

doublets for the transitions assigned. The combination of centrifugal distortion effects and coupling of internal torsion to over-all rotation will require further analysis and is being delayed until the structure (discussed later) can be determined more accurately from additional isotopic data. Since no b-type transitions were observed, it has been impossible to determine experimentally the  $a$  moment of inertia. However, the quantity  $(B + C)/2$  has been determined for this nearly symmetric prolate top for  $^{74}\text{GeH}_3\text{NCO}$ ,  $^{72}\text{GeH}_3\text{NCO}$ , and  $^{70}\text{GeH}_3\text{NCO}$  and is tabulated in Table II.

**Table II.** Rotational Constants  $[(B + C)/2]$  of Germeryl Isocyanate<sup>a</sup>

Species	$(B + C)/2$ , Mc/sec
$^{74}\text{GeH}_3\text{NCO}$	1839.14
$^{72}\text{GeH}_3\text{NCO}$	1853.25
$^{70}\text{GeH}_3\text{NCO}$	1868.11

<sup>a</sup> Since torsion-vibration-rotation analysis has not been performed, a simple averaging of the reported doublets was used and  $(B + C)/2$  was calculated in the rigid rotor approximation.

The rotational isotopic shifts contain essentially no information about the Ge-N-C angle because of the large  $a$  coordinate ( $a$  is the figure axis) and small  $b$  coordinate of germanium for any assumed structure. For any structure, an  $a$  coordinate of  $1.0119 \pm 0.0003$  Å will fit the isotopic shift in  $(B + C)/2$ . Accordingly only the absolute value of this quantity contains structural information. In terms of the "average structural parameters" employed by Griffiths<sup>2</sup> ( $r(\text{Ge-H}) = 1.53$  Å,  $r(\text{Ge-N}) = 1.81$  Å,  $r(\text{N-C}) = 1.21$  Å,  $r(\text{C-O}) = 1.17$  Å, and the H-Ge-H angle =  $111^\circ$ ), the Ge-N-C angle deviates from linearity by 35 to  $40^\circ$ . That is, the angle which best reproduces the quantity  $(B + C)/2$  for  $\text{GeH}_3\text{NCO}_3$  corresponds more closely to the angle found consistent with the microwave data of  $\text{CH}_3\text{NCO}$ <sup>4b</sup> than with the value expected assuming a linear or near-linear skeleton.

Because of the large uncertainties associated with the above assumed parameters, further considerations are required before the range for the Ge-N-C angle can be fixed and the conclusion drawn that there is little ( $p \rightarrow d$ ) <sub>$\pi$</sub>  bonding in  $\text{GeH}_3\text{NCO}$ . The quantity  $(B + C)/2$  can be fit by many combinations of structural parameters. In particular, if there is ( $p \rightarrow d$ ) <sub>$\pi$</sub>  bonding, one would expect the Ge-N bond to be shorter than the value employed by Griffiths and the N-C bond length could approximate the corresponding very short value of 1.15 Å found in  $\text{SiH}_3\text{NCO}$ .<sup>3</sup> The effect of such changes would be to open the Ge-N-C angle. To estimate the effect of such changes a calculation was carried out using the parameters listed in Table III (model I), which allows for the maximum back-bonding that might be expected based on that observed for  $\text{SiH}_3\text{NCO}$ . The C-O bond length assumed was that found by electron diffraction for  $\text{CH}_3\text{NCO}$ ,<sup>4a</sup> since it is close to the 1.179 Å for the same bond in  $\text{SiH}_3\text{NCO}$ . It is seen that the Ge-N-C angle deviation from linearity must be at least  $26^\circ$  to fit the observed value of  $(B + C)/2$ . Also listed in Table III is a second set of assumed parameters (model II) based on the electron diffraction data of  $\text{CH}_3\text{NCO}$ .<sup>4a</sup> The Ge-N distance used was that chosen by Griffiths. This set of param-

**Table III.** Structural Models

	I	II
Ge-H, <sup>a</sup> Å	1.53	1.53
H-Ge-H, deg <sup>a</sup>	111	111
Ge-N, Å	1.76 <sup>b</sup>	1.81 <sup>a</sup>
N-C, Å	1.15 <sup>c</sup>	1.19 <sup>d</sup>
C-O, <sup>d</sup> Å	1.18	1.18
$\angle\text{Ge-N-C}$ , deg	154	143

<sup>a</sup> Reference 2. <sup>b</sup> Estimated assuming back-bonding similar to that found in  $\text{SiH}_3\text{NCO}$ . <sup>c</sup> Reference 3. <sup>d</sup> Reference 4a.

eters requires a Ge-N-C angle which deviates from linearity by  $37^\circ$  to fit  $(B + C)/2$  for  $\text{GeH}_3\text{NCO}$ . A longer Ge-N bond would close the Ge-N-C angle even more.

It seems clear from the above calculations and experimental data that (1) the molecule is indeed bent as reported by Griffiths;<sup>2</sup> (2) the deviation from linearity is probably at least  $26^\circ$  assuming "maximum back-bonding" and the Ge-N-C skeletal bond angle may well approach the value of  $40^\circ$  found for the C-N-C skeletal bond angle in  $\text{CH}_3\text{NCO}$ ;<sup>4b</sup> (3) it does not seem likely that ( $p \rightarrow d$ ) <sub>$\pi$</sub>  bonding makes a very significant contribution to the Ge-N bonding in this molecule.

It is to be hoped that an investigation of the  $^{15}\text{N}$  and  $^{13}\text{C}$  isotopes will enable us to fix the molecular parameters more precisely in the near future. At that time we hope to report also on the barrier to internal rotation, the dipole moment, quadrupole coupling constants, and torsion-vibration interactions for this molecule.

**Acknowledgment.** One of us (R. N.) wishes to thank the President of Manhattan College for a starter grant which enabled him to begin construction of the microwave spectrometer used in this work. We are also grateful to the Chemistry Departments of New York University and Manhattan College for financing the extension of our operating frequency range to 26 Gc/sec and for supporting this particular investigation. K. R. R. acknowledges with thanks the support extended to him, in the form of a graduate fellowship during the summer of 1967, by the National Science Foundation Institution Grant Committee of New York University.

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### Thermolysis of *trans*-Chloro(2-allylphenyl)bis(triethylphosphine)nickel(II)

Sir:

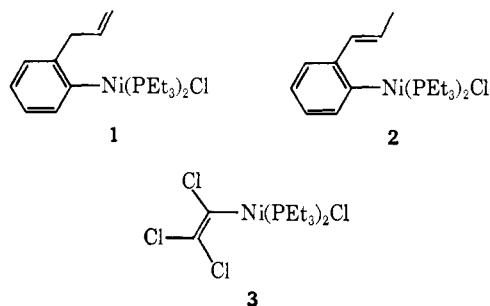
Treatment of *trans*-dichlorobis(triethylphosphine)-nickel(II) with 2-allylphenylmagnesium chloride in tetrahydrofuran-ether solution affords high yields of *trans*-chloro(2-allylphenyl)bis(triethylphosphine)nickel(II) (1). The yellow compound, mp  $63-65^\circ$ , possesses a *trans*-planar configuration and is monomeric in benzene solution.<sup>1</sup> As in other *ortho*-substituted arylnickel

(1) Details of the synthesis of 1, the palladium analog, and the corresponding styryl compounds will be published separately. The experi-

compounds,<sup>2</sup> the plane of the aromatic ring is forced perpendicular to the bonding plane of the transition metal system owing to nonbonding interactions between the phosphine ligands and the alkenyl substituent. Compound **1** is of interest because the benzylic hydrogens and the olefinic bond are both potential reactants with the transition metal at an apical site in the planar complex. We report herein the characterization of some products from the thermolysis of **1**.

Heating solutions of **1** in tetrachloroethylene at 85–90° results in the formation of indene as the major hydrocarbon product, identified by nmr and infrared spectra after glpc collection. Two minor products exhibited glpc retention times identical with those of *trans*- $\beta$ -methylstyrene and allylbenzene on three different columns.<sup>4</sup> No other monomeric products derived from the allylphenyl ligand were detected. Neither indane, 2,2'-diallylbiphenyl, nor other dimeric hydrocarbon products were present in >1% yield. The yields of indene varied with the reaction time employed, 58% being afforded during 3 hr at 85–90° (52% after 18 hr). Yields of the two minor components ranged from 2 to 4%.

The fate of the nickel moiety is partially accounted for in the characterization of three compounds. In addition to small amounts (2%) of *trans*-dichlorobis(triethylphosphine)nickel(II), a compound, **2**, mp 94–96° (11% yield), derived from double-bond migra-



tion in **1** is formed. The olefinic bond has the *trans* configuration as indicated by a band at 968  $\text{cm}^{-1}$  ( $\text{CHCl}_3$  solution) attributed to the C–H out-of-plane deformation vibration. Further evidence is found in the nmr spectrum ( $\text{CDCl}_3$ ). Both vinyl protons are deshielded to the extent that their resonances overlap with those of the aromatic protons to give a complex array of peaks from  $\tau$  2.26 to 3.45. This is expected for the isomer with the *trans* double bond since rotation of the propenyl group would cause both vinyl protons to experience environments in close proximity to the metal, whereas only the  $\alpha$  proton in the *cis* isomer can reside near the metal.<sup>5</sup> The methyl proton resonance

mental procedures were essentially the same as those reported by Chatt and Shaw<sup>2</sup> and by Calvin and Coates<sup>3</sup> for the preparation of other aryl-nickel and -palladium compounds.

(2) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

(3) G. Calvin and G. E. Coates, *ibid.*, 2008 (1960).

(4) The presence of *trans*- $\beta$ -methylstyrene was confirmed by its spectral identification in a mixture with indene after column chromatography of the hydrocarbon products on alumina. A control experiment demonstrated that allylbenzene does not isomerize to  $\beta$ -methylstyrene on the column under the conditions used. All reactions were carried out in a nitrogen atmosphere in deoxygenated solvents. Satisfactory analyses were obtained for all new compounds. The organonickel compounds were isolated *via* column chromatography on alumina (pH 3.8) eluting with ether–pentane mixtures.

(5) Because the plane of the aromatic ring in these compounds is perpendicular to the bonding plane, the protons of *ortho* substituents on the aromatic ring are above the metal and the bonding plane in a region

consists of a doublet at  $\tau$  8.03,  $J = 5.9$  Hz. *trans*- and *cis*- $\beta$ -methylstyrene have corresponding coupling constants of 6.0 and 6.7 Hz, respectively. Protonation of **2** with anhydrous HCl in ether affords a hydrocarbon with a glpc retention time identical with that of *trans*- $\beta$ -methylstyrene.

A third nickel compound, **3**, isolated in 41% yield, is a yellow diamagnetic solid, mp 92.0–92.8° (dec 190–200°), possessing two triethylphosphine ligands and the elements of tetrachloroethylene. *Anal.* Found: C, 36.29; H, 6.80; Cl, 30.68; Ni, 12.79; P, 13.58; mol wt (cryoscopic in benzene), 459. It exhibits a pronounced thermal stability and a marked resistance to attack by atmospheric oxygen and was recovered (95%) after its ether solution was treated with HCl for 2 days. We have prepared the same compound in 67% yield by treatment of nickel acetylacetonate, in the presence of triethylphosphine, with triethylaluminum, using the general procedure of Wilke for the preparation of bis(triethylphosphine)(ethylene)nickel(0).<sup>6</sup> The infrared spectrum possesses no band readily attributable to a C=C stretching vibration and exhibits no strong absorption in the 300–400- $\text{cm}^{-1}$  region that can unambiguously be assigned to a Ni–Cl stretching vibration.<sup>7</sup> The nmr spectrum ( $\text{CDCl}_3$ ) consists of partially overlapping multiplets centered near  $\tau$  8.3 and at 8.75 (Et<sub>3</sub>P protons). The high-field resonance is an apparent 1:4:6:4:1 quintet (four peaks are free from overlap) similar to that found in *trans*-bis(triethylphosphine)platinum complexes<sup>8</sup> and attributable to coupling<sup>9</sup> of the CH<sub>3</sub> protons with the two phosphorus nuclei and with the CH<sub>2</sub> protons. The electronic spectrum in hexane exhibits  $\lambda_{\text{max}}$  219  $\text{m}\mu$  ( $\epsilon$  27,800), 243 (16,600), 293 (3960), and 314 (8960).

Tetrachloroethylene adducts of platinum<sup>10</sup> and palladium,<sup>11</sup> derived from reaction of tetrachloroethylene with tetrakis(triethylphosphine)platinum(0) and the corresponding palladium compound, have been reported. Based on infrared spectra the palladium compound has been assigned the chloro(trichlorovinyl)-bis(triethylphosphine)palladium structure, and the platinum compound has been assigned the bis(triethylphosphine)(tetrachloroethylene)platinum structure. The latter compound has recently been converted to a compound believed to be the chloro(trichlorovinyl)bis(triethylphosphine)platinum isomer.<sup>12</sup>

The scant information offered by spectral data for **3** induced us to obtain chemical evidence which would allow a distinction between the two structural classes mentioned above. Treatment of **3** with sodium iodide in acetone afforded a 53% yield of **4**, mp 148–149°. The infrared spectra of **3** and **4** (650–4000  $\text{cm}^{-1}$ ) are essentially identical. Reaction of *o*-tolyllithium with **3** gave a 34% yield of **5**, mp 155–156°, which on treatment with HCl in ether gave **3** and toluene. The thermal decomposition of benzenediazonium-2-carboxylate in the presence of **3** in methylene chloride afforded an 8%

where they are believed to be deshielded because of their close proximity to the metal. This phenomenon has been observed in a number of *ortho*-substituted aryl-nickel compounds we have prepared.

(6) G. Wilke and G. Herrmann, *Angew. Chem.*, **74**, 693 (1962).

(7) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

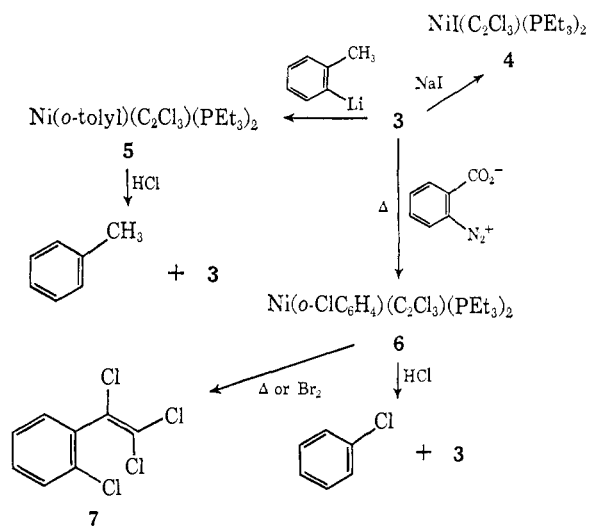
(8) H. C. Clark and W. S. Tsang, *J. Am. Chem. Soc.*, **89**, 533 (1967).

(9) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

(10) W. T. Bland and R. D. W. Kemmitt, *Nature*, **211**, 963 (1966).

(11) P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968).

(12) W. T. Bland and R. D. W. Kemmitt, *J. Chem. Soc.*, **A**, 1278 (1968).



yield of a compound believed to be **6**, mp 155.5–156.5,<sup>o</sup> which, on thermolysis in tetrachloroethylene or on treatment with bromine in hexane, afforded **7**. Reaction of **6** with HCl in ether afforded small amounts of **3** and chlorobenzene.

The above series of reactions suggests strongly that **3** is chloro(trichlorovinyl)bis(triethylphosphine)nickel(II), presumably derived from oxidative addition of tetrachloroethylene to a nickel(0) species generated in the decomposition of **1**. The compound exists in the *trans* configuration suggested by the low dipole moment of 1.95 D and the general features of the Et<sub>3</sub>P proton resonances. In view of the evidence for the generation of benzyne *via* the thermal decomposition of benzenediazonium-2-carboxylate,<sup>13</sup> the formation of **6** possibly results from "insertion" of benzyne into the nickel-chlorine bond of **3**. The formation of **6** appears to be an example of a coupling reaction induced by oxidative addition of bromine to **6** and is probably related to the coupling reactions reported by Corey.<sup>14</sup>

**Acknowledgments.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of North Dakota grant-in-aid program for support of this research.

(13) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

(14) E. J. Corey and M. F. Semmelhack, *ibid.*, **89**, 2755 (1967).

(15) NDEA Predoctoral Fellow, 1965–1968.

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 Received July 3, 1968

### Optically Active Solvents in Nuclear Magnetic Resonance Spectroscopy. VII. Direct Determination of Optical Purities and Correlations of Absolute Configurations of Sulfoxides<sup>1</sup>

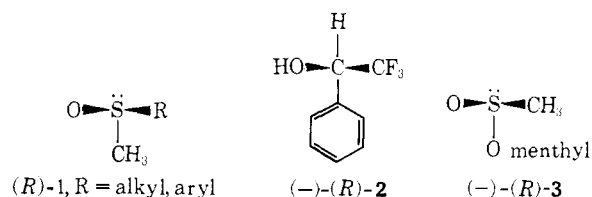
Sir:

While dissimilarly substituted sulfoxides, asymmetric by virtue of the tetrahedral configuration at sulfur, have not been resolved except through the agency of

(1) For part VI, see W. H. Pirkle, T. G. Burlingame, and S. D. Beare, *Tetrahedron Lett.*, in press.

other functional group "handles,"<sup>2</sup> optically active samples can be readily obtained through the Andersen synthesis<sup>3</sup> or *via* asymmetric oxidation of thioethers.<sup>4</sup> We herein report the first method, to our knowledge, for the direct determination of optical purities of sulfoxides.

In appropriate optically active solvents, the nmr spectra of enantiomeric type **1** sulfoxides are sufficiently different to allow not only direct determinations of enantiomeric purity, but also correlations of absolute configuration.



For example, in achiral solvents, the 100-MHz nmr spectrum of partially resolved methyl *t*-butyl sulfoxide, prepared<sup>5</sup> by the action of *t*-butylmagnesium chloride on a 1.78:1.00 mixture<sup>6</sup> of the two diastereomeric (–)-menthyl methanesulfonates (**3**),<sup>7</sup> shows two sharp singlets in a 3:1 ratio. However, in (–)-(R)-2,2,2-trifluorophenylethanol<sup>8</sup> (**2**), the methyl and *t*-butyl resonances of the two sulfoxide enantiomers have appreciably different chemical shifts, and the spectrum of the partially resolved sulfoxide consists of two unequally intense *t*-butyl resonances ( $\delta$  1.01 and 1.02, relative intensities 1.59:1.00) and two unequally intense methyl resonances ( $\delta$  2.09 and 2.07, relative intensities 1.63:1.00). Since by virtue of fast-exchange processes, the optical purity of the solvent affects only the chemical shift differences between the resonances of the enantiomers and not their relative intensities, this nmr method is, to our knowledge, the first method for the direct determination of the enantiomeric purity of a sulfoxide.

It is well known that sulfoxides associate with alcohols,<sup>9</sup> and it seems reasonable to assume that the spectral nonequivalence observed for enantiomers of unsymmetrical sulfoxides in optically active alcohol **2**

(2) One possible exception is the resolution of ethyl *p*-tolyl sulfoxide with platinum complexes containing optically active  $\alpha$ -methylbenzylamine: A. C. Cope and E. A. Caress, *J. Amer. Chem. Soc.*, **88**, 1711 (1966).

(3) K. K. Andersen, *Tetrahedron Lett.*, 93 (1962).

(4) U. Folli, D. Iarossi, F. Montanari, and G. Torre, *J. Chem. Soc.*, C, 1317 (1968), and references cited therein.

(5) M. Axelrod, P. Bickart, M. L. Goldstein, M. M. Green, A. Kjaer, and K. Mislow, *Tetrahedron Lett.*, 3249 (1968).

(6) Andersen has previously noted<sup>7</sup> a 0.02-ppm chemical shift difference between the methanesulfinyl resonances for the diastereomeric sulfonates (in chloroform) at 60 MHz, although the diastereomeric purity was presumably too low to be determined on the basis of relative peak heights. We have found that, at 100 MHz and 28°, the methanesulfinyl chemical shift difference ( $\Delta\delta_{\text{SOCH}_3}$ ) is increased to 3.4 Hz in (–)-alcohol **2**, greatly facilitating the ratio measurement. When racemic **2** is used as solvent the chemical shift difference is 1.7 Hz, while in (+)-**2** it is diminished to the extent that it is not observable.

(7) (a) K. K. Andersen, *J. Org. Chem.*, **29**, 1953 (1964). (b) For a modification of Andersen's procedure yielding ester **3** of higher diastereomeric purity, see J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5228 (1967).

(8) (a) For the absolute configuration of **2**, see H. M. Peters, D. M. Feigl, and H. S. Mosher, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April, 1967, No. O-67. (b) For the resolution of **2**, see D. M. Feigl, Ph.D. Thesis, Stanford University, 1966. A more convenient resolution of **2** will be reported shortly (W. H. Pirkle, S. D. Beare, and T. G. Burlingame, submitted for publication).

(9) C. P. Rader, *J. Amer. Chem. Soc.*, **88**, 1713 (1966), and references cited therein.