Journal of Organometallic Chemistry, 342 (1988) 143–152
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preparation of allylic lithium reagents with the allylic system partly incorporated into carbocyclic rings

Constantinos G. Screttas and Ioulia C. Smonou

Institute of Organic Chemistry, The National Hellenic Research Foundation, Athens 116 35 (Greece)

(Received July 7th, 1987)

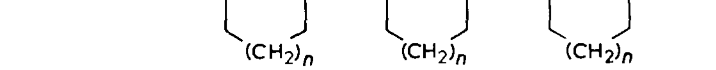
Abstract

A new method is described for preparation of allylic type organolithiums in which two of the allylic system carbons form part of a carbocyclic ring. It involves cleavage of the readily accessible allylic sulfides 1-phenylthiomethylcycloalkenes by the naphthalenelithium in tetrahydrofuran. Carbonation of the reagents has given mixtures of cycloalken-1-yl acetic acids and 2-methylenecycloalkane carboxylic acids, the distribution of which is strongly dependent on the ring size; thus the proportion of cycloalkenyl acetic acid, the endocyclic olefinic product, increases sharply on going from C_5 to C_8 ring derivatives and then considerably less sharply on going from C_8 to C_{10}, at which point the carbonation reaction has a high selectivity. It is concluded that the site of attack in the allylic anion by CO_2 is determined by the thermochemical stability of the product(s).

Introduction

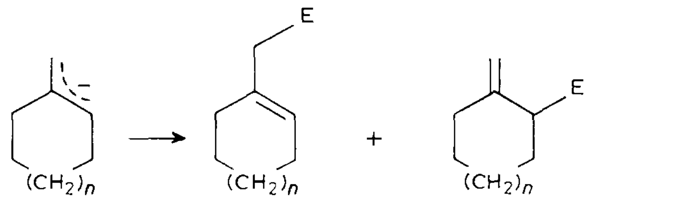
Allylic carbanionic reagents have the important property that their activity in C–C or C–element bond formation is accompanied by the introduction of an olefinic double bond that permits further chemical transformation [1a–c].

The three sp^2 hybridized carbon atoms which comprise the allylic system may be a part of an aliphatic chain (**1**) or of a ring system. In the latter case we can distinguish the following three alternatives (**2**–**4**) in which the number of the carbon atoms shared by the allylic and the ring systems are 3, 2, and 1, respectively.

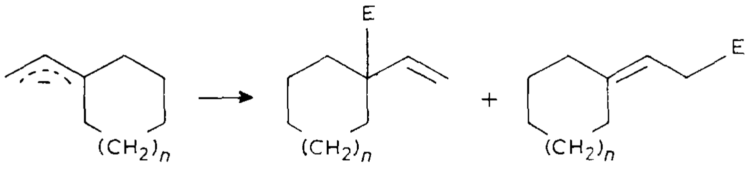


(1) (2) (3) (4)

Of the three cyclic allylic systems, types **3** and **4** are of interest because they are asymmetric, and as such should give two positional isomers **3a**,**3b** and **4a**,**4b** upon reaction with an electrophile E.



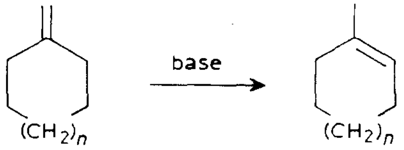
(**3**) (**3a**) (**3b**) (1)



(**4**) (**4a**) (**4b**) (2)

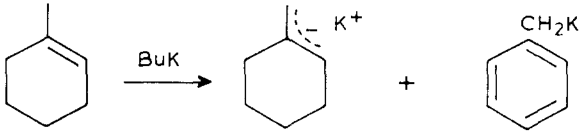
Such derivatives could be of considerable synthetic value. Recent advances in regioselectivity control mean that by use of appropriate additives one or the other of the major product of reactions such as 1 or 2 can be made selectively [1a–1c]. We describe here a method for synthesizing allylic organolithiums of the type **3**, and report on the distribution of their carbonation products as function of the ring size, from $n = 0$–5.

Base catalyzed isomerization of methylene cycloalkanes, (eq. 3) involves proton



(3)

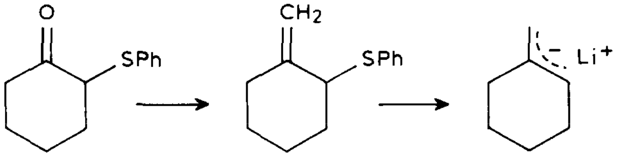
abstraction through an allylic-carbanionic transition state [2], and therefore reaction 3 could be relevant to the present work. To the best of our knowledge the only allylic organoalkali reagent which has been reported so far is one with $n = 3$; namely species **5**, made by metalation of 1-methylcyclohexene by butylpotassium; **5** was accompanied by 2–11% of benzylpotassium, i.e., the aromatization product (see eq. 4) [3]. Cohen [1b] prepared the corresponding lithium derivative by the sequence



(4)

(**5**)

depicted in eq. 5. His method involved cleavage of a C–S bond of the allylic sulfide **7** by lithium 1-(dimethylamino)naphthalene, sulfide **7** was obtained from the corresponding 2-phenylthiocyclohexanone, **6**, by a Wittig reaction. Also relevant is the work of Sowerby and Coates [4].



(5)

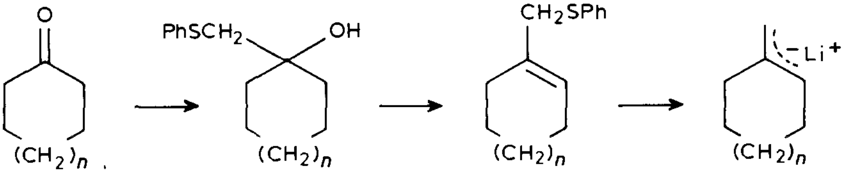
(**6**) (**7**)

Results and discussion

Our method makes use of reaction of the readily accessible reagent α-lithiothioanisole [5] with the appropriate cycloalkanone to give the intermediate (phenylthiomethyl)cycloalkanol (**8**). The latter is then dehydrated to the corresponding (phenylthiomethyl)cycloalkene (**9**), i.e., the allylic sulfide, which is finally converted into the corresponding lithium reagent by treatment with naphthalene-lithium in tetrahydrofuran [6] (eq. 6).

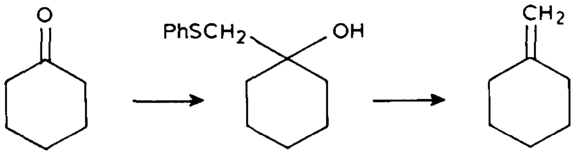
For the metalation of thioanisole we employed butyllithium and tetrahydrofuran (THF) [7]. Phenylthiomethylcycloalkanols (**8**) were obtained in 74–98% yields (Table 1). In Sowerby and Coates' work carbinols of this type were prepared by adding the DABCO complex of α-lithiothioanisole to cycloalkanones [4], the carbinols were then converted in situ into the corresponding esters and finally treated with lithium in liquid ammonia or naphthalene sodium in THF to afford the corresponding methylenecycloalkanes, as an alternative to Wittig reaction, eq. 7. This reaction involves Li_2O elimination from an unstable substituted 2-lithiooxyethyllithium [8].

From 4-(t-butyl)cyclohexanone we obtained the two epimeric alcohols with an equatorial/axial ratio of 1.0/2.72.



(6)

(**8**) (**9**) (**3**)



(7)

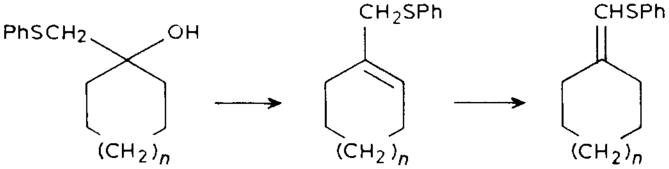
Table 1

Yields of cyclic allyllithiums (**3**) (based on the yield of isolated carboxylic acids after carbonation) and the distribution of *endo* and *exo* isomers

Starting sulfide	Yield (%)		*endo*/*exo* ratio [a]
	Acid	Ester	
1-Phenylthiomethyl-cyclopentene	80	94	45.8/54.2 (45.5) */(54.5)
1-Phenylthiomethyl-cyclohexene	87	100	58.8 */41.2
1-Phenylthiomethyl-2 (4-t-butyl)cyclohexene	64	100	71.0/29.0 (73.7)/(26.3)
1-Phenylthiomethyl-cycloheptene	46	80	80.9 */19.1
1-Phenylthiomethyl-cyclooctene	57	72	91.5/8.5 (95.5) */(4.5)
1-Phenylthiomethyl-cyclononene	55	79	(97.3) */(2.7)
1-Phenylthiomethyl-cyclodecene	51	82	(98.1) */(1.9)

[a] Based on the ^{1}H NMR spectrum of the mixture. Numbers in parentheses are the corresponding GLC ratios. Numbers with an asterisk are those used for the graph in Fig. 1.

A very important step in our synthesis was the dehydration of the phenylthiomethylcycloalkanols. This reaction could give two isomeric olefinic sulfides, one allylic and another vinylic (eq. 8).



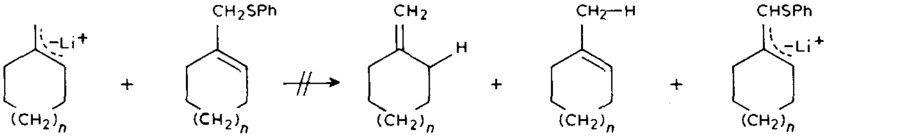
(8)

Both types of product were determined when the dehydration was carried out either with sodium hydroxide in ethylene glycol at 120 ° C or with *p*-toluenesulfonic acid in refluxing benzene. By use of potassium hydrogen sulfate at ca. 100 ° C as the dehydrating agent we obtained the allylic sulfide as the sole product.

The isomerization of vinylic to allylic sulfides by acid and/or base catalysis was briefly examined. Best results were obtained by boiling the mixture of the two olefinic sulfides in ethanolic sodium hydroxide for 20 h. Thus an originally 50/50 mixture of the two sulfides derived from the dehydration of phenylthiomethylcycloheptanol by the toluenesulfonic acid method, gave after the above treatment, a 3/1 mixture of allylic to vinylic sulfides. From this mixture the phenylthiomethylcycloheptene was separated by preparative GLC. The yields of the dehydration products were in the range 80–100%.

Transformation of the allylic sulfides to the relevant organolithium derivatives was carried out at -65 ± 5 ° C, using naphthalenelithium in THF [6]. The carbonation products were obtained in 45–90% yields (see Table 1). No effort was made to maximize the yield of the allylic organolithium in the step involving reaction with naphthalenelithium.

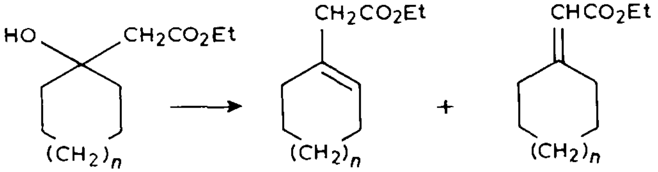
It is of importance that the carboxylic acids obtained by carbonating the mixture obtained from the allylic sulfide and $Li^+C_{10}H_8^{\cdot-}$ did not contain any detectable amount of a sulfur-bearing carboxylic acid. Such a product could result from transmetalation as depicted in eq. 9.



(9)

This type of reaction does occur in the case of acyclic allylic sulfides [9]. The difference between acyclic and cyclic allylic sulfides arises from the fact that the latter are much weaker carbon acids [10*].

In a carbanion such as **3** the three carbons which comprise the allylic system as well as the substituents attached to them should tend to be coplanar [2,11]. Coplanarity should be approached to the extent that it is permitted by the conformational requirement of the ring system and so it can reasonably be expected that the behaviour of the cyclic carbanions we are concerned with will depend on the ring size, and this appears to be the case so far as the distribution of the isomers of carbonation products is concerned. In most cases an estimate of the ratio of the cycloalkenyl acetic acid (*endo* product) to the methylenecycloakane carboxylic acid (*exo* product) could be obtained from the intergrated proton NMR spectra of the mixture, the resonances of the *exo-* and *endo*-cyclic olefinic protons being well separated. More accurate product ratios were obtained from GLC analysis of the ethyl ester mixtures, on the assumption that no fractionation occurred during esterification) in cases in which the yield of ester was considerably lower than theoretical. Authentic samples of the ethyl cycloalkenyl acetates, for use as analytical standards, were prepared by the Reformatsky reaction followed by acid-catalyzed dehydration of the ethoxycarbomethylenecycloalkanols (eq. 10).



(10)

In Fig. 1 a plot is shown of the proportion of *endo* product against the number of the carbon atoms in the ring. It can be seen that the proportion of *endo* product sharply increases up to C_8 and than less sharply from C_8–C_{10}. By extrapolation we can predict that for C_{12} or larger the carbonation reaction should become fully selective, and give just the *endo* product. It is tempting to associate the increasing relative yield of the *endo* product with decreasing conformational rigidity; in a less rigid ring system the allylic carbons and the substituents attached to them approach coplanarity [2,11], and this could make the *exo*-cyclic carbon the site of highest negative charge density. This interpretation, however, does not seem to fit the result from 4-(t-butyl)cyclohexanyl derivatives, see Table 1. In this case the increased

* A reference number with an asterisk refers to a note in the list of references.

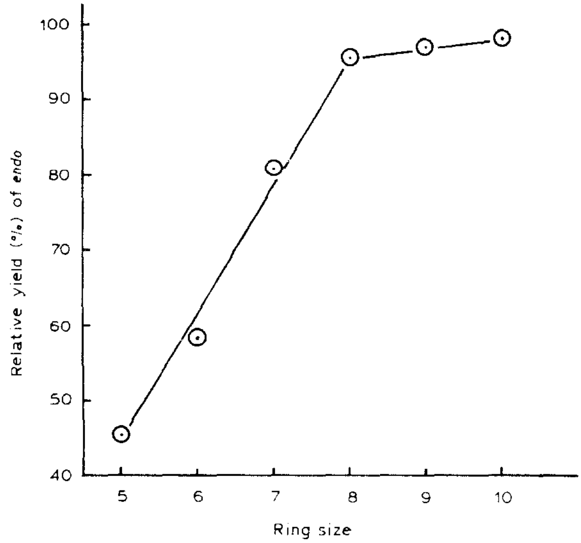


Fig. 1. Relative yield of cycloalken-1-yl acetic acids produced by carbonation of species **3** plotted against the number of carbon atoms in the alicyclic ring.

rigidity of the ring has exactly the opposite effect, the *endo* product being formed in over 10% higher yield than in the unsubstituted cyclohexanyl derivative. It has been noted previously that a plot of the relative yield of the *endo* product against the corresponding product yield of the dehydration of the ethoxycarbomethylenecycloalkanols (eq. 10), is linear with a near unit slope [12]. Thus two entirely different reactions, one electrophilic and the other nucleophilic, with different transition states, lead to very similar product distributions. This suggests the site of attack in the allylic anion **3**, is determined by the thermochemical stability of the product(s) [12].

Experimental

Reactions involving air sensitive reactants and/or products were carried out under argon. NMR spectra were recorded with a Varian FT80A spectrometer with $CDCl_3$, as solvent, and the chemical shifts are given in ppm downfield from TMS. GLC analyses and preparative separations were performed with a Pye Unicam GCV Gas chromatograph on (a) 4.5% Apiezon L on Chromosorb GAW/BMCS, 14′ × 3/8″ and (b) 10% Apiezon L, 6′ × 1/8″. Boiling points and melting points are uncorrected; the melting points were determined for samples in open capillaries with a Büchi apparatus. Tetrahydrofuran was purified by distillation from lithium aluminum hydride under argon shortly before use. The chemicals used were Merck or Fluka products, usually 98% pure of better, and were used as received.

1-(Phenylthiomethyl)cyclopentanol-1. To a stirred solution of 7.5 ml (ca. 50 mmol) of thioanisole in 40 ml of anhydrous peroxide-free THF at ca. −60 °C (Dry Ice/acetone bath) was added 28.5 ml of 1.75 *M* (50 mmol) butyllithium in cyclohexane. The mixture was stirred for 20 h at room temperature and then at

37 °C for 0.75 h. The brownish yellow solution was cooled in an ice water bath and the α-lithiothioanisole treated dropwise with a mixture of cyclopentanone (4.2 ml, ca. 48 mmol) with an equal volume of THF. The mixture was then diluted with 70 ml of toluene and treated with 60 ml of distilled water. The organic layer was separated, washed with water, then dried over $MgSO_4$, and the solvent was removed. The excess of thioanisole was then removed by vacuum distillation and fractionational distillation of the residue afforded a pure product b.p. 93–96 °C/0.05–0.1 mmHg. Yield 8.0 g, 95%. ^{1}H NMR: δ (ppm) 1.65, m, 8H (aliphatic); 2.63, s, 1H (OH); 3.17, s, 2H (SCH_2C); 7.27, m, 5H (aromatic). ^{13}C NMR: δ (ppm) C(1) 137.09; C(2) 128.85; C(3) 129.47; C(4) 126.06; C(5) 129.47; C(6) 128.85; C(7) 46.28; C(8) 81.72; C(9) 39.29; C(10) 23.97; C(11) 23.97; C(12) 3.29.

1-Phenylthiomethylcyclohexanol. Yield 83–87%, b.p. 118 °C/0.3 mmHg. ^{1}H NMR: δ(ppm) 1.49, m, 10H (aliphatic); 2.29, s, 1H (OH); 3.05, s, 2H (SCH_2); 7.26, m, 5H (Ph).

1-Phenylthiomethyl(4-t-butyl)cyclohexanol. Yield 83%. ^{1}H NMR: δ (ppm) 0.85, s, 9H (t-Bu); 1.64, m, 9H (aliphatic); 3.04, s, 2H (SCH_2); 3.20, s, 1H (OH); 7.34, m, 5H (Ph).

1-Phenylthiomethylcycloheptanol. Yield, 98%. ^{1}H NMR: δ (ppm) 1.52, m, 10H (aliphatic); 1.67, br m, 4H (CH_2–C–CH_2); 2.18, s, 1H (OH); 3.09, s, 2H (SCH_2); 7.24, m, 5H (Ph).

1-Phenylthiomethylcyclooctanol. Yield, 89%. ^{1}H NMR: δ (ppm) 1.52, m, 10H (aliphatic); 1.67, br m, 4H (CH_2–C–CH_2); 2.18, s, 1H (OH); 3.09, s, 2H (SCH_2); 7.24, m, 5H (Ph).

1-Phenylthiomethylcyclodecanol. Yield, 88%. ^{1}H NMR: δ (ppm) 1.52, m, 14H (aliphatic); 2.07, s, 1H (OH); 3.08, s, 2H (SCH_2); 7.32, m, 5H (Ph).

1-(Phenylthiomethyl)cyclohexene. A mixture of 15.55 g (83.6 mmol) of 1-(phenylthiomethyl)cyclohexanol-1 and 22 g (161.8 mmol) of potassium hydrogen sulfate was stirred at ca. 120 °C (oil bath temperature). The dark brown mixture was diluted with water and the product extracted with ether (3 × 80 ml portions). The combined extracts were washed with water (30 ml) dried over magnesium sulfate, and filtered, and the filtrate evaporated to small volume in a thin film evaporator. The residue was fractionated under reduced pressure to give a fraction (13.5 g, 79%) b.p. 85–90 °C/0.1 mmHg. GLC analysis revealed only one single component; ^{1}H NMR: δ (ppm) 1.54, m, 4H (aliphatic); 1.99, m, 4H (aliphatic); 3.42, s, 2H (SCH_2); 5.49, br s, 1H (olefinic); 7.21, m, 5H (Ph).

1-Phenylthiomethylcyclopentene. Yield, 92%; b.p. 73–78 °C/0.2 mmHg. ^{1}H NMR: δ (ppm) 1.85, m, 2H; 2.23, m, 4H; 3.56, s, 2H (SCH_2); 5.46, br s, 1H (olefinic); 7.21, m, 5H (Ph).

1-Phenylthiomethyl(4-t-butyl)cyclohexene. Yield 99%; ^{1}H NMR: δ (ppm) 0.85, s, 9H (t-Bu); 1.15, m, 2H; 2.10, m, 2H; 3.45, s, 2H (SCH_2); 5.48, br s, 1H (olefinic); 7.17, m, 5H (Ph).

1-Phenylthiomethylcycloheptene. Yield 83% as a 50/50 mixture with the vinylic isomer, 100–103 °C/0.2 mmHg. ^{1}H NMR: δ (ppm) 1.65, m, 8H (aliphatic); 2.25, m, 4H (aliphatic); 3.55, s, 2H (SCH_2); 5.68, tr, *J* 6.2 Hz, 1H (olefinic); 7.32, m, 5H (Ph).

1-Phenylthiomethylcyclooctene. Yield 90% b.p. 113–117 °C/0.05–0.1 mmHg. ^{1}H NMR: δ (ppm) 1.42, br s, 8 H (aliphatic); 2.15, m, 4H (aliphatic); 3.53, s, 2H (SCH_2); 5.53, tr, *J* 8.1 Hz, 1H (olefinic) 7.24, m, 5H (Ph).

1-Phenylthiomethylcyclononene. Yield, 100%; ^{1}H NMR: δ (ppm) 1.44, br s, 10H (aliphatic); 2.19, m, 4H (aliphatic); 3.56, s 2H (SCH_2); 5.47, tr, J 8.3 Hz, 1H (olefinic); 7.27, m, 5H (Ph).

1-Phenylthiomethylcyclodecene. Yield, 99%; ^{1}H NMR: δ (ppm) 1.38, br s, 12H (aliphatic); 2.32, m, 4H (aliphatic); 3.53, s 2H (SCH_2);5.34, tr, J 8.3 Hz, 1H (olefinic); 7.27, m, 5H (Ph).

Reaction of 1-(phenylthiomethyl)cyclooctene with naphthalenelithium

To a stirred solution of $Li^+C_{10}H_8^{\cdot-}$ prepared from 0.140 g lithium metal, 2.6 g (ca. 20 mmol) of naphthalene, and 20 ml of THF (with stirring for 15 h at room temperature) and cooled in a Dry Ice/acetone bath was added a solution of 2.1 g of the title sulfide in 9 ml of THF. The rate of addition of the sulfide solution was such that temperature was kept below $-63°$C. Upon completion of the addition the mixture had become brownish red. After a further 5 min stirring at ca. $-70°$C the mixture was carbonated with a slurry of crushed Dry Ice and diethyl ether. The mixture was allowed to warm to room temperature and then stirred with 70 ml of water, 2 ml of dimethyl sulfate, and 2 pellets of sodium hydroxide for 2 h. Toluene (100 ml) was then added, and the water layer was separated, washed with hexane (2×100 ml), and then acidified with 20% sulfuric acid. The liberated carboxylic acids were extracted with ether (3×100 ml). The combined ether extracts were dried over $MgSO_4$ for 12 h, then filtered and evaporated to dryness to leave 0.86 g (57%) of a mixture of α-cyclooctenyl acetic acid and 2-methylenecyclooctane carboxylic acid. The mixture gave the following ^{1}H signals: 1.35, m, (aliphatic); 2.20, m (aliphatic); 2.82, s, (CH_2COO); 3.35, m, (methenic); 4.78, m, (olefinic, *exo*), 5.32, t, J 8.1 Hz (olefinic, *endo*). Integration of the two well separated olefinic bands indicated a (*endo*)/(*exo*) product ratio of ca. 92/8.

Ethyl esters of 2-methylenecycloheptanecarboxylic and cyclohepten-1-yl acetic acids

A solution of 0.55 g (3.6 mmol) of a mixture of the title acids in 1.0 g of absolute ethanol (ca. 2 mmol) and 8 ml of dry benzene containing 0.25 g of p-toluenesulfonic acid was refluxed for 20 h, then diluted with 25 ml of benzene. The mixture was washed with 2×40 ml portions of saturated $NaHCO_3$ solution, then with 2×40 ml portions of saturated sodium chloride, and dried over $MgSO_4$ and filtered. The filtrate was evaporated to constant weight. Yield of ethyl esters 0.65 g, 80%. GLC analysis gave a ratio **B**/**A** of 80.91/19.09. Preparative GLC afforded samples of the pure ethyl esters.

Ethyl cyclopenten-1-ylacetate [13]. ^{1}H NMR: δ (ppm) 1.24, t, J 7.0 Hz, 3H (CH_2CH_3) 1.90, m, 2H (aliphatic); 2.32, m, 4H (aliphatic); 3.07, s, 2H (CH_2COO); 4.08, q, J 7.0 Hz, 2H (CH_2CH_3); 5.48, s, 1H (olefinic) ^{13}C NMR: C(1), 136.57; C(2), 127.91; C(3–6), 36.87; 34.99; 32.37; 23.35; C(7), 171.17; C(8), 60.29; C(9), 14.04.

Ethyl cyclohexen-1-ylacetate [13]. ^{1}H NMR: δ (ppm) 1.23, t, J 7.0 Hz, 3H (CH_2CH_3); 1.56, m, 4H (aliphatic); 1.98, br m, 4 H (aliphatic); 2.98, s, 2H (CH_2COO); 4.09, q, J 7.0 Hz (CH_2CH_3); 5.50, s, 1H (olefinic). ^{13}C NMR: δ (ppm) C(1), 131.21; C(2), 125.38; C(3–6) 28.42; 25.29; 22.76; 22.02; C(7), 43.56; C(8), 171.67; C(9), 60.20; C(10), 14.12.

Ethyl (4-t-butyl)cyclohexen-1-ylacetate. ^{1}H NMR: δ (ppm): 0.86, s, 9H (t-Bu); 1.25, t, J 7.1 Hz (CH_2CH_3); 1.84, m, 7H (aliphatic); 2.93, s, 2H (CH_2COO); 4.13,

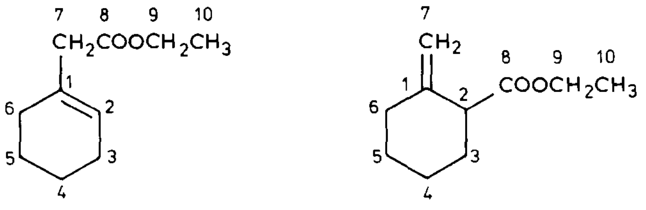


Fig. 2. Example of numbering of compounds.

q, J 7.1 Hz, 2H (CH_3); 5.57, br s, 1H (olefinic). ^{13}C NMR: δ (ppm) C(1/1), 131.01; C(2/2), 125.78; C(4/2), 43.75; C(5/3), 24.13; C(3,6/3), 29.93; 26.96; C(7/3), 43.12; C(8/1), 171.91; C(9/3), 60.34; C(10/4), 14.26; C(11/1), 32.14; C(12–14/4), 27.20.

Ethyl cyclohepten-1-ylacetate [13]. ^{1}H NMR: δ (ppm) 1.27, t, J 7.1 Hz, 3H (CH_2CH_3); 1.61, m, 6H (aliphatic); 2.12, m, 4H (aliphatic); 2.97, s, 2H (CH_2COO); 4.14, q, J 7.1 Hz (CH_2CH_3); 5.68, t, J 6.3 Hz 1H (olefinic). ^{13}C NMR: δ (ppm) C(1), 137.64; C(2), 130.66; C(3–7), 32.91; 32.33; 28.46; 26.96; 26.52; C(8), 45.61; C(9), 172.22; C(10), 60.38; C(11), 14.25.

Ethyl cycloocten-1-ylacetate [14]. ^{1}H NMR: δ (ppm) 1.25, t, J 7.1 Hz, (CH_2CH_3); 1.48, s, 8H (aliphatic); 2.17, br m, 4H (aliphatic); 2.97, s, 2H, (CH_2COO); 4.13; q, J 7.1 Hz, 2H (CH_2CH_3); 5.52, t, J 8.1 Hz, 1H (olefinic).

Ethyl 2-methylene(4-t-butyl)cyclohexane carboxylate. ^{1}H NMR: δ (ppm) 0.85, s, 9H (t-Bu); 1.24, t, J 7.2 Hz, 3H (CH_2CH_3); 1.28, m, 2H (aliphatic); 1.75, m, 1H (CH-Bu-t); 2.26, m, 4H (aliphatic); 3.29, m, 1H (CHCOO); 4.15, q, J 7.2 Hz (CH_2CH_3); 4.75, s, 1H (olefinic); 4.81, s, 1H (olefinic). ^{13}C NMR: δ (ppm) C(1), 146.54; C(2), 49.17; C(3), 31.05; C(4), 43.64; C(5), 28.55; C(6), 32.91; C(7), 110.87; C(8), 173.69; C(9), 60.38; C(10), 14.28; C(11), 32.28; C(12–14), 27.44.

Ethyl 2-methylenecycloheptane carboxylate. ^{1}H NMR: δ (ppm) 1.28, t, J 7.1 Hz, 3H (CH_2CH_3); 2.31, m, 2H (aliphatic); 2.75, m, 8H (aliphatic); 3.24, m, 1H (CHCOO); 4.12, q, J 7.1, 2H (CH_2CH_3); 4.89, m, 2H (olefinic). ^{13}C NMR: δ (ppm) C(1), 149.16; C(2), 51.71; C(3–7), 34.52, 30.57, 30.41, 29.89, 26.61; C(8), 114.39; C(9), 174.72; C(10), 60.36; C(11), 14.16.

Ethyl 2-methylenecyclooctane carboxylate. ^{1}H NMR: δ (ppm) 1.22, t, J 7.1 Hz, 3H (CH_2CH_3); 1.54, br m, 10H (aliphatic); 2.30, br m, 2H (aliphatic); 3.10, m, 1H (CHCOO); 4.10, q, J 7.1 Hz, 2H (CH_2CH_3); 4.97, s, 2H (olefinic).

Ethyl 2-methylenecyclononane carboxylate. ^{1}H NMR: δ (ppm) 1.22, t, J 7.1 Hz, 3H (CH_2CH_3); 1.43, br m, 12H (aliphatic); 2.26, m, 2H (aliphatic); 3.62, m, 1H (CHCOO); 4.13, q, J 7.1 Hz, 2H (CH_2CH_3); 5.07, s, 2H (olefinic).

Ethyl cyclononen-1-ylacetate. ^{1}H NMR: δ (ppm) 1.24, t, J 7.1 Hz, 3H (CH_2CH_3); 1.45, s, 10H (aliphatic); 2.22, br m, 4H (aliphatic); 2.96, s, 2H (CH_2COO); 4.12, q, J 7.1 Hz, (CH_2CH_3); 5.43, t, J 8.2 Hz, 1H (olefinic). ^{13}C NMR: δ (ppm) C(1), 133.45; C(2), 129.75; C(3–9), 29.30, 26.72, 26.37, 25.94, 25.43, 25.09, 24.82; C(10), 43.41; C(11), 172.17; C(12), 60.34; C(13), 14.21.

Ethyl cyclodecen-1-ylacetate [15]. ^{1}H NMR: δ (ppm) 1.25, t, J 7.1 Hz, (CH_2CH_3); 1.41, br s, 12H (aliphatic); 2.28, m, 4H (aliphatic); 2.97, s, 2H (CH_2COO); 4.14, q, J 7.1 Hz, (CH_2CH_3); 5.33, t, J 8.2 Hz, 1H (olefinic). ^{13}C NMR: δ (ppm) C(1/1), 132.19; C(2/2), 130.36; C(3–10), 27.43, 26.99, 26.74, 26.51, 25.82, 24.50, 21.04, 20.70.

Ethyl 2-methylenecyclopentane carboxylate. ^{1}H NMR: δ (ppm) 1.25, t, J 7.0 Hz, 3H (CH_2CH_3); 1.78, m, 4H (aliphatic); 2.33, m, 2H (aliphatic); 3.26, br m, 1H (CHCOO); 4.12, q, J 7.0 Hz (CH_2CH_3); 4.98, m, 2H (olefinic). ^{13}C NMR: δ (ppm) C(1/1), 150.57; C(2/2), 48.93; C(3–5/3), 33.36, 30.23, 25.17; C(6/3), 107.70; C(7/1), 174.04; C(8/3), 60.40; C(9/4), 14.16.

Ethyl 2-methylenecyclohexane carboxylate. ^{1}H NMR: δ (ppm) 1.25, t, J 7.0 Hz, 3H (CH_2CH_3); 1.65, m, 6H (aliphatic); 2.16, m, 2H (aliphatic); 3.08, m, 1H (CHCOO); 4.13, q, J 7.0 Hz (CH_2CH_3); 4.58, s, 1H (olefinic); 4.78, s, 1H (olefinic). ^{13}C NMR: δ (ppm) C(1), 146.68; C(2), 49.66; C(3–6), 34.41, 30.37, 27.83; C(7), 109.13; C(8), 173.58; C(9), 60.30; C(1), 14.26.

References

1 For leading references see (a) Y. Yamamoto, Acc. Chem. Res., 20 (1987) 243; (b) T. Cohen and B.-S. Guo, Tetrahedron, 42 (1986) 2803; (c) P. Hope, Angew. Chem. Int. Ed. (Engl.), 23 (1984) 932; and references therein.
2 A. Schriesheim, R.J. Muller and C.A. Rowe, Jr., J. Am. Chem. Soc., 84 (1962) 3164.
3 E. Moret, P. Schneider, C. Margot, M. Stähle and M. Schlosser, Chimia, 39 (1985) 231.
4 R.L. Sowerby and R.M. Coates, J. Am. Chem. Soc., 94 (1972) 4758.
5 J. Corey and D. Seebach, J. Org. Chem., 31 (1966) 4097.
6 C.G. Screttas and M. Micha-Screttas, J. Org. Chem., 43 (1978) 1064; T. Cohen, W.M. Daniewski and R.B. Weisenfeld, Tetrahedron Lett., (1978) 4665; T. Cohen, and R.B. Weisenfeld, J. Org. Chem., 44 (1979) 3601.
7 C.G. Screttas and J.F. Eastham, J. Am. Chem. Soc., 88 (1966) 5668.
8 J. Barluenga, F.J. Fañanás, J. Villemaña and M. Yus, J. Org. Chem., 47 (1982) 1560.
9 C.G. Screttas and M. Micha-Screttas, unpublished observations.
10 Proton removal from an allylic position requires rehybridization ($sp^3 \rightarrow sp^2$) of the allylic carbon, a process which should be more probable if conformational constraints are absent see ref. 2 and 11.
11 D.J. Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York, 1965, p. 199.
12 C.G. Screttas and I.C. Smonou, J. Org. Chem., in press.
13 T. Miyashi, Y. Nishizawa, Y. Fujii, K. Yamakawa, M. Kamata, S. Akao, and T. Mukai, J. Am. Chem. Soc., 108 (1986) 1617.
14 L. Ruzicka and H.A. Boekenoogen, Helvetica, 9 (1926) 399.
15 Y. Murakami, Y. Aoyama, M. Kida and A. Nakao, Bull. Chem. Soc. Japan, 50 (1977) 3365.