the heats of combustion have been measured for the compounds, and the enthalpy of the *trans* isomer was found to be less than that of the *cis* by 1.39 ± 0.64 kcal./mole (liquid phase, 298° K.).

The present work was undertaken to obtain values of $\Delta F$, $\Delta H$, and $\Delta S$ for the isomerization of 9-methyldecalin in the liquid phase. The method employed, which has previously been described in detail,[6] involves equilibrating small samples of the isomers at several different known temperatures. With hydrocarbons a palladium on carbon catalyst has usually been suitable. The present work was carried out over the temperature range 557–611° K. At still lower temperatures the equilibration is very slow, while at higher temperatures excessive decomposition sets in. The equilibrated samples were analyzed by gas phase analysis, the equilibrium constant was calculated at each temperature, and from a plot of ln K against 1/T the thermodynamic constants for the reaction *cis*- $\rightleftharpoons$ *trans*-9-methyldecalin were found to be $\Delta H_{584} = -0.55 \pm 0.28$ kcal./mole, and $\Delta S_{584} = -0.5 \pm 0.5$ e.u. These values were not as accurate as those usually obtained by this method,[6] due partly to the somewhat restricted temperature range that was conveniently available and partly to the fact that the isomers are not easily separable by vapor phase chromatography. Under the best conditions found, the separation was still not complete, and the composition of a given sample could be determined only with an accuracy of ± 0.24%.

The value for $\Delta H$ found in the present work is in good agreement with both the theoretical value,[4] and with the value determined from the heat of combustion measurements.[5]

The entropy change expected for the reaction can be predicted by noting that both isomers have symmetry numbers of 1, and the *cis* is *dl* while the *trans* is *meso*. The calculated (gas phase) value is $\Delta S = -1.4$ e.u. The experimental value is correct in sign but smaller than this in magnitude. The same situation was noted with the unsubstituted decalins,[7-9] and is not completely understood. In that case the experimental gas phase values were in better agreement with theory than were the liquid phase values, and the same may be true here.

It can be seen (Table I) that the equilibrium composition of the 9-methyldecalins is essentially independent of temperature, 55 ± 1% over the range studied. The difference in energy between the isomers is sufficiently small that in substituted systems the position of the *cis-trans* equilibrium will be determined to an important extent by the nature of the substituents.

TABLE I

EQUILIBRATION DATA FOR THE REACTION *cis*-9-METHYLDECALIN $\rightleftharpoons$ *trans*-9-METHYLDECALIN

| T° K | Starting Isomer | Eq. % *trans* |
|---|---|---|
| 557 | *cis* | 55.98 |
| 557 | *trans* | 56.56 |
| 572 | *cis* | 56.21 |
| 580 | *trans* | 55.99 |
| 583 | *cis* | 55.70 |
| 597 | *cis* | 55.14 |
| 597 | *trans* | 55.27 |
| 611 | *trans* | 55.21 |

## EXPERIMENTAL

The compounds used in the present work were samples prepared earlier by Dauben, Rogan, and Blanz.[3] Equilibrium was established by heating the compound (100 mg.) with palladium on carbon (10%, 50 mg.) in a small sealed tube as previously described.[6] The times used for the equilibrations varied from 350 hr. at 577° K., to 46 hr. at 611° K. The equilibration was quenched and the sample was analyzed as described earlier. The column used for the analysis and which gave the best separation of the many columns tried was 14.5 feet long, and was packed with 9.5 g. of $\gamma$-methyl-$\gamma$-nitropimelonitrile on 33 g. of 60–80 mesh firebrick. The analyses were carried out at 95°. The ratio of the isomers in the mixture was taken as equal to the ratio of the products of the band heights and the half-band widths as determined graphically. Each sample was analyzed at least three times and the average deviation for all duplicate analyses was ±0.24%. The results are summarized in Table I. The calculation of the thermodynamic quantities from the data was carried out as described earlier.[6]

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# Preparation of Sodium 2,2-Dimethyl-2-silapentane-5-sulfonate, a Useful Internal Reference for N.S.R. Spectroscopy in Aqueous and Ionic Solutions

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Recently a study has been made[1] to develop, in so far as possible, an adequate internal referencing technique for nuclear spin resonance (N.S.R.)

spectroscopy in aqueous and ionic solutions. The now well accepted[2] internal reference, tetramethylsilane,[3] is virtually insoluble in such media. However, an ionic derivative of this compound, the anion 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was shown to possess a remarkably favorable balance of properties for general internal referencing of aqueous systems.[1] We here describe the preparation of this useful reference.

The method used was a slight modification of the well-known free-radical addition of bisulfite to olefins.[4,5] Owing to the very low solubility of allyltrimethylsilane in the usual reaction mixture, it was found virtually essential to add a co-solvent, methanol.[5] Alternative initiators (*t*-butyl hydroperoxide, and potassium persulfate) were tried but appeared to be inferior to Kharasch's nitrate-nitrite system.[4]

## EXPERIMENTAL

*Materials.* Allyltrimethylsilane was purchased from Peninsular ChemResearch, Inc., Gainesville, Fla., and was redistilled before use. The other ingredients were of reagent grade.

*Sodium 2,2-dimethyl-2-silapentane-5-sulfonate.* Into a 500-ml. flask equipped with magnetic stirrer were placed 50.0 g. (0.48 mole) of sodium bisulfite, 5.0 g. (0.072 mole) of sodium nitrate, 5.0 g. (0.059 mole) of sodium nitrate, 150 ml. of distilled water, 250 ml. of methanol, and 25.0 g. (0.22 mole) of allyltrimethylsilane. The flask was tightly stoppered to prevent loss of the volatile silane (the mixture became quite warm) and was stirred without external heat for 2–4 days, at which time a fluffy white precipitate was present. (At this point one might recover a substantial amount of unchanged allyltrimethylsilane by steam distillation; however we did not choose to do so.) The reaction mixture was taken to dryness on the steam bath; we used a rotary evaporator. The dried residue was extracted overnight with 200 ml. of absolute ethanol in a Soxhlet apparatus; the solution was filtered hot through fine filter paper (Whatman No. 5) to remove traces of inorganic salts, and was cooled to crystallize sodium 2,2-dimethyl-2-silapentane-5-sulfonate. Our best yield thus far has been 23.9 g. (46.1%) of the monohydrate of sodium 2,2-dimethyl-2-silapentane-5-sulfonate, after one recrystallization from ethanol; the compound was obtained as the monohydrate.

*Anal.* Calcd. for $C_6H_{14}NaO_3SiS \cdot H_2O$: $H_2O$, 7.7; C, 30.5, H, 7.25. Found: $H_2O$, 7.3 (Karl Fischer); C, 30.5; H, 7.2.

The anhydrous material may be obtained by drying at 130° *in vacuo.*

The monohydrate shows infrared absorption (Nujol mull) at 2.80, 2.88, and 6.20 $\mu$, absent in the anhydrous material; it also has strong sulfonate bands at 8.41 and 9.50 $\mu$ with other characteristic bands at 8.01, 11.65, 12.05, 13.24, 13.47, and 14.34 $\mu$.

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# Substituent Constants for the Trinitromethyl-, 1,1-Dinitroethyl-, and Related Groups[1]

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Some time ago we pointed out that the rates of reaction of *trans*-3-substituted acrylic acids with diphenyldiazomethane could be correlated with the Hammett *para* substituent constants for the groups used.[2] We wish now to present data on the rates of reaction of several nitro acids and to list the substituent constants for nitroalkyl groups. The rate data, shown in Table I, were obtained as described previously, as were the substituent constants listed in Table II. The substituent constants were calculated from the equations[2]

$$\log k = 0.072 + 1.623\ \sigma_{\text{para}}$$

and

$$\log k = -0.105 + 1.174\ \sigma^*$$

TABLE I

RATES OF REACTIONS OF ACIDS WITH $(C_6H_5)_2CN_2$ IN ETHANOL AT 30°

| Acid | $k$, L. Mole$^{-1}$ Min.$^{-1}$ |
|---|---|
| *trans*-$(O_2N)_3CCH{=}CHCO_2H$ | 25.3 |
| *trans*-$(O_2N)_2C(CH_3)CH{=}CHCO_2H$ | 11.5 |
| *trans*-$O_2NC(CH_3)_2CH{=}CHCO_2H$ | 2.49 |
| *cis*-$O_2NC(CH_3)_2CH{=}CHCO_2H$ | 3.47 |
| *trans*-$(O_2N)_2C(C_2H_5)CH{=}CHCO_2H$ | 13.0 |
| $(O_2N)_3CCH_2CH_2CO_2H$ | 3.76 |
| $(O_2N)_2C(CH_3)CH_2CH_2CO_2H$ | 2.03 |
| $(O_2N)_2C(C_2H_5)CH_2CH_2CO_2H$ | 2.18 |

TABLE II

SUBSTITUENT CONSTANTS

| Substituent | $\sigma_{\text{para}}$ | Substituent | $\sigma^*$ |
|---|---|---|---|
| Trinitromethyl | 0.820 | 3,3,3-Trinitropropyl | 0.579 |
| 1,1-Dinitroethyl | 0.609 | 3,3-Dinitrobutyl | 0.352 |
| 2-Nitro-2-propyl | 0.200 | 3,3-Dinitropentyl | 0.377 |
| *t*-Butyl | −0.197[a] | 2,2,2-Trinitroethyl | 1.62[b] |
| 1,1-Dinitropropyl | 0.642 | Trinitromethyl | 4.54[b] |

[a] From Ref. 3. [b] Obtained by multiplying the value for the substituents with one more methylene group by 2.8.[4]

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(1) Part IV in the series *Polar Effects on Rates and Equilibria.* This investigation was supported by the Department of the Navy, Bureau of Ordnance.

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