Table I. Partial Resolution[a] of Ni(*rac*-1,7-CT)(NCS)₂

Fraction	α_{obsd}, deg[b,c]	Concn, g/ml × 10^{4} [d]	$[\alpha]_{546}$, deg[e]
1	+0.264	9.95	+133
2	+0.559	20.4	+137
3	+0.745	32.9	+113
5	+0.139	34.6	+ 20
7	−0.210	25.7	− 41
10	−0.102	5.9	− 87
13	−0.052	3.1	− 83
14	−0.069	3.8	− 90

[a] This resolution was achieved chromatographically using a column packed with potato starch and 0.01 N HCl as the eluent. [b] Readings taken with a Rudolph Model 80 polarimeter using a 2-dm tube. [c] Standard deviation of values ±0.008°. [d] Determined spectrophotometrically. [e] Uncertainty ~±5°.

proof, the resolution of *dl*-Ni(1,7-CT)(NCS)₂ is significant as a novel example of optical activity due to the nitrogens of coordinated secondary amines.[5]
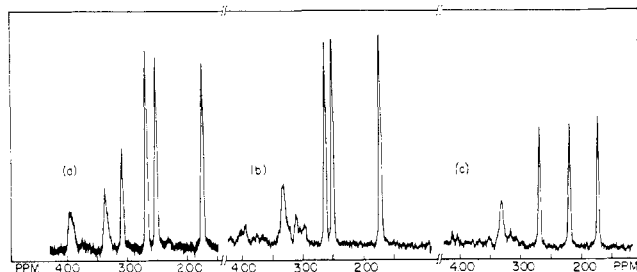

Figure 2. Pmr spectra of Ni(CT)(NCS)₂ isomers: (a) Ni(1,4-CT)-(NCS)₂ in neutral D₂O; (b) Ni(*rac*-1,7-CT)(NCS)₂ in acidic D₂O; (c) Ni(*meso*-1,7-CT)(NCS)₂ in acidic D₂O. Spectra calibrated in ppm downfield from external TMS.

Both pmr and visible spectra demonstrate that both pure Ni(*meso*-1,7-CT)²⁺ and pure Ni(*rac*-1,7-CT)²⁺ convert to the same equilibrium mixture of isomers in neutral aqueous solution or in acetone. However, if the solutions are distinctly acidic, the isomerization process is stopped. This is consistent with the long known pH dependence of hydrogen-exchange reactions involving coordinated amine groups.[6]

When separated from chloroform, Ni(*meso*-1,7-CT)-(NCS)₂ crystallizes with coordinated thiocyanates. Its spectrum and magnetic moment (3.2 BM) are typical of pseudo-octahedral nickel(II).[7] It is apparent (Figure 1) that the two extraplanar coordination sites are equivalent in the Ni(*meso*-1,7-CT)²⁺, but not in the *rac*-1,7-CT complex. The paramagnetic violet isomer is unstable and readily converts into the yellow diamagnetic form.

It is instructive to consider the only known (diamagnetic) isomer of Ni(1,4-CT)²⁺ along with the Ni(1,7-CT)²⁺ isomers. Three equally intense methyl resonances are most prominent in the pmr spectra (Figure 2) of all isomers: for NCS⁻ salts, Ni(*rac*-1,7-CT)²⁺, 2.67, 2.52, and 1.75 ppm; Ni(*meso*-1,7-CT)²⁺, at 2.69, 2.21, and 1.75 ppm; and Ni(1,4-CT)²⁺, 2.70, 2.54, and 1.75 ppm. Three resonances require the six methyl groups to be pairwise equivalent, a result easily accommodated if the two six-membered chelate rings

with a given isomer have identical conformations and if the secondary amines are configurationally stable toward inversion. This produces an axial *vs.* equatorial distinction between the *gem*-methyl groups.

Under conditions for rapid proton exchange (basic D₂O), the pmr spectra show that rapid flexing of the chelate rings occurs for both position isomers. At 35° the *gem*-methyl proton resonances of Ni(1,4-CT)²⁺ are merely broadened, but the bands collapse into a single resonance at 100°.

The imine methyl and the methylene protons of the six-membered chelate ring are readily identified by deuteration experiments. The proximity of these protons to the imine function[8,9] causes them to exchange for deuterium in basic D₂O.

The remainder of each pmr spectrum is assignable to the dimethylenic protons. This region provides a convenient and trustworthy method for distinguishing between the position isomers in this and similar systems. For Ni(1,4-CT)²⁺ the two dimethylene chains are different, but each has its two extremities identical. As a result, the most complex pattern expected would be two A₂B₂ patterns.[10,11] In the limit of slight distinction between the axial and equatorial hydrogens, the patterns would merely produce two distinct peaks, each of intensity 4. Figure 2 shows this to be the case: amine dimethylene, line at 3.11 ppm; imine dimethylene, A₂B₂ pattern at 3.92 ppm. In contrast, the two dimethylene chains are alike in either Ni(1,7-CT)²⁺ isomer, but the two ends of each chain are different. Conformational effects then cause each of the four protons to be distinct. This produces a complicated unsymmetrical ABCD pattern (Figure 2).

(5) Subsequent to submission of this report, the first convincing example of optical activity in a coordinated secondary amine appeared: B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966).

(6) J. W. Palmer, F. Basolo, and R. G. Pearson, *ibid.*, **82**, 1073(1960)

(7) J. L. Karn, Thesis, The Ohio State University, 1966.

(8) D. H. Williams and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 4644 (1965).

(9) D. A. Johnson, *Inorg. Chem.*, **5**, 1289 (1966).

(10) D. H. Williams, Thesis, The Ohio State University, 1964.

(11) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

(12) National Institutes of Health Postdoctoral Fellow, 4-F2·GM-28, 191-02.

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Reaction of Diazomethane with Silyl Ketones

Sir:

The reaction of diazomethane with ketones to give homologous ketones or epoxides is well documented.[1] It appeared of interest to investigate how the spectrally

(1) C. D. Gutsche, *Org. Reactions*, **8**, 364 (1954).

Table I. Reactions of Diazomethane with Silyl Ketones

$$RCOR' + CH_2N_2 \longrightarrow R_3SiOC(R')=CH_2 + R_3SiCH_2COR'$$

Ketone		Relative yields,[a,h] % (mp or bp, °C)	
R	R'	Siloxystyrene	β-Silyl ketone
Ph₃Si	Ph	60 (78–80)	40 (88–90)
Ph₃Si	p-ClC₆H₄	41 (80.5–82.0)	59 (121–121.5)
Ph₃Si	p-MeOC₆H₄	48[b]	52 (101–102)
Me₃Si	Ph	24 (78–84 (11 mm[c]))	76 (104 (3.1 mm))
(p-CF₃C₆H₄)₃Si	Ph	33[d]	67 (117–118.5)
(p-t-BuC₆H₄)₃Si	Ph	33[d]	66 (149–151)
α-NpMePhSi	Ph[e]	33 (oil)	67 (54–56)
Ph₃Si	Me	f	67[g]
Me₃Si	Me		82[g]
Ph₃Ge	Ph		81[g] (81–83)

[a] Relative yields were determined from the relative intensities of the nmr proton signals. [b] Compound not actually isolated, except as p-methoxyacetophenone, the decomposition product. The β-ketone was quite stable. [c] Compound slightly contaminated with phenacyltrimethylsilane. [d] Compound not isolated, except as acetophenone, the decomposition product. The β-ketone was quite stable. [e] Optically active enantiomer used. [f] The nmr spectrum of the first fraction eluted from silica gel with chloroform indicated that a small amount (<7%) of 2-triphenylsiloxypropene-2 might have been present. [g] Pure isolated material. [h] Under the experimental conditions (2–3 weeks at 0°) no unreacted ketone was detectable. Isolated yields of the β-ketones were in the range of 40–80% of the amounts estimated by nmr, but yields of siloxystyrenes rarely exceeded 50% due to decomposition during separation procedures.

abnormal carbonyl group of silyl ketones[2] would react with this reagent and whether products other than those normally observed would be formed.

When benzoyltriphenylsilane was kept at approximately 0° with excess ethereal diazomethane in the dark for several weeks, the crude product obtained by removal of the solvent showed infrared absorption at 6.0, 6.2, 7.6, 7.7, 7.8 and 9.4 μ, and the nmr spectrum showed doublets at $\delta = 4.34$ ($J = 2$ cps) and 4.77 ($J = 2$ cps) ppm, as well as a singlet at $\delta = 3.34$ ppm with intensities in the ratio of 3:3:4. Careful crystallization from ethanol afforded a compound, mp 78–80°, shown to be 1-triphenylsiloxystyrene by comparison of its properties with those of a sample prepared, following the general procedure of Kruger and Rochow,[3] from sodium bis(trimethylsilyl)amide, acetophenone, and triphenylchlorosilane: infrared: 6.2 (C=C), 7.6, 7.7, 7.8,[4] and 9.4 μ (Si–O–C); nmr: $\delta = 4.35$ (d, $J = 2$ cps, 1 H), 4.77 (d, $J = 2$ cps, 1 H), and 7.0–7.7 (m, 20 H) ppm.[5] This relatively unstable compound on treatment with a trace of KOH in wet ethanol gave acetophenone and triphenylsilanol. The other compound isolated from the reaction was the known phenacyltriphenylsilane[6] which had the typical β-silyl ketone carbonyl stretch at 6.0 μ and a singlet at $\delta = 3.34$ ppm in the nmr spectrum. Thus the spectral details of the crude reaction mixture are completely accounted for by the presence, in the ratio 60:40, of the siloxystyrene and the homologous β-silyl ketone. Similar results were obtained from a variety of other silyl ketones; the details are given in Table I. In general, the nature of the groups attached to silicon or the presence of various *para* substituents on aromatic rings had no very significant effect on the proportions of the two reaction products. In no case was any evidence observed for the formation of the alternative homologous ketone or for the epoxide. While the β-ketones were

reasonably stable compounds which could be readily isolated and purified, some of the siloxystyrenes were too unstable to isolate. They were identified by their characteristic nmr and infrared spectra and by their hydrolysis products, silanol and acetophenone.

The formation of the two types of reaction product may be logically explained as resulting from the addition of diazomethane to the carbonyl group to give an intermediate I, which may lose nitrogen,[7] giving II, prior to normal rearrangement to the β-ketone III.
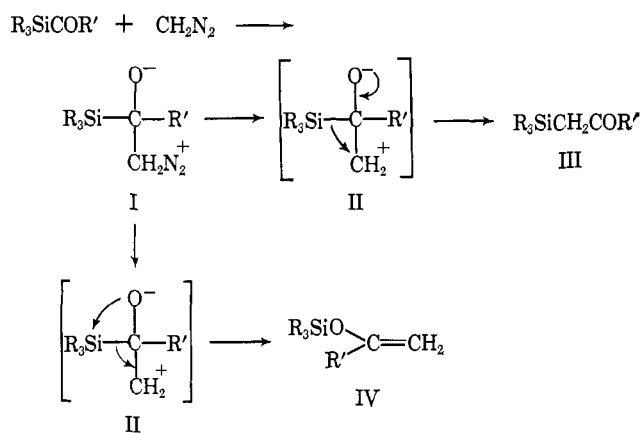
Alternatively, I (or II) may react by attack of the anionic oxygen on silicon leading to the formation of the siloxyalkene IV through silicon–oxygen bond formation and silicon–carbon bond cleavage. This route parallels closely that proposed for the related silylcarbinol to silyl ether rearrangement.[8,9]

When alkylsilyl ketones such as acetyltriphenylsilane or acetyltrimethylsilane[10] were treated with diazomethane, the major, if not exclusive, product was the β-silyl ketone. The decrease in siloxyalkene formation is in accord with the observed much slower rate of rearrangement to silyl ether of alkylsilylcarbinols com-

(2) A. G. Brook, R. Kivisikk, and G. E. LeGrow, *Can. J. Chem.*, **43**, 1175 (1965), and references cited therein.

(3) C. R. Kruger and E. G. Rochow, *J. Organometal. Chem.* (Amsterdam), **1**, 476 (1964).

(4) These three strong bands were observed in the infrared spectrum of every siloxystyrene isolated.

(5) Acceptable analyses were obtained for all new compounds and their infrared, nmr, and ultraviolet spectra were in accord with the proposed structures.

(6) A. G. Brook and J. B. Pierce, *Can. J. Chem.*, **42**, 298 (1964).

(7) R. Huisgen and C. Ruchardt, *Ann.*, **601**, 1, 21 (1956).

(8) A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

(9) A. G. Brook, G. E. LeGrow, and D. M. MacRae, *Can. J. Chem.*, in press.

(10) A. G. Brook, J. M. Duff, and P. F. Jones, *J. Am. Chem. Soc.*, in press.

pared to arylsilylcarbinols.[9,11] As might have been expected, on the basis that germylcarbinols do not rearrange to the corresponding germyl ether, when benzoyltriphenylgermane was treated with diazomethane phenacyltriphenylgermane was the only rearrangement product observed.

Further results, including the stereochemistry of the reaction at silicon, will be reported shortly.

(11) A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Am. Chem. Soc.*, **81**, 981 (1959).

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"Anomalous" Chemical Shifts in the Nuclear Magnetic Resonance Spectra of the 1,3,5-Trimethylcyclohexanes

Sir:

The nmr spectra of saturated cyclic organic molecules have been of considerable interest since the early work of Lemieux, *et al.*,[1] and Musher and Richards,[2]
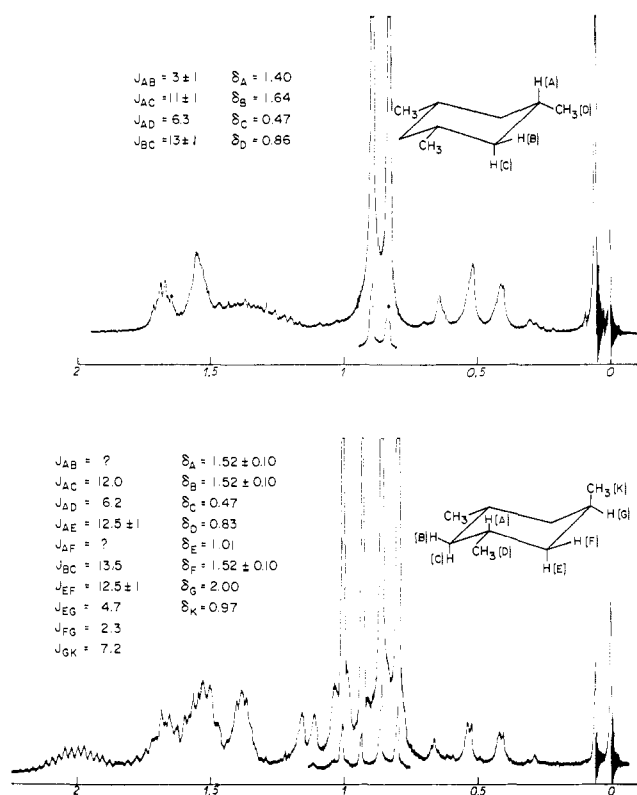

$J_{AB} = 3 \pm 1$ $\delta_A = 1.40$
$J_{AC} = 11 \pm 1$ $\delta_B = 1.64$
$J_{AD} = 6.3$ $\delta_C = 0.47$
$J_{BC} = 13 \pm 1$ $\delta_D = 0.86$

$J_{AB} = ?$ $\delta_A = 1.52 \pm 0.10$
$J_{AC} = 12.0$ $\delta_B = 1.52 \pm 0.10$
$J_{AD} = 6.2$ $\delta_C = 0.47$
$J_{AE} = 12.5 \pm 1$ $\delta_D = 0.83$
$J_{AF} = ?$ $\delta_E = 1.01$
$J_{BC} = 13.5$ $\delta_F = 1.52 \pm 0.10$
$J_{EF} = 12.5 \pm 1$ $\delta_G = 2.00$
$J_{EG} = 4.7$ $\delta_K = 0.97$
$J_{FG} = 2.3$
$J_{GK} = 7.2$

Figure 1 (top). The nmr spectrum of *cis,cis*-1,3,5-trimethylcyclohexane.
Figure 2 (bottom). The nmr spectrum of *cis-trans*-1,3,5-trimethylcyclohexane.

(1) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **79**, 1005 (1957); **80**, 6098 (1958).
(2) J. I. Musher and R. E. Richards, *Proc. Chem. Soc.*, 230 (1958). See also footnote 10 of J. I. Musher, *J. Am. Chem. Soc.*, **83**, 1146 (1961),

which showed the ability of nmr to distinguish among configurational isomers. Much of the work on the chemical shifts of carbocyclic molecules—as distinguished from saturated heterocycles, such as dioxane—has been, almost of necessity, restricted to observations on the carbinol protons of cyclohexanols.[1,3–5] The present empirical understanding of the effect of neighbor interactions on these chemical shifts is due to Eliel and co-workers[4] and to the recent work of Booth,[5] while attempts at the corresponding theoretical interpretation must be deemed relatively unsatisfactory,[3,6] particularly for nearest neighbor interactions.

Owing to the large numbers of protons involved, there have been very few carbocyclic molecules whose spectra were found to be sufficiently simple to provide even approximate complete analyses.[7] Thus, despite advances in the use of massive deuteration and variable temperature probes, the chemical shifts of the various protons in some simple cyclic hydrocarbons are not known. Muller and Tosch[8] have discussed some "anomalous" features of the 60-MHz spectra of some of these hydrocarbons, which have been recently interpreted by Booth,[5] and this, along with our own similar unpublished work,[3] has prompted the present study of the two isomers of 1,3,5-trimethylcyclohexane at 100 MHz.

The nmr spectra of *cis,cis*-1,3,5- (I) and *cis,trans*-1,3,5-trimethylcyclohexane (II) taken at 100 MHz in dilute solution in CCl_4 and referred to internal TMS[9] are given in Figures 1 and 2, respectively. Also given in the figures are the coupling constants in hertz (absolute values) and chemical shifts in parts per million which could be obtained from straightforward first-order analyses aided and checked by double irradiation methods. For example, the doublet to low field of the methyl peaks in II was shown to be the low-field part of a triplet in which proton E is coupled to protons A and F by irradiating G. Also, although the conservative numbers in the figure give the same chemical shift for the protons A, B, and F of II, they were shown to be strongly coupled since irradiation at δ 1.62 ± 0.03 caused both the quartet of C and the methyl doublet of D to collapse, which thus favors somewhat centering A and B at δ ~1.62 with F at δ ~1.45. Since the total number of spins in each molecule is 18, complete analyses were not possible and, unless otherwise indicated, the errors in the δ's and in the J's for the ring protons are 0.02 ppm and 0.2 Hz, respectively, being for the most part due to the first-

for a discussion of the significance of the relatively sharp signal of *cis*-decalin and the dimethylcyclohexanes.
(3) J. I. Musher, Ph.D. Thesis, Harvard Univerity, 1962 (unpublished). Some of the data in this thesis are reported in J. I. Musher, *J. Chem. Phys.*, **35**, 1159 (1961). See also J. I. Musher, *ibid.*, **37**, 192 (1962), and *Mol. Phys.*, **6**, 93 (1963), for some critical remarks on the theoretical interpretation.
(4) E. L. Eliel, M. H. Gianni, T. H. Williams, and J. B. Stothers, *Tetrahedron Letters*, 741 (1962).
(5) H. Booth, *Tetrahedron*, **22**, 615 (1966).
(6) See A. A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 43 (1966), for a review of the more recent literature.
(7) See, *e.g.*, (a) J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961); (b) A. Segre, *Tetrahedron Letters*, **17**, 1001 (1964).
(8) N. Muller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1167 (1962). The recent study of R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965), shows that the introduction of a methyl group at the angular position in adamantane shifts the adjacent methylene protons 0.30 ppm upfield.
(9) The peak at 7-Hz low field from TMS is due to hexamethyldisiloxane.