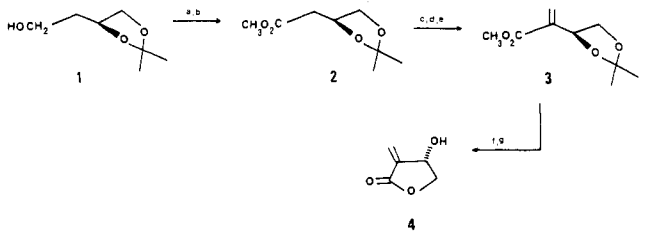
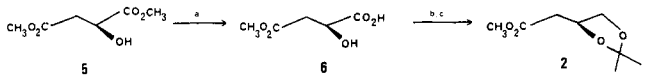
Scheme I[a]



[a] (a) $KMnO_4$, 18-crown-6, benzene; (b) ICH_3; (c) LDA, $CH_2{=}N^+(CH_3)_2I^-$; (d) ICH_3; (e) DBU; (f) $Ba(OH)_2$; (g) 1 N HCl.

Scheme II[a]



[a] (a) PLE; (b) $BH_3{\cdot}Me_2S$; (c) acetone, *p*-TsOH.

signal (H_A 2.52, H_B 2.72, J_{AX} = 6.4, J_{BX} = 7.0, J_{AB} = 15.9) for the group $CH_X(OD)CH_AH_BCO_2CH_3$ and an AMX signal (H_A 3.66, H_M 4.16, J_{AM} = 6.40; J_{MX} = 4.00; two dd) for the group $CH_X(OD)CH_AH_M(OD)$. If instead the other ester function had been hydrolyzed and then reduced, leading to compound $HOCH_2CH_2CH(OH)CO_2CH_3$, the NMR spectrum would have been different (in particular dt or even more complicated multiplets would have been present). The regioselectivity of the hydrolysis of the ester function with an α-OH group is therefore demonstrated.[10]

This half-ester was used toward the synthesis of tulipalin B (**4**), a natural product with cutaneous allergenic activity.[11] A lengthy synthesis of this compound has already been reported, starting from isopropylidene-D-glyceraldehyde.[12] We have developed two syntheses of tulipalin B on the basis of the malic acid derivatives.

The key compound **1**[13] in the first synthesis outlined in Scheme I is obtained from malic acid.

Oxidation of (−)-(**S**)-**1** with $KMnO_4$ in benzene containing 10% of 18-crown-6 and trapping the carboxylate with methyl iodide led to the ester **2** (43% yield; 40% of the starting compound **1** are recovered, $[\alpha]_D$ +17.0° (c 2.00, $CHCl_3$). Treatment[14] of the anion of **2** with Eschenmoser salt followed by permethylation and elimination of the resulting trimethylammonium salt (acetone, DBU) gave **3** in an 11% yield ($[\alpha]_D$ +15.7° (c 1.80, $CHCl_3$); 80% of **2** are recovered) which, after saponification and acid treatment, gave pure (−)-tulipalin B (**4**) ($[\alpha]_D$ −81° (c 1.32, $CHCl_3$), lit.[11] $[\alpha]_D$ −82° ($CHCl_3$)).

In Scheme II, the second synthesis involves dimethyl malate half-ester. Starting from optically pure dimethyl (*S*)-(−)-malate, we have obtained by the above described method the optically pure ester **6** ($[\alpha]_D$ +1.5° (*c* 1.80, $CHCl_3$) which, upon reduction with 2 equiv of $BH_3{\cdot}Me_2S$,[15] and treatment with acetone in the presence of *p*-TsOH gave compound **2** in 73% yield.

A sequence identical with that used in Scheme I led to tulipalin B. This short route was followed for the synthesis of (+)-tulipalin B.

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An Extremely Facile Ring Opening of Substituted 1-(Alkylthio)cyclopropenes via Vinylcarbene Intermediates

Summary: Thermal ring opening of 1-(methylthio)cyclopropenes **2** takes place readily to give indene and/or butadiene derivatives in good yields, and product analysis of the reaction in methanol as well as kinetic studies of **2b** gave strong evidence for the intermediacy of vinylcarbene in the ring opening of **2**.

Sir: In these 2 decades the chemistry of cyclopropene has attracted considerable interest because of its high strain energy.[1] Theoretical calculations suggest that the ring opening of cyclopropene proceeds directly to a diradical planar intermediate.[2] To explain the products of photochemical ring opening of cyclopropene, a diradical and/or a vinylcarbene intermediate has been postulated.[3] In contrast, a mechanistic studies on the thermal ring opening of cyclopropene have been scarce,[4] and to the best of our knowledge none of the effects of heteroatom substitution on the reactivity of cyclopropene has been reported. In this communication we report an easy route for the preparation and facile ring-opening reaction of 1-(alkylthio)cyclopropenes **2**.

To a suspension of 1,2-diphenyl-3-(methylthio)cyclopropenium bromide (**1a**)[5] in dry benzene was added methylmagnesium bromide (3 times excess) in one portion, and the mixture was stirred to give a clean solution. After 5 min the resulting solution was quenched with ice water and the organic layer was separated. ^1H NMR spectroscopic analyses revealed that the crude product was a mixture of two isomeric cyclopropenes (**2a** and **3a**). The major component was separated by column chromatography and confirmed to be 1,3-diphenyl-3-methyl-2-(methylthio)cyclopropene (**2a**).[6] Similar treatment of **1a** and **1b** with other Grignard reagents, R′MgX, yielded the corresponding cyclopropenes **2** in good yields together with isomeric cyclopropenes **3** (Table I).

It has been reported that tetraphenylcyclopropene rearranges at temperatures as high as 235–240 °C to give

(10) This result allowed the assignment of the signals of the esters in dimethyl malate ($CH(OH)CO_2CH_3$ δ 3.68; $CH_3CO_2CH_2$ δ 3.78).

(11) Tschesche, R.; Kammerer, F. J.; Wulff, G. *Chem. Ber.* **1969**, *102*, 2057. Barbier, P.; Benezra, C.; *J. Med. Chem.*, submitted for publication.

(12) Tanaka, A.; Yamashita, Y. *Agric. Biol. Chem.* **1980**, *44*, 199.

(13) Meyers, A. I.; Lawson, J. P. *Tetrahedron Lett.* **1982**, *23*, 4883.

(14) Alkylation of the α position of dimethyl malates has been reported to proceed with moderate yields. See: Seebach, D.; Wasmuth, D. *Helv. Chim. Acta* **1980**, *63*, 197. Papageorgiou, C.; Benezra, C. *Tetrahedron Lett.* **1984**, *25*, 1303.

(15) The first equivalent forms the borate between adjacent hydroxy groups.

(1) Recently extensive studies have been reported on the chemistry of cyclopropenes by two groups. For example: Padwa, A.; Cohen, L. A.; Gringrich, H. L. *J. Am. Chem. Soc.* **1984**, *106*, 1065. Zimmerman, H. E.; Fleming, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 622.

(2) Davis, J. H.; Goddard, W. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427.

(3) Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310.

(4) York, *E.* J.; Stevens, J. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680.

(5) Yoshida, H.; Nakajima, M.; Ogata, T.; Matsumoto, K.; Acheson, R. M.; Wallis, J. D. *Chem. Lett.* **1983**, 155; *Bull Chem. Soc. Jpn.* **1983**, *56*, 3015. Yoshida, H.; Nakajima, M.; Ogata, T.; Matsumoto, K. *Heterocycles* **1983**, *20*, 1013; *Bull. Chem. Soc. Jpn.* **1984**, *57*, 734.

(6) **2a**: oil; IR (neat) 1980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71 (3 H, s, Me), 2.39 (3 H, s, MeS), 6.9–7.6 (10 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 16.5 (q, MeS), 22.1 (q, Me), 31.9 (s, C-3), 116.0 (s), 117.6 (s), 125.3 (d), 125.9 (d), 126.1 (d), 127.2 (d), 127.8 (d), 128.0 (d), 128.6 (d), 146.8 (s); MS, *m/z* 252 (M^+).

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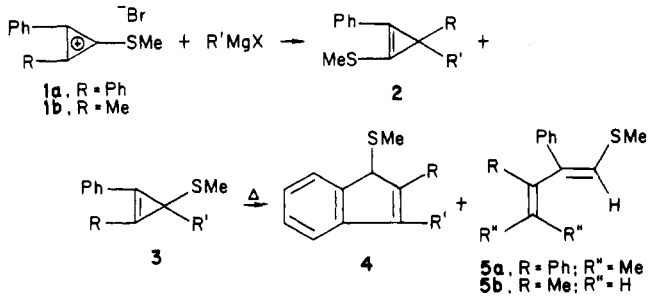
Table I. Reaction of 1a and 1b with Grignard Reagents

reactants		product (yield, %)	
1	R'X		
1a	MeI	**2a** (83)	**3a** (12)
1a	*i*-PrBr	**2b** (90)	**3b**
1a	PhBr	**2c** (64)	**3c** (23)
1b	MeI	**2d** (96)	**3d**
1b	PhBr	**2a** (82)	

Table II. Thermolysis of 2a–d and 3c in Benzene

reactn conditns			
reactant	temp, °C	time, h	product (yield, %)
2a	80	2	**4a** (87)
2b	80	30	**4b** (46), **5a** (44)
2c	25	3	**4c** (95)
2d	80	4	**5b** (82)
3c	200	100	recovery

Scheme I[a]



[a] For **2–4**: a, R = Ph, R' = Me; b, R = Ph, R' = *i*-Pr; c, R = Ph, R' = Ph; d, R = Me, R' = Me.

triphenylindene.[7] The ring opening reaction of 1-(methylthio)cyclopropenes **2a–d** took place easily either at room temperature or on heating at 80 °C, producing indene **4**[8] and/or butadiene derivative **5** in good yields as shown in Table II. In contrast, 3-(methylthio)-1,2,3-triphenylcycloprop-1-ene (**3c**)[9] was stable even at 200 °C.

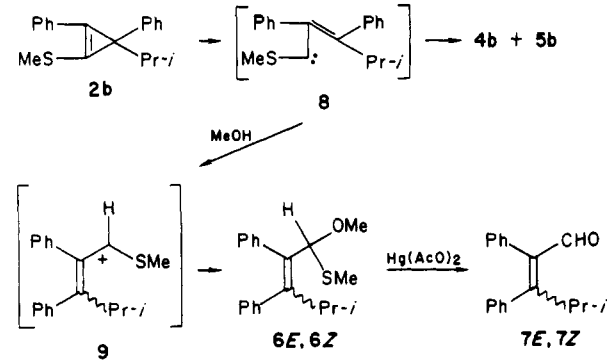
The relatively stable cyclopropene **2b** was subjected to precise studies for the ring-opening reaction. Thermolysis of **2b** in benzene gave indene **4b** and butadiene **5a** in a 1:1 ratio (Table II), whereas thermolysis of **2b** in boiling methanol afforded methyl ether **6E** and **6Z**[10] in a 51% yield along with **4b** and **5a** in 43% yield. Addition of triethylamine or sodium hydroxide to the methanol solution increased the total yield of **6E** and **6Z**; reaching up to 82%. The structures of **6E** and **6Z** were confirmed by ^{1}H NMR data as well as by conversion to aldehydes[11] **7E** and **7Z** on treatment with mercury(II) acetate in acetic acid.

Table III. Rate Constants for the Thermolysis of 2b

solvent (ε)	temp, °C	$10^5 k_1$, s^{-1}
CD_3OD (32.6)	60.2	2.69 ± 0.10
	65.3	4.57 ± 0.19, 4.41 ± 0.23,[a] 4.60 ± 0.25[b]
	69.8	7.37 ± 0.43
	75.0	11.8 ± 0.5
PhCl (5.61)	65.3	3.45 ± 0.15
$PhNO_2$ (34.6)	65.3	2.67 ± 0.17
PhCN (25.2)	65.3	2.77 ± 0.13
$MeNO_2$ (38.6)	65.3	3.01 ± 0.17
pyridine (12.3)	65.3	2.66 ± 0.16

[a] NaOD was added to the reaction mixture at (a) 0.07 and (b) 0.14 mol dm^{-3}.

Scheme II



We have performed a kinetic experiment[12] in order to find a reasonable mechanism for the ring opening of **2**. The disappearance of **2b** gave a good first-order rate constant k_1. The change of the solvent from chlorobenzene to nitromethane (ε 5.6–38.6) did not significantly affect the reaction rate.

Concerning formation of the methyl ether, the kinetic experiment ruled out a mechanism involving a nucleophilic attack of alkoxide onto the cyclopropene ring of **2b** to give **6E** and **6Z**. Addition of sodium hydroxide to the methanol solution had no effect on the rate constant (Table III).

Tetraphenylcyclopropene has been reported to rearrange to indene with the activation energy of 167 kJ/mol,[7] while the rearrangement of **2b** requires 98.6 kJ/mol.

These results indicate a sequence involving ring opening of **2b** to give a more stable vinylcarbene, stabilized by the adjacent alkylthio group,[13] followed by intramolecular hydrogen abstraction to afford **4b** and/or **5a** (Scheme II). In contrast to tetraphenylcyclopropene[7] and **3c**, the introduction of alkylthio groups on carbon-1 of the cyclopropene ring furnished the ring opening. The fact that the addition of a base to the methanolic solution of **2b** increased the yields of methyl ethers **6E** and **6Z** might be attributable to the high reactivity of methoxide with the protonated vinylcarbene (the (alkylthio)carbonium ion **9**[14]).

An oxacarbene intermediate, e.g., an oxygen analogue of **8**, has been postulated and trapped by methanol or

(7) Battiste, M. A.; Halton, B.; Grubbs, R. H. *Chem. Commun.* **1967**, 907.

(8) **4a**: mp 89–90 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (3 H, s, MeS), 2.23 (3 H, d, *J* = 2 Hz, Me), 4.72 (1 H, q, CH), 6.9–7.8 (9 H, m, Ar); ^{13}C NMR ($CDCl_3$) δ 9.2 (q, MeS), 11.8 (q, Me), 52.0 (d, CH), 119.0 (d), 123.7 (d),125.8 (d), 127.1 (d), 127.5 (d), 128.2 (d), 129.1 (d), 135.5 (d), 135.9 (s), 141.4 (s), 143.9 (s), 145.6 (s); MS, *m/z* 252 (M^+).

(9) Prepared from triphenylcyclopropenium perchlorate and methanethiol in the presence of triethylamine in 78% yield. **3c**: mp 121.5–122.5 °C; IR (KBr) 1820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, MeS), 7.0–7.9 (m, Ph); MS, *m/z* 314 (M^+).

(10) Although separation of **6E** and **6Z** by chromatography was unsuccessful, ^{1}H NMR data of the mixture showed two sets of signals assigned to be *E* and *Z* isomers in a 7:3 ratio. ^{1}H NMR ($CDCl_3$) **6E**, δ 0.78 (d, *J* = 7 Hz, 2 Me), 1.75 (s, MeS), 3.16 (s, MeO), 4.56 (s, CH), 6.6–7.6 (m, Ph), **6Z**; δ 0.99 (dd, *J* = 1.5 and 7 Hz, 2 Me), 2.13 (s, MeS), 3.46 (s, MeO), 5.29 (s, CH), 6.6–7.6 (m, Ph).

(11) A mixture of **7E** and **7Z** showed two sets of signals in the ^{1}H NMR spectrum corresponding to **6E** and **6Z**.

(12) The rate was followed at suitable time intervals by analyzing the ^{1}H NMR spectra of the methylthio group of **2b** by using methyl phenyl sulfide or dimethyl sulfone as an internal standard.

(13) Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; 221.

(14) Sulfur-substituted carbenes are known to serve either as a nucleophile or an electrophile, depending on the substituent and reaction conditions.[13] We feel, though not well-founded, that **8** is protonated prior to attack by methanol or methoxide ion since the electron-releasing property of the methylthio group would stabilize a carbonium ion intermediate **9** as revealed in the facile ring-opening reaction of **1a** with cyclic and acyclic 1,3-diketones.[5]

ethanol in the photochemical reaction of nortricyclanone and related compounds.[15]

In conclusion, an appropriate substitution of cyclopropenes with an alkylthio group permits a facile ring opening leading to indene and/or butadiene derivatives in good yields. Further studies on the reactions of 1 as well as other heteroatom-substituted cyclopropenes with various nucleophiles such as organolithium compounds, amines, and thiols are currently in progress.

(15) Yates, P. *Pure Appl. Chem.* **1968**, *16*, 93. We are indebted to a referee for calling our attention to this reference.

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New Functions of (Arene)tricarbonylchromium(0) Complexes as Hydrogenation Catalysts: Stereospecific Semihydrogenation of Alkynes and Highly Chemoselective Hydrogenation of α,β-Unsaturated Carbonyl Compounds[1]

Summary: An impressive stereo- and chemoselective catalytic hydrogenation procedure for alkynes to (*Z*)-alkenes) and α,β-unsaturated carbonyl compounds (to the saturated analogues) using (arene)$Cr(CO)_3$ catalysts is described.

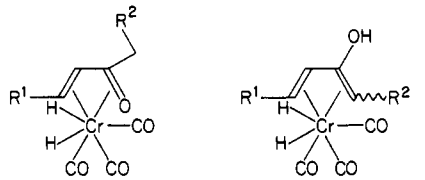
Sir: We report here that (arene)tricarbonylchromium(0) complexes, originally known as catalysts for the 1,4-hydrogenation of conjugated dienes,[2] serve as extremely useful catalysts for the hydrogenation of multiple bonds such as alkynes to (*Z*)-alkenes and α,β-unsaturated carbonyl compounds to saturated analogues. It appears that these catalysts are superior in the stereo- and chemoselectivity to ordinary catalysts including the Lindlar catalyst,[3] cationic rhodium complexes,[4] nickel boride catalysts,[5] and so on.

As shown in Table I, 1-phenyl-1-propyne (**1**) was stereospecifically hydrogenated to (*Z*)-β-methystyrene (**2**) by using the (arene)tricarbonylchromium(0) complexes as hydrogenation catalysts in very high yield (entries 1,2). Neither (*E*)-β-methylstyrene nor *n*-propylbenzene was detected by the GLC analysis of the crude reaction mixture in both cases. In contrast to the semihydrogenation of alkynes using ordinary catalysts mentioned above, even after prolonged reaction time, neither the overreduced product nor the *E* isomer was formed in the present partial hydrogenation reaction, thus characterizing (arene)tricarbonylchromium(0) complexes as catalysts for the hydrogenation of alkynes to (*Z*)-alkenes.

As the reference example, 1-phenyl-1-propyne (**1**) was hydrogenated by the Lindlar catalyst in the presence of quinoline (hexane solvent, 1 kg/cm^2 of H_2 pressure, 4.5 h). In this case a mixture of (*Z*)-β-methystyrene (**2**) (83%), (*E*)-β-methylstyrene (4%), and *n*-propylbenzene (10%) was formed along with recovery of the starting material (**1**) (3%).

Other alkynes such as 7-tetradecyne (**3**) and the propargyl alcohol derivative **4** were hydrogenated to the corresponding alkenes in excellent yields (entries 3,4,5). Also in these hydrogenations, the (*Z*)-alkenes were stereospecifically obtained without formation of the overreduced products (GLC analysis).

(Arene)tricarbonylchromium(0) complexes offer another synthetically useful reaction. Namely, α,β-unsaturated carbonyl compounds are chemospecifically hydrogenated to saturated analogues in the presence of nonconjugated double bonds.[6] For example, hydrogenation of the enone **5** gave the saturated ketone **6** in nearly quantitative yield without any isomerization of the terminal double bond (entries 6, 7). In striking contrast to this result, cyclic α,β-unsaturated ketones in which the enone system is rigidly constrained to a transoid geometry, such as 2-cyclohexenone (**7**), was found to remain unchanged under the hydrogenation conditions (entry 8), suggesting that a possible mechanism for the hydrogenation of enones involves the transition state **8** rather than **9**. Based on these



8 **9**

results, next we attempted the chemospecific hydrogenation of **10** having two enone functionalities. As was expected, specific hydrogenation proceeded quite well, affording the cyclic enone **11** in essentially quantitative yield (entry 9). To the best of our knowledge, this is the first example of the chemospecific hydrogenation of the enone functionality capable of adopting a cisoid geometry in the presence of the enone system constrained to a transoid conformation. The α,β-unsaturated ester **12**, though less reactive than α,β-unsaturated ketones, was also hydrogenated to the saturated analogue **13** in nearly quantitative yield (entry 10). Likewise the β-keto ester **14** was found to undergo hydrogenation probably via the enol form to give the hydroxy ester **15** albeit in low yield (entry 11).

Hydrogenation of 5-methyl-6-oxo-7(*E*)-tridecen-2-yne (**16**) provided the saturated ketone **17** with the *Z* double bond stereospecificially "in a single operation" (entry 12). In the case of the α,β-unsaturated imine **18**, hydrogenation afforded the secondary amine **19** in excellent yield (entry 13).

A representative procedure follows: 1(*E*)-11-Octadecadien-13-one (**5**) (570 mg, 2.1 mmol) and naphthalenetricarbonylchromium[7] (110 mg, 0.4 mmol) was dissolved in dry THF (20 mL). After deoxygenation by three freeze–

(1) This paper is dedicated to Professor Shun-ichi Yamada on the occasion of his 70th birthday.
(2) Farona, M. F. "Organometallic Reactions and Syntheses"; Plenum Press: New York and London, 1977; Vol. 6, pp 223–288.
(3) Marvell, E. N.; Li, T. *Synthesis* **1973**, 457.
(4) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143.
(5) Brown, C. A.; Brown, H. C. *J. Am. Chem. Soc.* **1963**, *85*, 1003. Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553. Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226.
(6) It was found that both α,β-unsaturated cyanides and α,β-unsaturated sulfones remained intact under the hydrogenation conditions. However, in the case of conjugated nitro olefins and α,β-unsaturated aldehydes, a complex mixture was obtained.
(7) Yagupsky, G; Cais, M. *Inorg. Chim. Acta* **1975**, *12*, L27. Cais, M; Fraenkel, D.; Weidenbaum, K. *Coord. Chem. Rev.* **1975**, *16*, 27.

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