

because the corresponding cobalt(III) compounds are well defined and have been known for a long time.<sup>7</sup> It is significant that the rhodium(III) isomers now have been prepared because it will be possible to make quantitative comparisons between these systems and the analogous cobalt(III) compounds. Work is now in progress on the kinetics and mechanism of hydrolysis, isomerization, and racemization of the rhodium(III) complexes.

The method described by Meyer and Kienitz<sup>3</sup> for the synthesis of  $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$  was tried several times but without success. Other attempts to prepare this compound also were unsuccessful.<sup>8</sup> The *cis*- and *trans*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$  finally were isolated from a reaction mixture obtained by gradually adding aqueous KOH to a refluxing water solution of  $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$  and  $\text{en}\cdot 2\text{HCl}$ . In a typical preparation 1.0 g. of  $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$  (0.0038 mole), 1.0 g. of  $\text{en}\cdot 2\text{HCl}$  (0.0076 mole), 0.43 g. of KOH (0.0076 mole) and 50 cc. of  $\text{H}_2\text{O}$  were heated to reflux. Over a period of 15 min. another 50 cc. of  $\text{H}_2\text{O}$  containing 0.43 g. of KOH (0.0076 mole) was added to the refluxing reaction mixture in 10 cc. increments. The color of this solution changed from dark red to bright yellow. Since the chloride salts are rather soluble and difficult to separate from KCl, 20 cc. of  $\text{HNO}_3$  (concd.) was added to the cold reaction mixture after concentration to one half the original volume. Yellow-orange crystals of *trans*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$  separated in 33% yield (0.45 g.). *Anal.* Calcd. for  $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$ : C, 13.5; H, 4.53; Cl, 19.9. Found: C, 13.9; H, 4.63; Cl, 20.1. Evaporation of this filtrate to 20–30 cc. at room temperature yields 0.15 g. of bright yellow *cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$ . Analysis of this isomer shows C, 13.9; H, 4.31; Cl, 20.0.

Although the chloride salts are fairly soluble, it has been possible to isolate *cis*- and *trans*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$  from a reaction mixture of the type described above. When the reaction is finished, instead of adding  $\text{HNO}_3$ , the solution is concentrated. The first crystals to separate are the *cis* isomer after which the more soluble *trans* form is obtained from the mother liquor.

Assignment of the geometric configuration to the two isomers was made on the basis of the resolution of the asymmetric *cis* isomer. A solution of 0.45 g. of *cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$  and 0.9 g. of dextro-ammonium  $\alpha$ -bromocamphor- $\pi$ -sulfonate in 15 cc. of  $\text{H}_2\text{O}$  was frozen in an ice-salt-bath. After melting, 0.25 g. of *l-cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2][d\text{-C}_{10}\text{H}_{14}\text{O}_4\text{SBr}]$  was collected on a filter and washed. This diastereoisomer was thoroughly ground with 2 cc. of a 1:1:1 mixture of ethanol:ether:HCl (concd.) and 0.19 g. of *l-cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$  was isolated. The specific optical rotation of a 0.4% aqueous solution of this compound has values of  $[\alpha]_{577m\mu} - 50^\circ$  and  $[\alpha]_{535m\mu} - 58^\circ$ .

Additional evidence in support of this structural assignment is offered by a comparison of the rhodium(III) isomers with the same cobalt(III) compounds of known structure. For example, the infrared spectra in the 3, 6, and 9  $\mu$  regions for the *cis* and for the *trans* isomers of the cobalt(III) and

rhodium(III) complexes are almost identical whereas the spectra of the *cis* differ from those of the *trans* isomers.<sup>9</sup> Likewise the *cis*-chloride and *trans*-nitrate salts are the less soluble forms for the cobalt(III) and also for the rhodium(III) complexes. Finally, the rate of acid hydrolysis of *cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]^+$  is faster than that of the *trans*-isomer as is also true for the analogous cobalt(III) complexes.

(9) M. L. Morris and D. H. Busch, *THIS JOURNAL*, **82**, 1521 (1960).

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#### SPIN DISTRIBUTION IN ALIPHATIC KETYL<sup>1</sup>

Sir:

Electron spin resonance experiments confirm the conclusion of Favorsky and Nazarov<sup>2</sup> that hexamethylacetone and pentamethylacetone react with alkali metals to form free radicals. Reduction of solutions of the ketones in tetrahydrofuran by potassium yields products whose hyperfine splittings correspond to the free radicals containing the same numbers of protons as the original molecules. The spectrum of the ketyl of hexamethylacetone has seventeen lines evenly spaced at an interval of 0.12 oersted and symmetrically distributed about  $g = 2.003$ . The intensities correspond to hyperfine interaction with eighteen equivalent protons. Nineteen lines are expected, but the two weakest ones, of expected intensity only  $2 \times 10^{-5}$  as great as the strongest one, are not detected by our spectrometer. Pentamethylacetone yields a symmetrical doublet with splitting of 2.38 oe.; each member of the doublet is further split into incompletely resolved components with interval about 0.1 oersted.

The spectrum of each compound contains additional components whose intensities correspond well with those expected from splitting by  $\text{C}^{13}$  in its natural abundance. In hexamethylacetone two replicas of the central pattern are found symmetrically disposed about it (Fig. 1). The interval between the replicas is 7.6 oe., the intensity of each 0.033 that of the central pattern. A second pair of patterns, with intensity 0.17 of the first pair is found with splitting 49.6 oe. The intensity of the first pair corresponds to the 6.6% of the molecules which have one  $\text{C}^{13}$  in any of six equivalent positions, of the second pair to the natural abundance of  $\text{C}^{13}$  in a single position. We conclude that the splitting of 7.6 oe. arises from  $\text{C}^{13}$  in the methyl position, the 49.6 oe. from  $\text{C}^{13}$  in the central carbon. No splitting from the quaternary carbons is found. Similarly in pentamethylacetone the splitting by  $\text{C}^{13}$  in the central position is 49.8 oe. and by  $\text{C}^{13}$  in a methyl position 13 oe. Splitting by the five methyl carbons are approximately equal.

The large splittings by the central carbon atoms are in the same range as those in methyl radical<sup>3</sup>

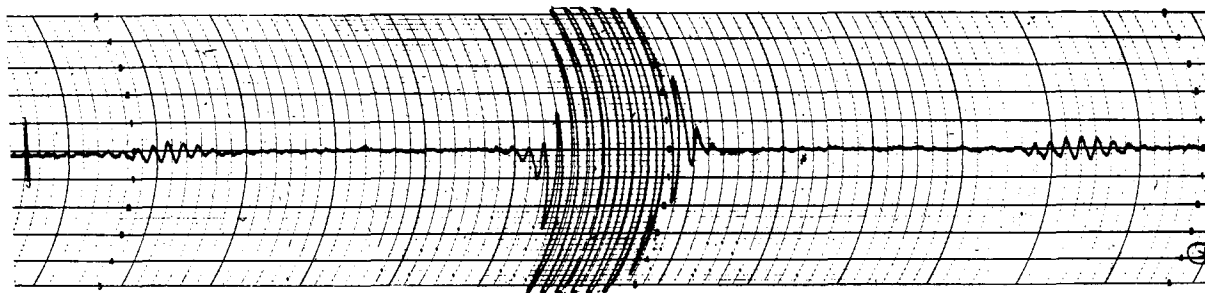
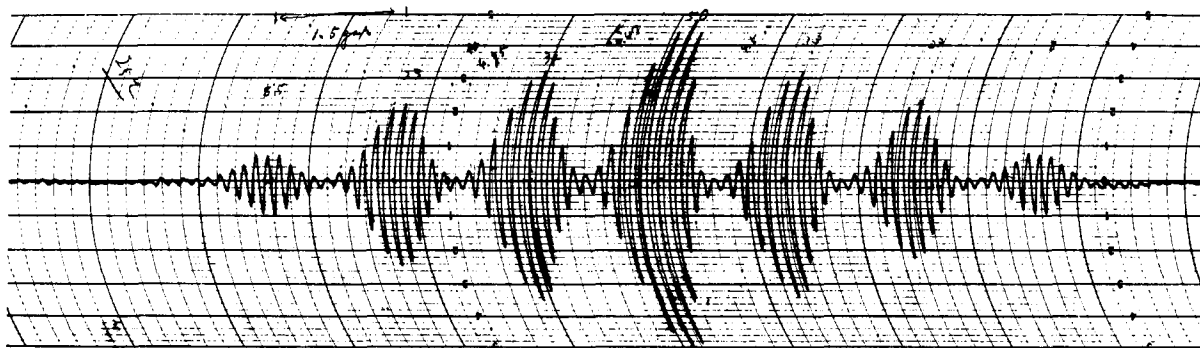
(1) This work was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract AF 49-638-469. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

(2) Favorsky and Nazarov, *Bull. soc. chim.*, [5] 1, 46 (1934).

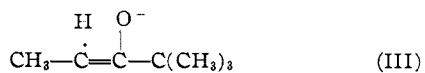
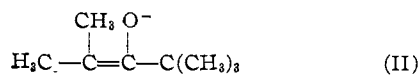
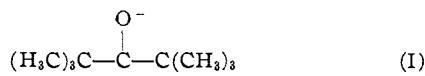
(3) T. Cole, H. O. Pritchard, N. R. Davidson and H. M. McConnell, *Mol. Phys.*, **1**, 406 (1958).

(7) "Gmelins Handbuch der anorganischen Chemie," **58B**, 228 (1930).

(8) G. M. Harris, private communication.

Fig. 1.— $-dX''/dH$  vs.  $H$  for potassium ketyl of hexamethylacetone in THF.Fig. 2.— $-dX''/dH$  vs.  $H$  for sodium ketyl of hexamethylacetone in THF.

and suggest structure I as the major ingredient in the ground state of each of the ketyls.



Splittings by the methyl carbons and by the unique proton in pentamethylacetone could be accounted for by admixture of conjugated structures such as II and III. (In view of the recent proliferation in names of conjugations we don't know which kind we are reporting.) Admixture of two or three per cent. of each of structure II and of about 0.5 per cent. of structure III could account for the observed splittings.

The absence of splittings by the quaternary carbons is not easily explained. Spin polarization of the  $\sigma$  bond between them and the central carbon might be expected to produce observable splittings. Probably other structures which produce spin density of opposite sign to that produced by I must be included.

When sodium or lithium is used as reducing agent, the splittings by protons and  $\text{C}^{13}$  in the ketyls are almost identical with those described in the preceding paragraphs. In addition, splittings by two equivalent alkali metal nuclei per paramagnetic molecule are found. The sodium compound in tetrahydrofuran yields seven evenly spaced lines at interval 1.58 oe. with intensities 1:2:3:4:3:2:1 (Fig. 2). The spectrum of the lithium ketyl is

somewhat more complex because of the presence of the isotopes  $\text{Li}^6$  and  $\text{Li}^7$ . The complexes with sodium and lithium are under further investigation.

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#### N.M.R. SPECTRA AND STRUCTURE OF ALUMINUM METHYL CHLORIDES

Sir:

Recently Brownstein, *et al.*,<sup>1</sup> have published n.m.r. data on  $\text{Al}_2(\text{CH}_3)_6$ ,  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  and  $\text{Al}_2(\text{CH}_3)_2\text{Cl}_4$ . The interpretation of their results for  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  and  $\text{Al}_2(\text{CH}_3)_2\text{Cl}_4$  is based on the methyl bridge model for these two molecules deduced from Raman Spectra by Van der Kelen and Herman.<sup>2</sup> However, for  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  a chlorine bridge structure was deduced from electron diffraction measurements by Brockway and Davidson,<sup>3</sup> from the infrared spectrum by Schomburg,<sup>4</sup> and from infrared and Raman work.<sup>5,6</sup> The vibrational spectrum of  $\text{Al}_2(\text{CH}_3)_2\text{Cl}_4$  gives evidence of a centrosymmetrical structure<sup>6</sup> but subsequent Raman work did not yet allow of a definite choice between the chlorine bridge model ( $\text{C}_{2h}$  symmetry) and the methyl bridge model ( $\text{D}_{2h}$  symmetry).

The n.m.r. spectra of Brownstein, *et al.*, were

(1) S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, *THIS JOURNAL*, **82**, 1000 (1960).

(2) G. P. Van der Kelen and M. A. Herman, *Bull. Soc. Chim. Belges*, **65**, 350 (1956).

(3) L. O. Brockway and N. R. Davidson, *THIS JOURNAL*, **63**, 3287 (1941).

(4) G. Schomburg, "Infrarot spektroskopische Untersuchungen an aluminum-organischen Verbindungen," Diss., Aachen, 1956.

(5) M. P. Groenewege, *Z. Physik Chemie, Neue Folge*, **18**, 147 (1958).

(6) M. P. Groenewege, *Revue Universelle des Mines (Liege)*, 9 Série, **15**, 461 (1959).