TABLE I

| °K. | Natural | D of liquid uranium in g./cm.³ | | | Atomic volume, cm.³/g. at. | Cubical coef. of expansion for natural uranium, $T^{-1}$ °K. $\times 10^6$ |
| | | $U^{238}$ | $U^{235}$ | $U^{233}$ | | |
|---|---|---|---|---|---|---|
| 1406 m.p. | 17.898 | 17.905 | 17.678 | 17.528 | 13.301 | 57.6$_0$ |
| 1500 | 17.801 | 17.807 | 17.582 | 17.432 | 13.374 | 57.9$_2$ |
| 2000 | 17.284 | 17.291 | 17.072 | 16.927 | 13.774 | 59.6$_5$ |
| 2500 | 16.768 | 16.774 | 16.562 | 16.421 | 14.198 | 61.4$_9$ |
| 3000 | 16.252 | 16.258 | 16.052 | 15.916 | 14.649 | 63.4$_4$ |
| 4200 b.p. | 15.01 ± 0.04 | 15.02 | 14.83 | 14.70 | 15.86 ± 0.04 | 69 |
| $D_0$ | 19.350 | 19.357 | 19.112 | 18.949 | | |
| $\alpha$ | $-10.310 \times 10^{-4}$ | $-10.330 \times 10^{-4}$ | $-10.200 \times 10^{-4}$ | $-10.110 \times 10^{-4}$ | | |

Three runs were made using different type sinkers and crucibles to avoid or minimize chemical contamination effects. The sinkers and crucibles used were a $ZrO_2$-coated molybdenum sinker and a $Al_2O_3$ crucible in run 1, a pure $Al_2O_3$ sinker and a $Al_2O_3$ crucible in run 2, and a $ZrO_2$-coated molybdenum sinker and a pure $ThO_2$ crucible in run 3. No noticeable chemical reaction was observed. All materials performed satisfactorily, those of run 3 being the best. All the measured values fitted the same straight line. The uranium (from Davison Chemical Co.) contained 0.220% $U^{235}$ and its actual uranium content was 99.9 wt.%. Impurities, in p.p.m., were: Fe and Ni, 200; O, 150; C, 90; Cu and Si, 50; N, 25; Al, 20.

The equation of the density of liquid uranium, determined by the method of least squares, is $D_{liq.}$ in g./cm.³ = $19.356 - 10.328 \cdot 10^{-4}\, T$, with a probable error of ±0.078%.

Details of our general method of density measurement, electrical heating, temperature control and surface tension correction are given in another publication.[2]

In recent papers[3,4] it was shown that the temperature range of liquid metals, i.e., the range from melting to the critical point, is far greater than for any other type of substance. It extends, in view of their elementary and atomic nature, far beyond the thermal limits of existence of any other solid or liquid; even the stablest of the latter dissociate into atoms at about 5000–6000°K. In contrast, the refractory metals such as Re, Ta and W *will be liquids* up to a critical temperature of about 20,000, 22,000, and 23,000°K., respectively.

It also was shown[3,4] that one can construct a liquid temperature range diagram of metals demonstrating the relationship between liquid (and saturated vapor) density vs. temperature over the whole liquid temperature range, from the melting point to the critical point, by using the theorem of corresponding states of van der Waals, the law of rectilinear diameter of Cailletet and Mathias and experimental data on heats and entropies of vaporization, vapor pressure and particularly experimental liquid density data over as wide a temperature range as possible. Density measurements have been carried out, at this Institute, on a large number of metals from their melting points to their

boiling points, such metals as Pb,[2] Ag,[5] Cu, Sn, and In.

It is clear now, from a study of the temperature range diagram of liquid metals, that liquid density is a straight line function of temperature far beyond the metal's normal boiling point, because the saturated vapor density of metal, which according to the law of rectilinear diameter causes deviation from linearity, assumes significant values only *substantially* above the normal boiling point. Thus, we can estimate the density of liquid uranium at its normal boiling point with reasonable accuracy.

T. W. Richards in his classical work[6] on the atomic volumes of separated lead isotopes proved F. Soddy's concept of the equality of atomic volumes of isotopes with a high degree of precision. Thus, we can calculate from our data the liquid densities of pure $U^{235}$, $U^{233}$ and $U^{238}$. The coefficients of the density equation $D_T = D_0 + \alpha T$ and density values for set temperatures for the three isotopes and the natural U-mixture are given in Table I.

(5) A. D. Kirshenbaum. J. A. Cahill and A. V. Grosse, *J. Inorg. & Nucl. Chem.*, in press (1961).

(6) T. W. Richards and C. Wadsworth, *J. Am. Chem. Soc.*, **38**, 221 (1916).

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NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. ABNORMAL SPLITTING OF ETHYL GROUPS DUE TO MOLECULAR ASYMMETRY. II.[1]

*Sir:*

Diethyl sulfite,[2-5] acetaldehyde diethyl acetal,[3] and cyclopropylcarbinyl ethyl ether[3] offer striking examples of the magnetic non-equivalence of the methylene hydrogens in compounds of the type $R-CH_2-O-XR_1R_2R_3$ (with R = $CH_3$ and X = S, C, P, etc.). Thus, the nuclear magnetic resonance (n.m.r.) spectra of such methylene protons are often typical of AB rather than $A_2$ systems.[6,7]

(1) Supported in part by the Office of Naval Research.

(2) H. Finegold, *Proc. Chem. Soc.*, 283 (1960).

(3) P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci.*, **47**, 49 (1961).

(4) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

(5) J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961).

(6) Cf. P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4565 (1957).

(7) (a) J. A. Pople, W. G. Schneider and H. Bernstein, "High-resolution Nuclear Magnetic Resonance Spectra," McGraw-Hill Book Co., Inc., New York, 1959, pp. 98, 119–123; (b) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., Chap. 2–3.

(2) A. D. Kirshenbaum, J. A. Cahill and A. V. Grosse, *J. Inorg. & Nucl. Chem.*, in press (1961).

(3) A. V. Grosse, "The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures," Report of the Research Institute of Temple University, September, 1960.

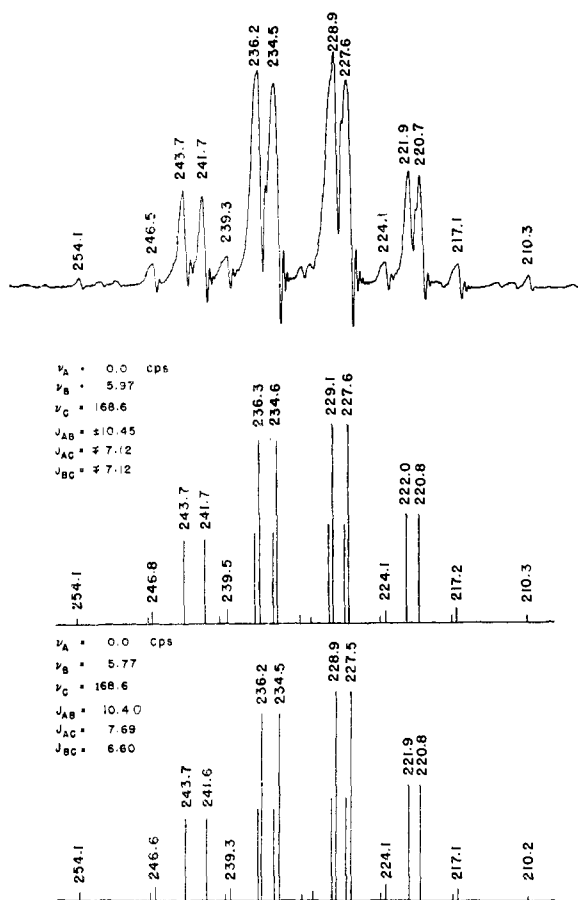(4) A. V. Grosse, *J. Inorg. & Nucl. Chem.*, in press (1961).

Fig. 1.—Observed and calculated n.m.r. spectra of a 50% (volume) solution of diethyl sulfite in benzene at 60 Mc. with tetramethylsilane as an internal reference taken as zero.

Excellent agreement has been obtained between theoretical and observed spectra of the ethoxy groups of acetaldehyde diethyl acetal. The calculations were based on an $ABC_3$ type system but led to a quite unanticipated assignment of different coupling constants (7.35 and 6.68 cps.) between the A and B methylene protons and the $C_3$ methyl protons of the ethoxy group. The origin of the multiplicity of the n.m.r. resonances which was first reported by Finegold for the methylene groups of diethyl sulfite has been discussed by Waugh and Cotton.[4] We have now completed a detailed investigation of the spectrum of diethyl sulfite and believe our results are of considerable importance to the general problem of analysis of complex spectra and the relation of coupling constants to structure in saturated organic molecules.

Although the spectrum of diethyl sulfite might be expected to offer only a more or less trivial example of an $ABC_3$ type, the manner of its sensitivity to solvent changes[8] turned out to be at first baffling and then illuminating. The methylene resonances of 50% diethyl sulfite–50% benzene are shown in Fig. 1. A series of iterative calculations demonstrated that this spectrum could be fitted to within experimental error by assigning a 1.09
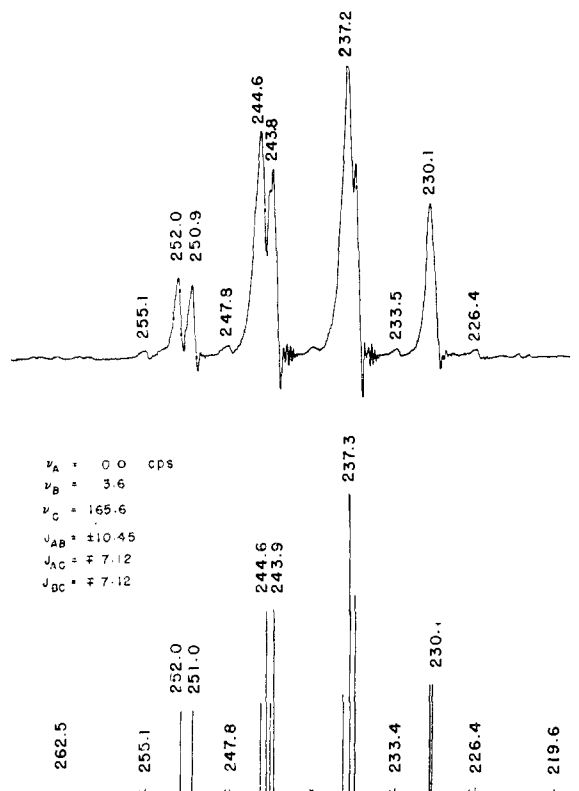
Fig. 2.—Observed and calculated n.m.r. spectra of neat diethyl sulfite at 60 Mc. with tetramethylsilane as an internal reference taken as zero.

cps. ($J_{AC} = 7.69$ cps. and $J_{BC} = 6.60$ cps.) difference between the spin–spin coupling constants for the different methylene hydrogens and the methyl hydrogens. The other parameters had unexceptional values, thus, $\nu_B - \nu_A = 5.77$ cps., $\nu_C - \nu_A = 168.6$ cps., $J_{AB} = 10.45$ cps. and $J_{CC} = 12.50$ cps.[9]

With neat diethyl sulfite, the chemical shift between A and B is smaller (cf. Fig. 2) but we were not able to compute a satisfactory theoretical spectrum by varying the chemical shifts and keeping the coupling constants constant. Matters were improved considerably when the $J_{AC}$ and $J_{BC}$ coupling constants were set about 2 cps. apart along with a smaller $\nu_A - \nu_B$ but, even after more than a hundred trials, the over-all agreement could not quite be brought to within experimental error.

The difficulties appeared to be resolved when (following a suggestion from Dr. Marjorie C. Caserio) we explored the possibility of assigning coupling constants of opposite signs. Complete success was obtained with $J_{AB}$ having an opposite sign from $J_{AC}$ and $J_{BC}$ (see Fig. 2). With these relative signs, the theoretical spectra agreed within experimental error with the experimental spectra when $J_{AC}$ was taken as equal to $J_{BC}$. Furthermore, the change between diethyl sulfite in benzene solution and neat liquid could be ascribed as only due to changes in chemical shifts with no changes in the coupling constants.

Complete agreement between the computed 40 Mc. and observed 40 Mc. spectra of diethyl sulfite

in benzene solution was achieved only with the coupling constants of opposite signs. The spacings between the lines shown in Fig. 1 at 241.7 and 243.7 cps. and 221.9 and 220.7 cps. (Fig. 1) were reduced to 1.4 and 0.1 cps., respectively, at 40 Mc. With coupling constants of the same sign, the computed spacings for these lines were 0.8 and 0.9 cps., respectively.

On the basis of these results, we believe that the relative signs of $J_{AC}$ and $J_{BC}$ must be taken as being indeed different from $J_{AB}$. Interestingly, this conclusion could only have been reached by treatment of the spin system as $ABC_3$, not as the $ABX_3$ approximation in which a change in the sign of $J_{AB}$ relative to $J_{AC}$ and $J_{BC}$ does not affect the theoretical spectrum.

The results can be regarded as disquieting in two connections. First, the difference in sign between the geminal and vicinal H–H couplings runs counter to the theoretical predictions of Karplus and Gutowsky[10] for substances with normal bond angles. Second, in analogy with the findings of Castellano and Waugh[11] for ABC systems, rather different sets of spin-coupling and chemical-shift parameters were found to give nearly identical theoretical spectra for diethyl sulfite in benzene and each of these corresponds amazingly well to the experimental spectrum at 60 Mc. Indeed, the previously mentioned excellent agreement between theoretical and experimental spectra obtained for acetaldehyde diethyl acetal now has been duplicated with $\nu_B - \nu_A = 9.23$ cps., $\nu_C - \nu_A = 146.3$ cps., $J_{AC} = 9.30$ cps. and $J_{AC}$ equal to $J_{BC} = 7.03$ cps. with $J_{AB}$ opposite in sign to $J_{AC}$ and $J_{BC}$.

Clearly, caution and judgment must be exercised in use of the iterative method of obtaining spin-spin coupling constants since there seems to be no assurance that a "final" solution is truly unique.[7b,11]

**Acknowledgment.**—We are deeply indebted to Dr. Stanley L. Manatt and the Computing Center of the Jet Propulsion Laboratory for the IBM 7090 calculations of the theoretical spectra.

(10) H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, 31, 1278 (1959); M. Karplus, *ibid.*, 30, 11 (1959).

(11) S. Castellano and J. S. Waugh, *ibid.*, 34, 295 (1961).

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## STERICALLY CONTROLLED GRIGNARD REACTIONS. A NEW SIMPLE ROUTE TO 17α-METHYLATED STEROID ANALOGS

*Sir:*

We wish to report a convenient new synthesis of 17α-methylated steroid derivatives which has made possible the preparation of highly active progesterone homologs. When the readily available methyl 3β-hydroxy-17α-methyl-5-etienate (I)[1] was refluxed in anisole for one hour in presence of *excess* methylmagnesium bromide, the corresponding sterically hindered *ketone*, 17α-methylpregnenolone II[1] was obtained in 70% yield. The latter substance was converted to the known[1] 17α-methyl-

(1) Pl. A. Plattner, H. Heusser, P. Th. Herzig, *Helv. Chim. Acta*, 32, 270 (1949).



I

II, R' = H
III, R' = CH₃
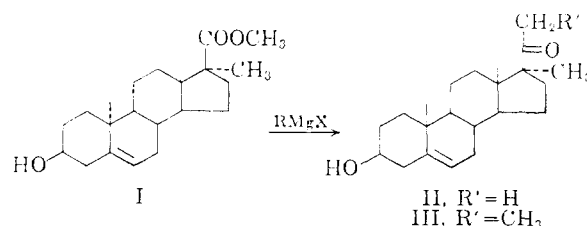
progesterone by Oppenauer oxidation. Only about 20% of the "normal" product, the corresponding carbinol 17α,20-dimethyl-5-pregnene-3β,20-diol, was formed and conveniently separated by chromatography.

Analogously, the 5α,6α epoxide obtained by peracetic acid treatment of I, m.p. 170–171°, $[\alpha]D$ −67.2, gave in similar yields 3β,5α-dihydroxy-6β,-17α-dimethylpregnan-20-one, m.p. 188–192°, which was directly oxidized by chromic acid to the 3,20-dione, m.p. 230–233°, and converted by methanolic sodium hydroxide to 6α,17-dimethylprogesterone, m.p. 137–140°, $[\alpha]D$ +90.5, $\lambda_{max}$ 239 mμ, log ε 4.2. The latter substance, and the corresponding 6-dehydro derivative, m.p. 143–146°, $[\alpha]D$ +87.1, $\lambda_{max}$ 292 mμ, log ε 4.4, obtained by chloranil dehydrogenation, were orally at least as active, in the Clauberg test, as 19-nor-17α-ethynyltestosterone, and twenty times more active than 17α-methylprogesterone.

NOTE ADDED IN PROOF.—6,17-Dimethyl-6-dehydroprogesterone is as active orally as 6α-methyl-17-acetoxyprogesterone. It is devoid of any androgenic properties.

Treatment of I with ethylmagnesium iodide in anisole gave 17α,21-dimethylpregnenolone III, m.p. 145–148°, with no detectable amount of carbinol being formed. Oppenauer oxidation gave 17α,21-dimethylprogesterone, m.p. 157–159°, $[\alpha]D$ +107.7, $\lambda_{max}$ 241 mμ, log ε 4.2² in 70% over-all yield. Further transformations of these methylated steroids together with a report on their 6-halogenated derivatives[3] will be presented in a more detailed paper.

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RECEIVED SEPTEMBER 20, 1961

## INERTIAL EFFECTS OF SUBSTITUENTS ON HOT ATOM CAPTURE[1]

*Sir:*

Hot hydrogen atoms can replace hydrogen and other atoms and groups with high collision efficiency.[2] The course of these reactions has been shown to be largely controlled by steric factors.[2] However certain results, particularly on alkyl replacement, have not found explanation. This letter reports a remarkable new effect in the hot hydrogen displacement of halogen atoms from