

# $^{13}\text{C}$ NMR Chemical Shift Assignments for Some *n*-Butylthiomethylene Ketones

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The  $^{13}\text{C}$  NMR spectra of a series of 2-(*n*-butylthiomethylene) cycloalkanones and 2-(*n*-butylthiomethylene) 1-decalones were recorded and unequivocally assigned by the study of correlation signals in DQCOSY and HETCOR experiments. The effect caused by the introduction of the *n*-butylthiomethylene group in comparison with the corresponding parent compounds is discussed.

KEY WORDS 2-(*n*-Butylthiomethylene) cycloalkanones 2-(*n*-Butylthiomethylene) decalones  $^{13}\text{C}$  NMR chemical shifts

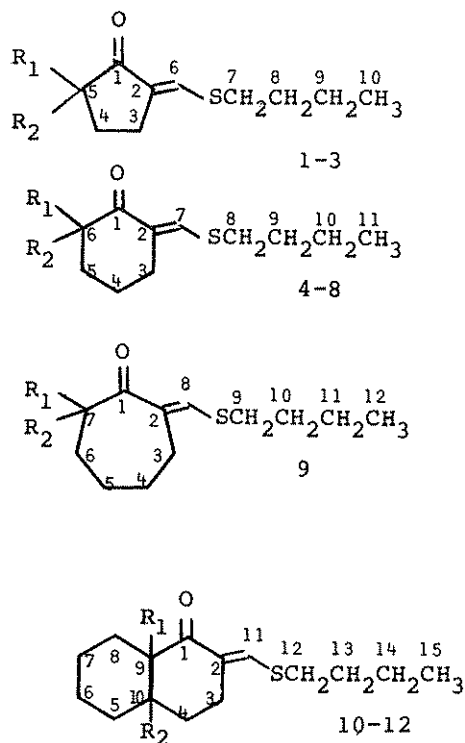
## INTRODUCTION

The *n*-butylthiomethylene group introduced into the  $\alpha$ -position to a carbonyl function has been utilized as a blocking group for the selective preparation of alkyl-substituted ketones,<sup>1,2</sup> to obtain sulphur-substituted 1,3-dienes<sup>3</sup> and as an activating function of the carbonyl group to promote a new ring expansion reaction of

cycloalkanones.<sup>4</sup> However, and in spite of their utility in direct rather than conjugate nucleophilic addition reactions, only a very limited number of 2-(*n*-butylthiomethylene) cycloalkanones and decalones with few  $^{13}\text{C}$  NMR data have been reported.<sup>5-9</sup>

We have prepared a variety of these *n*-butylthiomethylene derivatives of substituted and unsubstituted cyclopentanones (1-3), cyclohexanones (4-8), cycloheptanone (9), *trans*-1-decalone (10) and *cis*- and *trans*-9-methyl-1-decalones (11-12) (Scheme 1), some of them for the first time, and report here the unequivocal assignments of their  $^{13}\text{C}$  NMR chemical shifts through DQCOSY and HETCOR experiments.

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Compound	$\underline{R}_1$	$\underline{R}_2$
1	H	H
2	$\text{CH}_3$	H
3	$\text{CH}_3$	$\text{CH}_3$
4	H	H
5	$\text{CH}_3$	H
6	$\text{CH}_3$	$\text{CH}_3$
7	$\text{CH}_3$	$\text{C}_2\text{H}_5$
8	$\text{CH}_3$	$\text{C}_3\text{H}_7$
9	H	H
10	H	H ( <i>trans</i> )
11	$\text{CH}_3$	H ( <i>cis</i> )
12	$\text{CH}_3$	H ( <i>trans</i> )

Scheme 1

Table 1.  $^{13}\text{C}$  chemical shifts of *n*-butylthiomethylene cycloalkanones 1-9 and decalones 10-12 in comparison with the parent compounds

compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	Other
1 Cyclopentanone <sup>12</sup>	203.0	132.5	28.0	19.3	38.2	137.3	34.2	32.5	21.4	13.4						$\alpha\text{-CH}_3$ 14.8
2 2-Me-cyclopentanone <sup>12</sup>	219.4	38.1	23.2	23.2	38.1	137.4	34.3	32.6	21.5	13.5						$\alpha\text{-CH}_3$ 23.8, $\alpha'\text{-CH}_3$ 23.8
3 2-Me-cyclopentanone <sup>12</sup>	204.8	132.5	26.2	28.6	43.7	137.4	34.3	32.6	21.5	13.5						$\alpha\text{-CH}_3$ 16.0
4 Cyclohexanone <sup>12</sup>	220.9	37.5	20.7	31.9	43.9	137.9	34.1	32.4	21.4	13.3						$\alpha\text{-CH}_3$ 14.7
5 2-Me-cyclohexanone <sup>12</sup>	206.5	131.7	24.3	35.1	45.4	137.9	34.1	32.4	21.4	13.3						$\alpha\text{-CH}_3$ 26.1, $\alpha'\text{-CH}_3$ 26.1
6 2,2-Di-Me-cyclohexanone <sup>12</sup>	195.2	130.2	27.2	22.7	22.5	138.7	141.9	33.7	32.2	21.1	13.1					$\alpha\text{-CH}_3$ 25.2, $\alpha'\text{-CH}_3$ 25.2
7 Cyclohexanone <sup>12</sup>	211.5	41.9	27.1	25.0	27.1	41.9	141.7	34.0 <sup>a</sup>	32.5	21.5	13.4					$\alpha\text{-CH}_2$ 31.0, $\beta\text{-CH}_3$ 8.0
8 2-Me-cyclohexanone <sup>12</sup>	197.7	130.1	27.5	21.2	31.0	42.5	140.9	33.5	32.1	21.0	13.0					$\alpha\text{-CH}_2$ 40.9, $\beta\text{-CH}_2$ 16.9
9 Cycloheptanone <sup>14</sup>	212.9	41.8	28.0	25.2	36.2	45.3	141.9	33.8	32.3	21.3	13.2					$\alpha\text{-CH}_3$ 14.5, $\alpha'\text{-CH}_3$ 24.3
10 <i>trans</i> -1-Decalone <sup>13</sup>	201.0	129.6	27.9	18.4	37.7	42.1	141.9	33.8	32.3	21.3	13.3					Angular $\text{CH}_3$ 26.2
11 <i>trans</i> -1-Decalone <sup>13</sup>	215.0	38.2	27.6	21.5	41.1	45.1	141.7	34.0 <sup>a</sup>	32.5	21.4 <sup>a</sup>	141.5	34.0	32.5	21.4 <sup>a</sup>	13.4	Angular $\text{CH}_3$ 25.9
12 <i>cis</i> -9-Me-1-decalone <sup>13</sup>	201.5	130.5	28.0	18.3	34.1 <sup>a</sup>	45.7	141.7	34.0 <sup>a</sup>	32.5	21.5	13.4					Angular $\text{CH}_3$ 15.8
<i>trans</i> -9-Me-1-decalone <sup>13</sup>	201.2	130.3	27.9	18.2	34.5	45.5	141.7	33.9	32.4	21.4	13.3					Angular $\text{CH}_3$ 15.7
9 Cycloheptanone <sup>14</sup>	199.7	135.2	28.9	28.5	31.1	24.9	42.9	135.2	33.7	32.3	21.3	13.3				Angular $\text{CH}_3$ 26.2
10 <i>trans</i> -1-Decalone <sup>13</sup>	215.0	43.9	24.4	30.6	30.6	24.4	43.9	26.5	53.4	39.7	141.3	34.2 <sup>a</sup>	32.6	21.6	13.5	Angular $\text{CH}_3$ 25.9
11 <i>trans</i> -1-Decalone <sup>13</sup>	197.6	130.7	27.1	30.2	34.2 <sup>a</sup>	25.7	26.1	26.5	55.1	45.0	141.7	33.9	32.3	21.3	13.2	Angular $\text{CH}_3$ 15.8
12 <i>cis</i> -9-Me-1-decalone <sup>13</sup>	212.3	41.8	25.5	33.1	34.4	25.2	25.9	26.5	55.1	45.0	141.5	34.0	32.5	21.4 <sup>a</sup>	13.4	Angular $\text{CH}_3$ 15.8
<i>trans</i> -9-Me-1-decalone <sup>13</sup>	200.2	128.9	23.0	26.2	28.8	25.3	23.9	34.8	46.6	42.2	141.7	33.9	32.3	21.3	13.2	Angular $\text{CH}_3$ 15.7
<i>cis</i> -9-Me-1-decalone <sup>13</sup>	216.2	37.9	22.9	26.6	28.9	25.2	22.9	34.1	49.5	44.7	141.5	34.0	32.5	21.4 <sup>a</sup>	13.4	Angular $\text{CH}_3$ 15.7
<i>trans</i> -9-Me-1-decalone <sup>13</sup>	201.7	129.5	24.9	26.3	28.4	25.9	21.4 <sup>a</sup>	33.4	45.3	41.1	141.5	34.0	32.5	21.4 <sup>a</sup>	13.4	Angular $\text{CH}_3$ 15.7
<i>trans</i> -9-Me-1-decalone <sup>13</sup>	215.9	37.5	26.3	27.7	27.9	26.3	21.4	32.6	48.4	46.1	141.5	34.0	32.5	21.4 <sup>a</sup>	13.4	Angular $\text{CH}_3$ 15.7

<sup>a</sup> Assignments may be interchanged.

## RESULTS AND DISCUSSION

The synthesis of cycloalkanones 1-9 and decalones 10-12 was carried out by the introduction of the hydroxymethylene group at C-2 of the starting ketone, followed by reaction with *n*-butanethiol in the presence of *p*-toluenesulphonic acid as previously described.<sup>1</sup> The configuration of the *n*-butylthiomethylene ketones prepared is mainly *E* [ $\delta(\text{C}=\text{CHSBu}) = 7.35\text{--}7.55$ ], although a small percentage of the *Z* isomer (<5-7%) at  $\delta$  6.65-6.75 was detected in most cases. The assignment was based on the well known differentiating effect promoted by the carbonyl group on the  $\beta$ -protons with a *Z* or *E* relationship to the carbonyl in cisoid  $\alpha,\beta$ -unsaturated ketones.<sup>10</sup> The ring junction configuration in decalones 11 and 12 was determined by the larger peak width at half-height of the angular methyl group for the *trans*-fused isomer (0.86 Hz for 12) than for the *cis*-fused isomer (0.29 Hz for 11).<sup>11</sup> This assignment was further confirmed by the  $^{13}\text{C}$  NMR data (Table 1). All the compounds were fully characterized by their spectroscopic properties (IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectra).

In all cases the carbonyl carbon absorptions of the *n*-butylthiomethylene cycloalkanones prepared are not only, as expected, consistently shielded by an average of  $-14.6 \pm 1.8$  ppm compared with the non-substituted ketones, but also follow the same trend as their parent counterparts on methyl substitution.<sup>12</sup> In addition, we have found that in the cyclopentanone series, C-3 of 1 and 2 is significantly deshielded (+4.8 ppm for 1 and +5.5 ppm for 2) in comparison with their parent ketones. C-4, on the other hand, is shielded by  $-3.3$  to  $-3.9$  ppm whereas the C-5 in 1 and 2 is hardly affected. Absorption of C-4 at 28.6 ppm in the 5-methyl-substituted cyclopentanone 2, in comparison with the non-methylated ketone 1 at 19.3 ppm, suggests that the introduction of the methyl group has taken place at the pseudo-equatorial position owing to the higher  $\beta$  effect (*ca.* 9.1 ppm) in comparison with that promoted by a pseudo-axial oriented methyl group (*ca.* 6.0 ppm).<sup>12</sup>

In the cyclohexanone series (4-6) a regular trend is observed when the  $^{13}\text{C}$  absorptions are compared with those of the parent ketones, i.e. cyclohexanone, 2-methylcyclohexanone and 2,2-dimethylcyclohexanone.<sup>12</sup> Thus, whereas the C-3 absorptions are virtually unchanged ( $\Delta\delta$  0.1-0.5 ppm), the remaining carbons are regularly shielded, i.e. C-4 by an average of  $-3.2 \pm 0.9$  ppm, C-5 by  $-4.3 \pm 0.9$  ppm and C-6 by  $-3.0 \pm 0.2$  ppm.

C-3 in 2-(*n*-butylthiomethylene)cycloheptanone (9) is clearly deshielded (+4.5 ppm) and C-4 is shielded ( $-2.1$  ppm) when compared with the same carbons in cyclo-

heptanone. Absorptions of the other carbons, i.e. C-5 to C-7, are only slightly affected ( $\Delta\delta$  +0.5 to  $-1.0$  ppm).

In decalones 10-12 it is worth noting the regular upfield shift (*ca.*  $-2.4 \pm 0.7$  ppm) of C-9 compared with that of the parent decalones,<sup>13</sup> whereas C-10 is more shielded in *trans*-decalones ( $-5.3$  for 10 and  $-5.0$  ppm for 12) than in *cis*-decalones ( $-2.5$  ppm for 11). The remaining  $^{13}\text{C}$  absorptions of the *cis*-methyldecalone 11 resemble those of the underivatized compound ( $\Delta\delta \leq \pm 1$  ppm), whereas for the *trans*-decalones 10 and 12 only C-4 of 10 is significantly shielded ( $-2.9$  ppm) in comparison with the parent decalone. It must finally be noted that the  $^{13}\text{C}$  absorption of the angular 9-methyl in the decalones 11 and 12 can be a reliable parameter for ascertaining the ring junction configuration ( $\delta$  15.80 ppm for the *trans* junction and  $\delta$  26.2 ppm for the *cis* junction), as has been found in methyldecalins<sup>14</sup> and 2-decalones.<sup>13,15</sup>

## EXPERIMENTAL

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in 5 mm o.d. tubes for 0.2-0.4 M solutions in  $\text{CDCl}_3$  using TMS as internal reference. The spectra were recorded on a Bruker WP-80-SY spectrometer operating at 80 MHz ( $^1\text{H}$ ) and on a Varian Unity 300 NMR spectrometer at 300 MHz ( $^1\text{H}$ ) and 75 MHz ( $^{13}\text{C}$ ) at 25°C. The measurement conditions for  $^1\text{H}$  NMR were pulse angle 40°, acquisition time 4 s, spectral width 6000 Hz, pulse width 15  $\mu\text{s}$ , 16K data points with zero-filling up to 64K and Gaussian resolution enhancement. For  $^{13}\text{C}$  NMR the parameters were pulse angle 30°, acquisition time 1 s, pulse delay 2 s, spectral width 20 000 Hz, 20K data points with zero-filling up to 64K and 1 Hz exponential filtering.

$^{13}\text{C}$  DEPT experiments were run to assert C-H multiplicities under the previously established conditions using as an average  $^1J(\text{CH}) = 140$  Hz.<sup>16</sup> Two-dimensional experiments were run only for selected  $^1\text{H}$  or  $^{13}\text{C}$  windows with full quadrature detection. In all cases a 2-s recycling time and squared sine-bell filtering in both dimensions were generally employed. DQCOSY and HETCOR experiments were generally recorded using  $1024 \times 1024$  and  $2048 \times 1024$  data points, respectively, and the acquisition time was 1 s for DQCOSY and 0.3 s for HETCOR.

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