Methyl isonitrile. To 14.1 g (0.1 mole) methyl iodide in 100 ml purified nitrobenzene was added 33 g (0.11 mole) triphenyl methylphosphonium dicyanoargentate. The odour of an isonitrile was detected after few minutes. The clear reaction mixture was refluxed at 80°C for 30 min whereupon the low-boiling product was distilled off. Yield, 3.6 g. NMR in CCl_4 showed a contamination of approximately 10 % of unreacted methyl iodide and no signal due to methyl cyanide. The total yield of methyl isonitrile is thus more than 80 %. No trace of methyl cyanide could be detected by IR using a gas cell.

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Proton Chemical Shifts in Some Benzhydryl Compounds

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Many authors have recently given attention to the NMR shifts of different kinds of protons for the identification of organic compounds. Quite some effort has been devoted to collecting and compiling the proton shift values for compounds with selected functional groups (Ref. 1 and references therein).

Generally it is now accepted that the Shoolery rule on the additivity of substituent effects on proton shifts is quite successful for methyl and methylene protons, while for compounds of the general type $XYZC-H$, *i.e.*, methine protons, Shoolery's rule is rather unreliable.[2]

Attempts have been made to correlate proton chemical shifts and charge densities in different series of compounds.[3] Beside electron density changes around the proton due to the electronegativity of substituents, other factors, as magnetic anisotropy[4] and electrostatic field effects,[5] are important. For numerous substituted aliphatic hydrocarbons a linear relationship could be established between Taft's $\sum\sigma^*$ values and chemical shift, using the anisotropy correlations ($\Delta\sigma$) due to Reddy and Goldstein,[6] except for highly polar substituents like CN, COR, NO_2, and COOH.[7,8] By correcting the chemical shifts for lone pair dipole moment in substituents this relationship has been improved.[9] The importance of the combined effect of the electric dipole moment and the anisotropic magnetic susceptibility of substituents has been particularly stressed by Zürcher.[10]

Recently a good correlation between proton chemical shifts and proton charge densities has been obtained,[11] but limited to substituents of the same row of the periodic system, suggesting that proton chemical shifts and charge densities have a different sensitivity to valence electron configuration.

To try to shed further light on the effect of polyatomic, highly polar substituents, the proton chemical shifts of some benzhydryl compounds have been determined. In a recent compilation of proton chemical

shifts of acyclic methine compounds, only benzhydryl bromide is included.[1] The benzhydryl substrates offer a special case where both the normal- and the iso-pseudohalide derivatives are easily synthesized.[12] The results are listed in Table 1.

Table 1. Resonance position of methine proton in Ph_2CHX, recorded in MeCN and CCl_4. The positions are given in ppm units relative to MeCN and TMS respectively.

X	MeCN	CCl_4
H	2.01	3.93
OH	3.82	5.74
OMe	3.34	5.11
Cl	4.32	6.02
Br	4.48	6.18
N_3	3.94	5.60
CN	3.43	5.01
NC	4.17[a]	5.79
NCO	4.07	5.73
NCS	4.21	5.90
NCSe	4.30	5.98
SCN	4.08	5.73
SeCN	4.29	6.05
COOH	3.13	[b]
NH-CHO	4.05	5.73

[a] $J_{NCH} = 1.8$ cps.
[b] Not sufficiently soluble.

Attempts to predict the resonance position by means of Shoolery's rule gave poor results. No correlation was found between positions of methine protons in benzhydryl compounds and methylene protons in the corresponding benzyl compounds.[13] This can probably be explained on the basis of the benzhydryl groups' deviation from sp^3 hybridization. Furthermore, it is known from molar Kerr constants that benzhydryl derivatives have configurations highly dependent upon substituents.[14,15] Interestingly, a rather good correlation was found between positions of methine protons in the benzhydryl compounds and the methyl protons in the corresponding t-butyl compounds.[16]

Considering the electronegativity of the iso-pseudohalides, one may use the pK_a values of the corresponding acids, HNCX, as a valuable parameter,[17] which indicates that electronegativity is increasing in the order NCSe < NCS < NCO. However, the resonance position indicates the opposite order.

For the normal SCN and SeCN derivatives, the shielding is decreasing from sulphur to selenium, which is opposite to the series dimethyl ether ($\delta = 3.17$), dimethyl sulfide ($\delta = 2.06$) and dimethyl selenide ($\delta = 1.93$).[18]

Here it must be emphasized that the group dipole moment of the SeCN group, 3.48 D, is 0.49 Debye units higher than that of the SCN group, 2.99 D. Group moments of other pseudohalide groups have been published.[20,21]

All pseudohalide groups contain multiple bonds, and several resonance forms contribute. The different canonical forms will contribute as a function of the other substituents present. It is interesting to note that the difference in chemical shift between NCS and SCN for methyl compounds, 0.76, drops to 0.47 for the iso-propyl compounds and to 0.17 in the benzhydryl case.[22] As one moves further away from sp^3-hybridization of the central atom, the effect of electronegativity of the substituents on the chemical shifts seems to decrease.

Because of the ambident nature of the SeCN and the SCN ions, the usual methods for preparation of organic selenocyanates and thiocyanates usually give mixtures of the normal and iso derivatives. Analytical methods that can distinguish the isomeric products, like UV and IR, have not been entirely satisfactory, especially for small amounts of one component in the other, because of the similarities of the absorptions.[23-25] NMR provides a valuable analytical method for kinetic studies of substitution reactions and studies on isomerizations.

Experimental. All spectra were examined on a JEOL NMR C-60 H spectrometer, and a Spin-decoupler JNM-SD 30 counter was used to determine the resonance positions. The benzhydrylbromide (I) and benzhydrol (II) were examined over a concentration range 0.4 M − 0.01 M, and the dilution effect was less than 1 cps in (I), but about 14 cps in (II), in both cases in downfield direction. The figures listed in the table are at a concentration of 0.2 M except for benzhydrol, where the shifts at infinite dilution are listed. The dilution shift for benzhydrol is probably due to the shift of the monomer-dimer equilibrium.[26] The compounds were either commercial, or prepared according to the literature: $Ph_2CHSeCN$ and $Ph_2CHNCSe$, Ref. 23; Ph_2CHSCN and Ph_2CHNCS, Ref. 27; Ph_2CHCN, Ref. 30; and Ph_2CHNC, Ref. 31.

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The Absolute Configuration of Terrestrol

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The main component of the marking perfume of male bumble bees of the species *Bombus terrestris* L. has been shown [1] to be one of the optical isomers of 3,7,11-trimethyldodeca-6*trans*,10-dien-1-ol (I). In order to have a less cumbersome name, particularly in connexion with biological work, the name terrestrol is now proposed for this compound. Both enantiomers of (I) have recently been synthesized in this laboratory.[2] Owing to the comparatively low optical rotation of the molecule and the small amount of the natural product available the observed rotation was only $\alpha_{5463}{}^{23}$ $-0.018°$, which was too small to allow safe conclusions regarding the absolute configuration. An attempt was therefore made to determine the configuration by comparing the gas chromatographic retention times of stereoisomeric esters obtained through esterification of terrestrol with the enantiomers of 2-methylbutanoic acid, and through preparation of the bornyl ethers, respectively. No gas chromatographic separation of these stereoisomers could be achieved, however. Next, the alcohols were converted into the corresponding aldehydes (II), which were further converted into cyclic