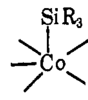
is in striking contrast to the racemization of R_3C^*H on the surface of group VIII metals.[9]

It has been shown that a wide variety of compounds containing a transition metal–silicon bond may be prepared by the action of R_3SiH on transition metal complexes.[6,10,11] An interesting study by Chalk and Harrod[11] has shown further that compounds containing a silicon–cobalt bond undergo exchange with organosilicon hydrides (8). A cobalt complex formed by expansion of its coordination sphere to accommodate two silicon centers (I) has been postulated as a probable mechanism.[11] Speier has proposed a similar scheme for chloroplatinic acid catalyzed SiH–SiD exchange in solution whereby a single metal center coordinates two silicons (II).[5] Our present finding of retention of configuration for Si*H–Si*D exchange catalyzed by chloroplatinic acid or platinum–ethylene complex $((C_2H_4)PtCl_2)_2$ is consistent with intermediates such as I or II. Our studies on the dynamic stereochemistry and mechanisms of organosilicon reactions catalyzed by group VIII metals are continuing.

$$R_3SiCo(CO)_4 + R'_3SiH \rightleftarrows R_3SiH + R'_3SiCo(CO)_4 \qquad (8)$$



I

Si_2PtH_2

II

The SiH–SiD exchange reactions (4) were carried out by mixing the desired catalyst with a solution of 0.248 g (1 mmole) of optically active α-naphthylphenylmethylsilane and 0.151 g (1 mmole) of racemic phenylmethylethyldeuteriosilane in 5 ml of the designated solvent and stirring the mixture in an atmosphere of dry nitrogen. Scrambling of hydrogen and deuterium between the two available silanes (4) was complete in 10 min at room temperature over palladium or nickel but took considerably longer when 5% platinum on carbon was used. Infrared spectroscopy was used to determine the extent of exchange by comparing the relative intensities of the SiH band, ~4.75 μ, and the SiD band, ~6.25 μ, in each of the products.

Rapid exchange of deuteriosilane with hydrogen gas also occurred at room temperature. Optically active α-naphthylphenylmethyldeuteriosilane, 0.25 g, in 2.5 ml of pentane was shaken in a Parr hydrogenator under 1–2 atm of hydrogen gas in the presence of 25 mg of the designated catalyst, and the deuterium was rapidly replaced with hydrogen (5). Reaction was slower with platinum on carbon than when nickel or palladium catalysts were used. Retention stereochemistry was observed in all cases.

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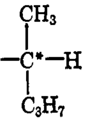
[9] R. L. Burwell, *et al., J. Am. Chem. Soc.*, **79**, 5142 (1957). Isotopic exchange between (+)-3-methylhexane and deuterium on palladium and nickel catalysts have shown that nearly every exchange of the hydrogen atom at position 3 leads to racemization under the conditions of this study. In contrast to this, nearly every exchange between R_3Si^*H and deuterium (5) in the presence of palladium and nickel occurs with retention of configuration.



$$C_2H_5-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large C_3H_7}{|}}{C^*}}-H$$

[10] W. Jetz and W. Graham, *ibid.*, **89**, 2773 (1967).

[11] A. J. Chalk and J. F. Harrod, *ibid.*, **89**, 1646 (1967).

Nonequivalence of the Nuclear Magnetic Resonance Spectra of Enantiomers in Optically Active Solvents. IV. Assignment of Absolute Configuration

Sir:

We wish to report an expeditious method for assigning the absolute configuration of alkylarylcarbinols (**1**). The nmr chemical shifts of enantiomeric nuclei in type **1** carbinols differ sufficiently in optically active α-(1-naphthyl)ethylamine (**2**) solvent to allow direct comparison of the relative intensities of the resonances of these nuclei.[1] Figure 1 demonstrates that, in dex-

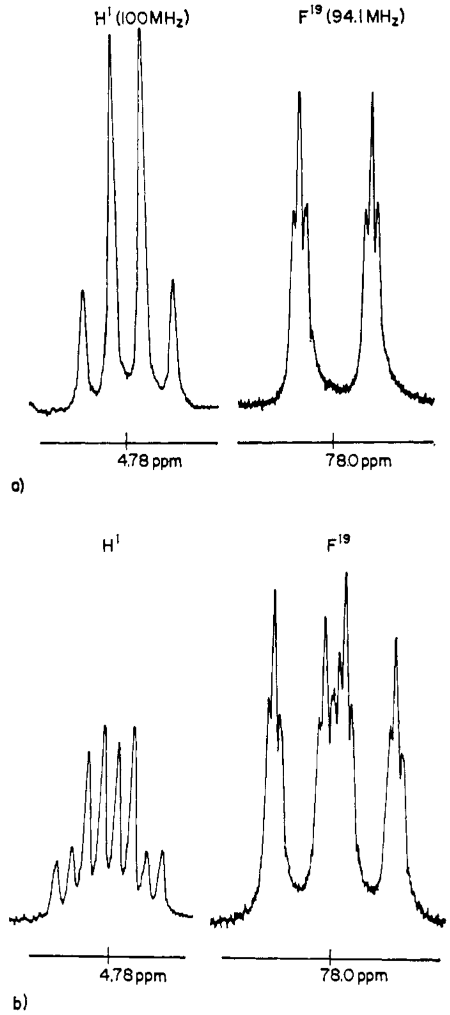


Figure 1. Portions of the nmr spectra of partially resolved 2,2,2-trifluorophenylethanol ($[\alpha]^{22}D$ 2.19° (neat)) in (a) racemic and (b) optically active α-(1-naphthyl)ethylamine ($[\alpha]^{25}D$ +80° (neat)). The carbinyl proton resonances are downfield from tetramethylsilane while those of fluorine are upfield from fluorotrichloromethane. The carbinyl proton–fluorine spin–spin coupling is 6.9 Hz. The spectra were obtained by N. Bhacca of Varian Associates.

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[1] (a) W. H. Pirkle, *J. Am. Chem. Soc.*, **88**, 1837 (1966); (b) T. G. Burlingame and W. H. Pirkle, *ibid.*, **88**, 4294 (1966); (c) W. H. Pirkle and T. G. Burlingame, *Tetrahedron Letters*, in press.

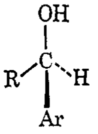
Table I. Correlation of Nmr Data with Absolute Configuration of Alkylarylcarbinols[p]

Ar	R	$[\alpha]^{25\pm 1}$D, deg[a]	% optical purity[b]	Relative field position of largest enantiomeric resonance Carbinyl proton	Fluorine	Absolute configuration of predominate enantiomer Known	Predicted
Phenyl	CH_3	9.38	21.9	High		**3**[q]	
Phenyl	C_2H_5	2.61	9.0	High		**3**[r]	
Phenyl	*i*-C_3H_7	3.09	6.5	High		**3**[r]	
Phenyl	$C(CH_3)_3$	1.78[c]	6.5	High		**3**[r]	
Phenyl	Cyclobutyl	1.81	7	High			**3**
α-Naphthyl	CH_3	17.5[d]	17	High		**3**[s]	
β-Naphthyl	CH_3	−14.8[e]	18.6	Low			**3a**
2-Phenanthryl	CH_3	34.0[f]	26	High			**3**
3-Phenanthryl	CH_3	9.5[g]	12	High			**3**
9-Anthracyl	CH_3	1.54[h]	6	High			**3**
Phenyl	CF_3	−5.34	13	Low	High	**3a**[2]	
m-$CH_3C_6H_4$	CF_3	1.5	7	High	Low		**3**
m-BrC_6H_4	CF_3	*i*	11	Low	High	**3a**[t]	
p-BrC_6H_4	CF_3	*i*	11	Low	High	**3a**[t]	
o-$NO_2C_6H_4$	CF_3	*j*	5	*o*	High	**3a**[t]	
m-$NO_2C_6H_4$	CF_3	*j*	5	*o*	High	**3a**[t]	
p-$NO_2C_6H_4$	CF_3	*j*	5	*o*	High	**3a**[t]	
2,4-$(NO_2)_2C_6H_3$	CF_3	*k*	5	Low	High	**3a**[t]	
3,5-$(NO_2)_2C_5H_3$	CF_3	*k*	5	Low	High	**3a**[t]	
α-Thienyl	CF_3	−6.6[l]	32	Low	High		**3a**
α-Naphthyl	CF_3	−1.5[m]	8.0	Low	High		**3a**
β-Naphthyl	CF_3	−3.7[n]	11.5	Low	High		**3a**

[a] Neat unless otherwise specified. [b] Determined by nmr unless otherwise specified. [c] *c* 13.0, benzene. [d] *c* 6.5, pyridine. [e] *c* 1.8, pyridine. [f] *c* 4.1, chloroform. [g] *c* 25, chloroform. [h] *c* 6.4, ethanol. [i] Present in a 60:40 mixture of the *meta* and *para* isomers for which $[\alpha]^{22}$D −2.45° (*c* 11.0, ethanol). A partially resolved sample (11% optical purity) of *p*-bromo-2,2,2-trifluorophenylethanol, $[\alpha]^{25.5}$D −1.5° (*c* 12.0, ethanol), was shown by nmr to have configuration **3a**. [j] Present in a 24:48:28 mixture of the *ortho*, *meta*, and *para* isomers for which $[\alpha]^{24}$D −2.4° (*c* 4.5, ethanol). [k] Present in a mixture of isomers. [l] *c* 18.7, chloroform. [m] *c* 16.4, chloroform. [n] *c* 17.2, chloroform. [o] Obscured. [p] The alkylarylcarbinols in this table either have physical properties corresponding to those previously reported or have elemental compositions and nmr and infrared spectra in accord with their assigned structures. Unless otherwise noted, the partially resolved carbinols were obtained by asymmetric reduction of the corresponding ketones. [q] J. A. Mills and W. Klyne, *Progr. Stereochem.*, **1**, 177 (1954). [r] R. MacLeod, F. J. Welch, and H. S. Moser, *J. Am. Chem. Soc.*, **82**, 876 (1960). [s] V. Prelog, E. Philbin, E. Watanabe, and M. Wilhelm, *Helv. Chim. Acta*, **39**, 1086 (1956). [t] Since these samples were obtained from electrophilic substitutions upon partially resolved 2,2,2-trifluorophenylethanol (levorotatory), the absolute configurations of the predominant enantiomers must be that shown in **3a**.

trorotatory amine **2**, partially resolved 2,2,2-trifluorophenylethanol gives rise to distinct fluorine and carbinyl proton resonances for each enantiomer, and that the resonances derived from the two enantiomers are of unequal intensity.

In each set of partially overlapping multiplets shown in Figure 1b, the more intense multiplet arises from the dextrorotatory carbinol enantiomer of known absolute configuration **3**.[2] Similarly, we have determined the nmr spectra of 13 alkylarylcarbinols of known absolute configuration and find that the enantiomers of stereochemistry **3** have their carbinyl proton resonances at higher field than do their mirror images (**3a**). Moreover, when R is trifluoromethyl, the fluorine resonances of those enantiomers having configuration **3** appear at lower field than do those of configuration **3a**. Based on



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the correlations shown in Table **I**, the absolute configurations of nine other alkylarylcarbinols are assigned. These assignments agree with those obtained by application of Brewster's empirical rules.[3]

If the naphthyl (or phenyl[1a]) system of the optically active amine solvent is replaced with a cyclohexyl group, the nmr spectral nonequivalence of enantiomeric alkylarylcarbinols can no longer be observed at 60 MHz and 35°. Furthermore, introduction of two nitro groups onto the aromatic ring of partially resolved 2,2,2-trifluorophenylethanol enhances the magnitude of the observed nonequivalence *without changing its sense*.

Although many aspects of the interactions between amine **2** and alkylarylcarbinols are not yet understood, a hypothesis capable of accounting for the nmr observations is offered. Under the experimental conditions, short-lived diastereomeric hydrogen-bonded carbinol-amine solvates are formed. The diastereomers need have neither identical spectra nor identical formation constants. Of the various conformations possible for each diastereomer, it seems likely that only those in which the carbinyl protons (or trifluoromethyl groups) are near the diamagnetically anisotropic naphthyl (or phenyl[1a]) system will contribute appreciably to the observed spectral nonequivalence. The hypothesis that conformations similar to **4** are the major contributors to the observed spectral nonequivalence allows explanation of the presently available experimental data.[4] In

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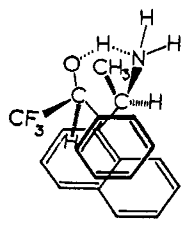
(2) H. M. Peters, D. M. Feigl, and H. S. Mosher, Abstracts of papers presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(3) See E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 401, and references therein.

(4) In structure 4, it has been assumed that *d*-α-(1-naphthyl)ethylamine has the *R* configuration (Cahn, Ingold, Prelog convention) as does *d*-α-phenylethylamine. This is the configuration predicted by Brewster's rules.[3]



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4, the aromatic rings of the amine and the carbinol overlap, the carbinyl proton being held above the naphthyl system where it is heavily shielded. The more distant trifluoromethyl group experiences comparatively less shielding by the naphthyl group. In the analogous conformer derived from enantiomer **3a**, the positions of the carbinyl proton and the trifluoromethyl group are reversed. The net average result is that the carbinyl proton of enantiomer **3a** is less shielded than is that of **3**, while the trifluoromethyl group of enantiomer **3a** is more highly shielded than is that of **3**. Weak charge-transfer interactions between the aromatic systems may stabilize conformations such as **4**. Such interaction may be invoked to account for the unusually large degree of spectral nonequivalence exhibited by the enantiomers of 2′,2′,2′-trifluoro-2,4-dinitrophenylethanol and 2′,2′,2′-trifluoro-3,5-dinitrophenylethanol when optically active amine **2** is used as a solvent.[1c] Significantly, a carbon tetrachloride solution 1.0 *M* in naphthalene and 0.01 *M* in 2′,2′,2′-trifluoro-2,4-dinitrophenylethanol shows absorption at 385 mμ which is not present in the spectra of the individual components. Enhanced long-wavelength absorption is characteristic of charge-transfer complex formation.

The foregoing model is probably oversimplified; steric effects doubtlessly important in determining conformational preferences have not been explicitly discussed. Even so, the model is an aid in rationalizing the observations. Tests of the validity of this model are in progress.

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Bis(trichloromethyl) Nitroxide. A Novel Electron Spin Resonance Spectrum

Sir:

Nitroxide radicals (R_2NO) stabilized by fluorocarbon substituents have recently been prepared and identified by their electron spin resonance spectra.[1-3] Nitroxide radicals carrying hydrocarbon substituents are also known and normally require a tertiary carbon adjacent to the nitrogen, or aromatic substituents, in order to achieve stability.[4,5] The identification, by electron spin resonance spectroscopy, of a relatively stable nitroxide radical containing chlorocarbon substituents, namely, bis(trichloromethyl) nitroxide, is now reported. It is believed that this is the first observed example of an esr spectrum containing resolved hyperfine splitting due to β-chlorine nuclei.

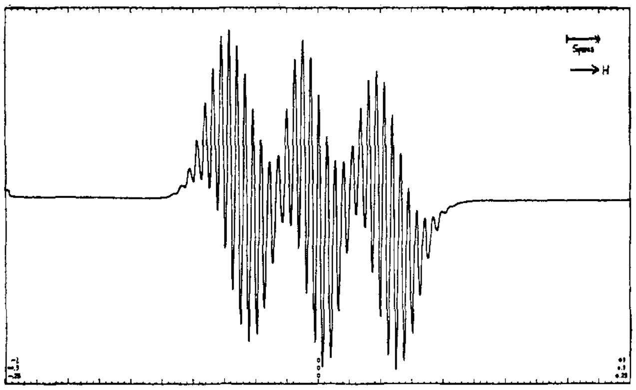

Figure 1. The electron spin resonance spectrum of bis(trichloromethyl) nitroxide.

Trichloronitrosomethane, a blue liquid at room temperature, was prepared by the method previously described[6] and stored at 77°K. The electron spin resonance spectrum shown in Figure 1 was obtained by measurement on trichloronitrosomethane at room temperature in the dark. This spectrum clearly demonstrates the presence, in trichloronitrosomethane, of a small concentration of a free radical containing several magnetic nuclei. A similar but less intense spectrum was obtained by measurement on a dilute solution of trichloronitrosomethane in carbon tetrachloride.

All the features of the spectrum may be interpreted in terms of the radical bis(trichloromethyl) nitroxide. Interaction of the unpaired electron with the ^{14}N nucleus gives rise to the main triplet with a splitting of 11.8 ± 0.1 gauss. Each component of this triplet is split further into a series of hyperfine lines with a coupling of 1.25 ± 0.05 gauss. Some overlapping of these lines occurs in the center of the spectrum, but examination of the amplified wings of the spectrum reveals all the expected hyperfine structure for bis(trichloromethyl) nitroxide. The tenth line of each hyperfine series is the most intense, approximately 600 times more so than the outermost line. This suggests that there are 19 hyperfine lines in each component of the main triplet. Such a pattern can arise by interaction of the unpaired electron with six equivalent chlorine nuclei. The theoretical intensity ratio of the strongest to the weakest line in the spectrum of an electron in this situation is 580:1.

The isotropic nitrogen splitting is larger than that observed for bis(trifluoromethyl) nitroxide,[1,2] much smaller than in dialkyl nitroxides,[7] and slightly smaller than in potassium nitrosodisulfonate (Fremy's salt).[8] This suggests that the magnitude of the nitrogen coupling is related to the electron-withdrawing power of the substituents. The rather poor resolution of the chlorine hyperfine lines may be attributed to the presence of two

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[1] W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, **87**, 802 (1965).
[2] P. J. Scheidler and J. R. Bolton, *ibid.*, **88**, 371 (1966).
[3] W. D. Blackley, *ibid.*, **88**, 480 (1966).
[4] A. K. Hoffmann and A. T. Henderson, *ibid.*, **83**, 4671 (1961).
[5] H. Wieland and M. Offenbacher, *Ber.*, **47**, 211 (1914).
[6] H. Sutcliffe, *J. Org. Chem.*, 30, 3221 (1965).
[7] J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, **35**, 1507 (1961).
[8] G. E. Pake, J. Townsend, and S. I. Weissmann, *Phys. Rev.*, **85**, 682 (1952).