m, 3H, Ar-*H*), 8.0-8.45 (m, 2H, Ar-*H*); MS: m/e(%) relative intensity: 315(M^+-141, 49), 221(100), 203(16), 194(12), 193(62), 178(11), 143(13), 128(15), 125(34), 115(51), 91(25), 77(28), 51(11). Anal. Calcd for $C_{28}H_{24}O_4S$: C, 73.66; H, 5.29. Found: C, 73.39; H,5.23.

1-Allyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (6b): 66%; m.p. 118-119 °C; IR($CHCl_3$): ν_{max} 3010, 1640, 1600, 1500, 1450, 1420, 1320, 1190, 1150, 1090, 1030, 980, 930, 840, 690 cm^{-1}; NMR ($CDCl_3$): δ 1.65 and 2.35 (each d, J = 8 Hz, 2H, *-CH_2- parts of cyclopropane*), 2.06 (dd, J = 8, 16 Hz, 1H, AB system of *allylic protons*) and 2.90 (dd, J = 5, 16 Hz, 1H, AB system of *allylic protons*), 4.63-5.25 (m, 2H, *CH_2*=CH-), 5.35-6.30 (m, 1H, CH_2=*CH*-), 6.60-8.40 (m, 15H, Ar-*H*); MS: m/e(%) relative intensity: 265(M^+-141, 53), 233(26), 171(76), 143(100), 125(61), 115(19), 95(20), 91(17), 77(95), 67(44). Anal. Calcd for $C_{24}H_{22}O_4S$: C,70.94; H, 5.42. Found: C, 70.87; H, 5.45.

1-Butyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (6c): 56% (butyl bromide) and 87% (butyl iodide); m.p. 130-132 °C; IR($CHCl_3$): ν_{max} 2970, 1600, 1500, 1450, 1420, 1320, 1310, 1190, 1140, 1090, 1030, 980, 940, 690 cm^{-1}; NMR($CDCl_3$) : δ 0.40 - 2.07 (m, 9H, *methyl and methylene protons*), 1.5 and 2.3 (each d, J = 7 Hz, 2H, *-CH_2- parts of cyclopropane*), 6.26-7.33 (m, 10H, Ar-*H*), 7.37-7.77 (m, 3H, Ar-*H*), 7.77-8.20 (m, 2H, Ar-*H*); MS: m/e(%) relative intensity: 281(M^+-141, 22), 223(10), 203(8),187(60), 159(19), 145(61), 125(51), 91(36), 77(100), 67(17), 55(41). Anal. Calcd for $C_{21}H_{18}O_4S$: C, 71.06; H, 6.20. Found: C, 71.31; H, 6.11.

1-Methyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (6d): 87%; m.p. 115-117 °C ; IR ($CHCl_3$): ν_{max} 3050, 1600, 1500, 1450, 1320, 1200, 1160, 1150, 1080, 980, 940, 880, 690, 620,cm^{-1}; NMR

($CDCl_3$): δ 1.4 (s, 3H, *CH_3*-C-), 1.47 and 2.33 (each d, J=7 Hz, 2H, *-CH_2- parts of cyclopropane*), 6.55-7.47 (m, 10H, Ar-*H*) 7.5-8.3 (m, 5H, Ar-*H*); MS: m/e(%) relative intensity: 239(M^+-141), 223(11), 197(64), 145(100), 125(81), 91(15), 77(82), 69(23). Anal. Calcd for $C_{22}H_{18}O_4S$: C, 69.45;H, 5.29. Found: C, 69.16; H, 5.40.

1-Ethyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (6e): 72% ;m.p. 111-113 °C; IR($CHCl_3$): ν_{max} 3080, 3018, 1600, 1500, 1450, 1420, 1310, 1190, 1155, 1080, 970, 940, 690, 640 cm^{-1}; NMR($CDCl_3$): δ 0.93 (br.t, J=7 Hz, 3H, *CH_3*-CH_2-), 2.00 (m, 2H, CH_3-*CH_2*-), 1.5 and 2.23 (each d, J =7 Hz, 2H, *-CH_2-, parts of cyclopropane*), 6.3-8.2 (m, 15 H, Ar-*H*); MS: m/e(%) relative intensity : 253(M^+-141,13), 223(11), 175(6), 159(100), 131(87), 115(14), 91(32), 77(100), 65(18), 55(47), 41(52). Anal. Calcd for $C_{23}H_{22}O_4S$: C, 70.05; H, 5.58. Found: C, 69.70; H, 5.52.

1-Pentyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (6f): 75%; m.p. 120-121 °C; IR($CHCl_3$): ν_{max} 2960, 1600, 1500, 1450, 1420, 1320, 1310, 1190, 1140, 1090, 1030, 980, 940, 690 cm^{-1}; NMR($CDCl_3$): δ 0.60-2.33 (m, 11H, *methyl and methylene protons*), 1.53 and 2.27 (each d, J = 7 Hz, 2H, *-CH_2 - parts of cyclopropane*), 6.33 - 7.53 (m, 10H, Ar-*H*), 7.53-7.90 (m, 3H, Ar-*H*), 7.90-8.33 (m, 2H, Ar-*H*); MS: m/e(%) relative intensity: 295(M^+-141, 21), 210(19), 159(19), 125(30), 115(23), 105(14), 91 (34), 77(100), 55(38), 41(22). Anal. Calcd $C_{26}H_{28}O_4S$: C, 71.56; H, 6.42 Found: C, 71; H, 6.37.

1-Hexyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (6g): 80%; m.p. 104-105 °C; IR($CHCl_3$): ν_{max} 2950, 1600, 1500, 1450, 1420, 1320, 1190, 1140, 1090, 1030, 980, 940, 690, cm^{-1}; NMR($CDCl_3$): δ 0.80-2.13 (m, 10H, *methyl and methylene protons*), 1.53 and 2.26 (each d, J = 7 Hz, 2H, *-CH_2- parts of cyclopropane*), 6.50-7.55 (m, 10H, Ar-*H*), 7.55-8.0 (m, 3H, Ar-*H*), 8.00-8.30 (m, 2H, Ar-*H*); MS: m/e(%) relative intensity: 309 (M^+-141, 45), 215(48), 173(141), 125(56), 105(26), 91(49), 77 (100), 55(27). Anal. Calcd for $C_{27}H_{30}O_4S$: C, 71.97; H, 6.71. Found: C, 72.26; H, 6.68.

1-Heptyl-2,2-diphenoxy-2-(phenylsulfonyl)cyclopropane (6h): 70%; m.p. 73-75 °C; IR($CHCl_3$): ν_{max} 2950, 1600, 1500, 1450, 1420, 1320, 1310, 1190, 1040, 1090, 690 cm^{-1}; NMR($CDCl_3$): δ 0.55-2.17 (m, 15H, *methyl and methylene protons*), 1.53 and 2.26 (each d, J = 7 Hz, *-CH_2- parts of cyclopropane*), 6.40-7.36 (m, 10H, Ar-*H*), 7.40-7.39 (m, 3H, Ar-*H*), 7.80-8.23 (m, 2H, Ar-*H*); MS: m/e (%) relative intensity: 323(M^+-141, 100), 229(57), 187(42), 145(13), 125(48), 91(35), 77(65), 67(14), 55 (22); Anal. Calcd for $C_{28}H_{32}O_4S$: C, 72.38; H, 6.94. Found: C, 72.25; H, 6.89.

1-Octyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (6i): 81%; m.p. 81-83 °C; IR($CHCl_3$): ν_{max} 2940, 1600, 1500, 1450, 1420, 1320, 1310, 1190, 1140, 1090, 1030, 980, 940, 900, 840, 690 cm^{-1}; NMR($CDCl_3$): δ 0.63-2.13 (m, 17H, *methyl and methylene protons*), 1.53 and 2.27 (each d, J =7 Hz, *-CH_2- parts of cyclopropane*), 6.47-7.40 (m, 10H, Ar-*H*), 7.50-7.80 (m, 3H, Ar-*H*), 7.90-8.25 (m, 2H, Ar-*H*); MS: m/e(%) relative intensity: 337(M^+-141, 100), 243(53), 223(19), 201(40), 183(14), 145(15), 125(57), 91(49), 77(88), 67(23), 55(36). Anal. Calcd for $C_{29}H_{34}O_4S$: C, 72.78; H, 7.16 Found: C, 72.71; H, 7.18.

Preparation of Unsaturated Esters 8 and 9.

General Procedure:

Phenyl 2-butenoate (8a): To a stirred solution of 1-methyl-2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane (**6d**) (0.76 g, 2 mmol) in dichloromethane (6 ml) was added drop by drop a solution of 4 *M* solution of titanium(IV) chloride in dichloromethane (2.5 ml) at 0 °C under an argon atmosphere. The reaction mixture became red brown immediately. After stirring at 0 °C to room temperature overnight (20 h), the reaction mixture was quenched with a saturated potassium fluoride solution (20 ml) and extracted with dichloromethane (3x20 ml). The combined extracts were washed with 2*N* NaOH (20 ml) and a saturated NaCl solution (20 ml) and then dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude liquid product obtained (0.64 g) (without purification) was dissolved in dry THF (8 ml) and treated with DBU (0.6 ml, 4 mmol) under an argon atmosphere. The resulting mixture was stirred at room temperature overnight (14 h), then diluted with ethyl acetate (50 ml) and water (20 ml). The organic layer was separated and washed successively with a saturated NH_4Cl solution (3x10 ml), water (20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The crude brown liquid product was purified by PLC (silica gel, 5% ethyl acetate in hexane) to afford a colorless liquid product of **8a** (0.14 g, 41%; b.p. 48 °C/0.3 torr): IR(neat): ν_{max} 3050, 1740, 1660, 1590, 1500, 1440, 1380, 1320, 1300, 1250, 1200, 1150, 1100, 1070, 1020, 970, 840, 750, 720, 710, 690 cm^{-1}; NMR(CCl_4): δ 1.94 (dd, J = 7, 2 Hz, 3H, *CH_3*-CH=CH-), 5.97 (d, J = 16 Hz, 1H, =*CH*-CO), 677-7.63 (m, 6H, -*CH*=CHCO-and Ar-*H*); MS: m/e(%) relative intensity: 162(M^+,7), 96(16), 77(7), 69(100), 65(13).

***A mixture of* phenyl 2-pentenoate (8b) *and* phenyl 3-pentenoate (9b):** 38% (85:15); liquid; IR (neat) : ν_{max} 3050, 2975, 1740, 1650, 1500, 1340, 1290, 1250, 1200, 1160, 1120, 1025, 980, 960, 860, 770, 750, 720, 690 cm^{-1}; NMR(CCl_4): δ 1.15 [t, J = 7 Hz, 3H, CH_3CH_2- (**8b**)], 1.80 [m, 3H, CH_3CH=C-(**9b**)], 2.33 [quint, J = 7 Hz, 2H, CH_3CH_2-CH=C (**8b**)], 3.20 [m, 2H, -CH=CHCH_2CO (**9b**)], 163 [m, 2H, -CH=CH-CH_3 (**9b**), 5.93 [d, J = 16 Hz, 1H, CO-CH=CH- (**8b**) , 6.80-7.60 [m, 11H, CH=CHCO- (**8b**), Ar-H (**8b** and **9b**)]; MS: m/e (%) relative intensity: 176(M^+, 9), 94(19), 83(100), 82(31), 77(4), 65(12), 55(35).

Phenyl 2,4-hexadienoate (8c): 31%; liquid; IR(neat): ν_{max} 3050, 2950, 1730, 1640, 1620, 1500, 1450, 1380, 1330, 1240, 1200, 1120, 1080, 1000, 925, 780, 760, 720, 710, 690 cm^{-1}; NMR(CCl_4): δ 1.83-2.17 (m, 3H, CH_3-CH=CH), 5.83-6.50 (m, 3H, -CH=CH- CH_3, -CH=CH-COOPh), 7.00-7.80 (m, 6H, -CH=CH-COOPh and Ar-H); MS: m/e(%) relative intensity : 188(M^+, 8.77), 96(6), 95(100), 94(6), 67(31), 65(16), 51(3). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.03. Found: C, 76.89; H, 6.28.

***A mixture of* phenyl 2-heptenoate (8d) *and* phenyl 3-heptenoate (9d):** 43%; (86:14); liquid; IR (neat): ν_{max} 3050, 2975, 2950, 2900, 1740, 1650, 1600, 1500, 1470, 1460, 1320, 1300, 1250, 1160, 1120, 1030, 980, 820, 780, 750, 690 cm^{-1}; NMR(CCl_4): δ 0.70-1.85 and 1.85-2.60 (m, *alkyl protons* of **8d** and **9d**), 3.20 [m, 2H, -CH=CHCH_2COO- (**9d**)], 5.63 [m, 2H, -CH=CH-CH_2CO (**9d**)], 5.96 [d, J = 16 Hz, 1H, -CH=CH-COOPh (**8d**)], 6.80-7.70 [m, 11H, -CH =CH-COOPh (**8d**), Ar-H (**8d** and **9d**)]; MS: m/e(%) relative intensity: 204(M^+, 6), 111(100), 94(14), 81(16), 77(8), 65(15), 55(97). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.49; H, 7.76.

***A mixture of* phenyl 2-octenoate (8e) *and* phenyl 3-octenoate (9e):** 45%; (85:15); liquid; IR(neat): ν_{max} 3050, 2950, 2850, 1740, 1650, 1600, 1470, 1460, 1310, 250, 1200, 1160, 1140, 1120, 1020, 980, 750, 720, 690 cm^{-1}; NMR (CCl_4): δ 0.70-1.90 and 1.93-2.60 (m, *alkyl protons* of **8e** and **9e**), 3.23 [m, 2H, -CH=CHCH_2COOPh (**9e**)], 5.65 [m, 2H, -CH=CH- CH_2-COOPh (**9e**)], 5.93 [d, J = 16 Hz, 1H, -CH=CH-COOPh (**8e**), 6.85-7.70 [m, 11H, -CH=CH-COOPh (**8e**), Ar-H (**8e** and **9e**)]; MS: m/e(%) relative intensity: 246(M^+, 5), 154(10), 153(100), 94(8), 69(14), 55(18). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.30; H, 8.24.

***A mixture of* phenyl 2-nonenoate (8f) *and* phenyl 3-nonenoate (9f):** 49% (84:16); liquid; IR (neat): ν_{max} 3050, 2950, 2850, 1740, 1650, 1600, 1500, 1460, 1310, 1300, 1250, 1200, 1160, 1140, 1120, 970, 930, 820, 750, 720, 690 cm^{-1}; NMR(CCl_4): δ 0.60-1.80 and 1.80-2.50 (m, *alkyl protons* of **8f** and **9f**), 3.16 [m, 2H,-CH=CH-CH_2COOPh (**9f**)] 5.60 [m, 2H, -CH=CH-COOPh (**9f**)], 5.9 [d, J = 16Hz, 1H, -CH=CHCOOPh (**8f**)], 6.80-7.60 [m, 11H, -CH=CH-COOPh (**8f**), Ar-H (**8f** and **9f**)]; MS: m/e(%) relative intensity : 232(M^+, 9), 140(8), 139(100), 94(23) ,81(9), 77(4), 69(24), 55(27). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.54; H, 8.68. Found: C, 77.19; H, 8.55.

***A mixture of* phenyl 2-decenoate (8g) *and* phenyl 3-decenoate (9g):** 43 % (86:14); liquid; IR (neat): ν_{max} 3050, 2950, 2850, 1740, 1650, 1600, 1470, 1310, 1250, 1200, 1110, 980, 750, 690 cm^{-1}; NMR(CCl_4): δ 0.60-1.90 and 1.90-2.55 (m, *allylic protons* of **8g** and **9g**), 3.20 [m, 2H, -CH=CHCH_2COOPh (**9g**)], 5.60 [m, 2H, -CH=CH-CHCOOPh (**9g**) 5.93 [d, J = 16 Hz, 1H, -CH=CH-COOPh (**8g**)], 6.80-7.55 [m, 11H, -CH=CH-COOPh (**8g**)), Ar-H (**8g** and **9g**)]; MS: m/e(%) relative intensity : 246(M^+, 5), 15(10), 153(100), 94(8), 69(14), 55(18). Anal. Calcd for $C_{12}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.46; H, 8.90.

***A mixture of* phenyl 2-undecenoate (8h) *and* phenyl 3-undecenoate (9h):** 39% ; liquid ; IR(neat): ν_{max} 3050, 2950, 2850, 1740, 1650, 1600, 1500, 1470, 1460, 1315, 1300, 1250, 1200, 980, 760, 720, 690 cm^{-1}, NMR(CCl_4): δ 0.65-1.86 and 1.86-2.50 (m, *alkyl protons* of **8h** and **9h**), 3.16 [m, 2H, -CH=CHCH_2COOPh (**9h**)], 5.56 [m, 2H, -CH=CHCH$_2$COOPh (**9h**)], 5.90 [d, J = 16 Hz, 1H, -CH=CH-COOPh (**8h**)], 6.76-7.50 [m, 11H, -CH =CH-COOPh (**8h**), Ar-H (**8h** and **9h**)]. MS: m/e(%) relative intensity: 260(M^+, 5), 168(11), 167(100), 94(11), 83(16), 77(3), 69(13). Anal.Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.16; H, 9.33.

Preparation of 2-Alkyl Cyclopropanone Acetals 12.

General Procedure:

Compound **6** (1.5 mmol) was dissolved in a mixture of absolute MeOH (10 ml) and dry THF (2 ml). 6% Na-Hg (2.87 g, 7.5 mmol) was added and the mixture was stirred under argon atmosphere at room temperature overnight (18 h). The mixture was diluted with water (20 ml) and extracted with ethyl acetate (3x25 ml). The combined extracts were washed with water (15 ml), brine (15 ml) and dried over anhydrous $MgSO_4$.

The organic phase was concentrated to give a crude product, which was purified by preparative thin-layer chromatography (PLC) (silica gel, 5% ethyl acetate in hexane) to afford **12**.

2-Methyl-1,1-(diphenoxy)cyclopropane (12a): 91%; m.p. 93-94 °C (hexane); IR($CHCl_3$): ν_{max} 3040, 1600, 1490, 1470, 1380, 1280, 1230, 1180, 1160, 1110, 1080, 1030, 985, 940, 900, 700 cm^{-1}, NMR(CCl_4): δ 0.63-0.90 (m, 1H, *cyclopropyl proton*), 0.90-1.70 (m, 5H, *CH_3*-CH- and *cyclopropyl protons*), 6.70-7.40 (m, 10H, Ar-*H*); MS: m/e(%) relative intensity; 147(M^+-93, 29), 131(16),119(14), 105(100), 91 (40), 77(45), 69(6), 65(12), 55(11). Anal. Calcd for $C_{16}H_{16}O_2$: C,79.97; H, 6.71. Found: C, 80.12; H, 7.00.

2-Ethyl-1,1-(diphenoxy)cyclopropane (12b): 79%; a viscous liquid, which was crystallised on keeping in a refrigerator (m.p. 38-39 °C): IR(neat): ν_{max} 2980, 1600, 1500, 1469, 1390, 1330, 1220, 1170, 1080, 1030, 920, 900, 860, 820, 750, 695 cm^{-1}, NMR(CCl_4): δ 0.70-2.03 (m, 8H, *methyl and cyclopropyl protons*), 6.65-7.83 (m, 10H, Ar-*H*); MS: m/e(%) relative intensity : 254(M^+, 0.1), 161(26) 131(22), 119(64) 105 (6), 91 (100), 77 (69), 65 (20), 55 (39). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.29; H, 7.13. Found: C, 80.20; H, 7.10.

2-Allyl-1,1-(diphenoxy)cyclopropane (12c) : 86% ; liquid; IR(neat): ν_{max} 3100, 1640, 1600, 1490, 1440, 1380, 1300, 1270, 1220, 1170, 1080, 1030, 1000, 940, 755, 695 cm^{-1}. NMR(CCl_4): δ 0.7-0.97 (m, 1H, *cyclopropyl proton*), 0.97-1.75 (m, 2H, *cyclopropyl protons*), 1.75-2.75 (m, 2H, *-CH_2*-CH=CH_2), 4.80-5.26 (m, 2H, *CH_2*=CH), 6.50-6.23 (m, 1H, *-CH*=CH_2), 6.70-7.50 (m, 10H, Ar-*H*); MS: m/e(%) relative intensity: 266(M^+, 0.12), 173(23), 131(84), 118(23), 91(77), 77(100), 69(33), 65(21), 55(48). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.25 ; H, 8.44. Found: C, 81.06; H, 8.45.

2-Butyl-1,1-(diphenoxy)cyclopropane (12d): 93%; m.p. 47-48 °C ; IR(neat): ν_{max} 2950, 1600, 1500, 1450, 1380, 1340, 1280, 1220, 1170, 1080, 1030, 980, 940, 900, 760, 700 cm^{-1}; NMR(CCl_4): δ 0.6-1.90 (m, 12H, *cyclopropyl and butyl protons*), 6.70-7.50 (m, 10H, Ar-*H*); MS: m/e (%) relative intensity : 281(M^+-1, 1.36), 239(4), 225(5), 189(22) 161(5), 147(53), 131(18), 105(18), 91(100), 77(9), 69(4), 55(16). Anal.Calcd for $C_{19}H_{22}O_2$: C, 80.80; H, 7.86. Found: C, 80.83; H, 7.82.

2-Pentyl-1,1-(diphenoxy)cyclopropane (12e) : 77%; liquid; IR(neat): ν_{max} 3050, 2950, 1600, 1500, 1460, 1390, 1340, 1290, 1230, 1170, 1080, 1030, 940, 900, 760, 700 cm^{-1}; NMR(CCl_4): δ 0.6-2.0 (m, 14H, *cyclopropyl and pentyl protons*), 6.67-7.50 (m, 10H, Ar-*H*); MS: m/e(%) relative intensity : 296(M^+, 0.39), 295(2), 253(0.4), 239(8), 225(13), 161(54), 131(16), 105(18), 91(100), 77(35), 69(2), 65(8); Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.35; H, 8.13.

2-Hexyl-1,1-(diphenoxy)cyclopropane (12f): 83%; liquid; IR(neat): ν_{max} 3050, 2950, 1600, 1490, 1460, 1390, 1340, 1295, 1220, 1170, 1080, 1030, 940, 900, 760, 700 cm^{-1}. NMR(CCl_4): δ 0.60-1.90 (m, 16H, *cyclopropyl and hexyl protons*), 6.60-7.40 (m, 10H, Ar-*H*); MS: m/e(%) relative intensity : 309(M^+-1, 1.11), 217 (20) 175 (41), 105 (29), 91 (100), 77 (37), 65 (7), 55 (28). Anal. Calcd for $C_{21}H_{26}O_2$: C,81.25; H, 8.44. Found :C, 81.05; H, 8.12.

2-Heptyl-1,1-(diphenoxy)cyclopropane (12g): 88% ; 48-49 °C ; IR(Neat): ν_{max} 3050, 2950, 1600, 150, 1460, 1390, 1340, 1280, 1220, 1160, 1080, 1030, 940, 900, 760, 700 cm^{-1}; NMR (CCl_4): δ 0.65-1.95 (m, 18H, *cyclopropyl and heptyl protons*), 6.65-7.50 (m, 10H, Ar-*H*); MS: m/e(%) relative intensity : 324 (M^+, 0.56), 323(2), 23(9), 231(24), 225(15), 202(12), 189(54), 131(18) 119(15), 105(25), 91(100), 77 (29), 55(23). Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.44; H, 8.69. Found: C, 81.63; H, 8.70.

2-Octyl-1,1-(diphenoxy)cyclopropane (12h): 86%; liquid; IR(neat): ν_{max} 3050, 2950, 2870, 1600, 1500, 1460, 1340, 1300, 1280, 1220, 1160, 1080, 1030, 940, 900, 790,760, 700 cm^{-1}, NMR(CCl_4): δ 0.6-2.0 (m, 20H, *cyclopropyl and octyl protons*), 6.73-7.50 (m, 10H, Ar-*H*); MS: m/e(%) relative intensity: 338 (M^+, 0.59), 337(2), 245(24), 203(56), 131(19), 119(16), 105(26), 94(23), 91(100), 77(25), 69(8), 55 (11); Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61: H 8.93. Found: C, 81.85; H, 8.94.

2-Benzyl-1,1-(diphenoxy)cyclopropane (12i): 91%; liquid; IR(neat): ν_{max} 3040, 2920, 1600, 1590, 1500, 1460, 1380, 1340, 1280, 1200, 1160, 1080, 1030, 940, 900, 760, 700 cm^{-1}; NMR(CCl_4): δ 0.75-2.00 (m, 3H, *cyclopropyl protons*), 2.40-3.23 (m, 2H, *-CH_2*- Ph), 6.7-7.4 (m, 15H, Ar-*H*); MS m/e(%) relative intensity: 223(M^+-93, 63), 181(77), 165(7), 145(8), 131(34), 117(39), 103(15), 91(100), 77(96), 65 (26), 55(46); Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37. Found; C, 83.74; H, 6.35.

ACKNOWLEDGEMENT

We would like to thank Mrs. Pucharin Poochaiwatananon, Miss Amporn Srisuttipruet and Miss Kingkaew Serikul for carrying out the IR, ^{1}H-NMR-, MS-spectra as well as elemental analyses.

REFERENCES AND NOTES

1. Taken in part from the *M.Sc Thesis* of JR, Mahidol University, **1993**.
2. See for examples : a) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12* ,66. b) Wong, H. N. C.; Hon, M. Y; Tse, C. H.; Yip, Y. C; Tanko, J; Hudlicky, T.*Chem. Rev.* **1989**, *89*, 165.
3. (a) Trost, B.M. *Topics in Current Chemistry : Small Ring Compounds in Organic Synthesis,* **1986**,Vol. *133*, p 1-81. (b) Krief, A. *ibid.* **1987**, Vol. *135*, p 1-71. (c) Reissig, H.U. *ibid.* **1988**, Vol. *144*, p 75-135.
4. Kuwajima, I; Nakamura, E. *Topics in Current Chemistry: Small Ring Compounds in Organic Synthesis*, **1990**, Vol. *155*, p 1-38.
5. Pisutjaroenpong, S. *M.Sc. Thesis,* Mahidol University, **1985**; Pohmakotr, M; Pisutjaroenpong, S. *Tetrahedron Lett.*. **1985**, *26*, 3613.
6. Fedorynski, M; Dybowska, A; Jonczyk, A. *Synthesis* **1988**, 548.
7. For reviews of homoenolate equivalents, see: (a) Werstiuk, N. H.; *Tetrahedron*, **1983**, *39*, 205; (b) Stowell, J. C. *Chem. Rev.* **1984**, *84*,409; (c) Hoppe, D. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 932. Some recent reports, see: Fang, J. M.; Chang, C. J. *J. C. S. Chem. Commun.* **1989**, 1787; Najera, C.; Yus, M. *J. C. S. Perkin Trans. I* **1989**, 1387; Plewe, M.; Schmidt, R. R. *Synthesis* **1989**, 534; Ghosez, L.; Carretero, J. C. *Tetrahedron Lett.*. **1988**, *29*, 2059; Kim, S.; Lee, P H. *Tetrahedron Lett.* **1988**, *29*, 5413; Dziadulewicz, E.; Hodgeson, D.; Gallagher, T. *J. C. S. Perkin Trans I* **1988**, 3367 and references cited therein; Barluenga, J.; Fernandez, J. R.; Yus, M. *J. C. S. Chem. Commun.* **1987**, 1534.
8. *Ref. 3c* and references cited therein.
9. Bhatt, M.V; Babu, J.R. *Tetrahedron Lett.*. **1984**, *25*, 3497. For a recent review for the cleavage of ethers,see : Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249.
10. For the $TiCl_4$-mediated ring opening of 2,2-dialkoxy(cyclopropane)carboxylic esters, see: Saigo, K; Shimada, S.; Shibasaki, T; Hasegawa, M. *Chem Lett.*. **1990**, 1093. Shimada, S; Saigo, ; Hashimoto, Y; Maekawa, Y; Yamashita, T; Yamamoto, T; Hasegawa, M, *ibid*, **1991**, 1475.
11. The term " Cyclopropanone Enolate " has been recently used by Nakamura: Nakamura, E.; Isaka, M.; Matsuzawa, S. *J. Amer. Chem. Soc.* **1988**, *110*, 1297.
12. For some recent syntheses of substituted cyclopropanone acetals, see: Nakamura, E. *Synlett* **1991**, 535 and references cited therein.
13. Brasen, W. R. ; Hauser, C. R. *Organic Synthesis* Coll. Vol. *IV*, **1941**, p. 509.