solved in water and heated with sodium carbonate. The liberated base was extracted with ether. The ethereal solution was washed thoroughly with water until neutral and evaporated. The base was converted into the D-glutamic acid salt and purified as described above. The purified base gave a triacetyl derivative melting at 98–100° ($[\alpha]^{22}\text{D}$ +19.2 (0.1 g. in 10 cc. of chloroform)).

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RECEIVED SEPTEMBER 21, 1953

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THE PREPARATION OF D-HOMOPROGESTERONE AND D-HOMO-11-DEOXYCORTICOSTERONE ACETATE

Sir:

The sustained interest in the cortical hormones made it desirable to determine the effect of a six-membered D ring on cortical-hormonal activity. D-Homoprogesterone and D-homo-11-deoxycorticosterone acetate were prepared as the first part of this program.

Ethynylation of 3β-hydroxy-D-homoandrost-5-en-17a-one[1] (I) produced D-homo-17aα-pregn-5-en-20-yne-3β,17aβ-diol (II), m.p. 262–264°; $[\alpha]^{23}\text{D}$ −108° (0.5% in $CHCl_3$); (*Anal.* Calcd. for $C_{22}H_{32}O_2$: C, 80.4; H, 9.8. Found: C, 80.2; H, 9.8); and, in low yield, D-homopregn-5-en-20-yne-3β,17aα-diol (III), m.p. 220–222°; $[\alpha]^{23}\text{D}$ −76° (1% in $CHCl_3$); (*Anal.* Found: C, 80.2; H, 10.0.) Treatment of either II or III with formic acid[2] gave, after hydrolysis, 3β-hydroxy-D-homopregna-5,17(17a)-dien-20-one (IV), m.p. 233–235°; $[\alpha]^{23}\text{D}$ +35° (0.5% in $CHCl_3$); $\lambda_{\text{max.}}$ 233 mμ, ϵ 8,930; (*Anal.* Calcd. for $C_{22}H_{32}O_2$: C, 80.4; H, 9.8. Found: C, 80.7; H, 9.9.) plus an unidentified compound, $C_{22}H_{30}O$, m.p. 171–172°. Hydrogenation of IV yielded 3β-hydroxy-D-homopregn-5-en-20-one (V), m.p. 205–206°, $[\alpha]^{23}\text{D}$ −25° (1% in $CHCl_3$); (*Anal.* Calcd. for $C_{22}H_{34}O_2$: C, 80.0; H, 10.4. Found: C, 79.8; H, 10.3) which on Oppenauer oxidation gave the desired D-homoprogesterone, m.p. 158–160°; $[\alpha]^{23}\text{D}$ +167° (1% in $CHCl_3$); $\lambda_{\text{max.}}$ 242 mμ, ϵ 16,600; (*Anal.* Calcd. for $C_{22}H_{32}O_2$: C, 80.4; H, 9.8. Found: C, 80.5; H, 9.6.) Since attempts to isomerize D-homoprogesterone, by heating in acidic and in basic solution, failed, the configuration of the side chain at 17a is probably β.

Perfusion of D-homoprogesterone through surviving adrenal glands yielded neither D-homocorticosterone nor 17aα-hydroxy-D-homocorticosterone.

D-Homo-11-deoxycorticosterone acetate was prepared from V by use of the method devised by H. Ruschig.[3] Compound V was condensed with dimethyl oxalate using sodium methoxide in benzene. The sodium enolate so obtained was iodinated in methanol at −15°, then cleaved to 3β-hydroxy-21-iodo-D-homopregn-5-en-20-one (VI) with sodium methoxide at room temperature. The crude iodo compound (VI) was converted, by means of potassium acetate in acetone, to 3β,21-dihydroxy-D-homopregn-5-en-20-one 21-acetate (VII), m.p. 188–190°; (*Anal.* Calcd. for $C_{24}H_{36}O_4$: C, 74.2; H, 9.3. Found: C, 74.3; H, 9.6.) Oppenauer oxidation of VII yielded D-homo-11-deoxycorticosterone acetate (VIII), m.p. 152–154°; $[\alpha]^{23}\text{D}$ +150° (0.45% in $CHCl_3$); $\lambda_{\text{max.}}$ 241 mμ, ϵ 16,200; (*Anal.* Calcd. for $C_{24}H_{34}O_4$: C, 74.6; H, 8.9. Found: C, 74.9; H, 8.9). Compound VIII showed no appreciable ability to prevent sodium excretion in adrenalectomized rats,[4] but it did possess approximately 10% of the activity of 11-deoxycorticosterone acetate in the maintenance of life in adrenalectomized rats on a sodium deficient diet.[5]

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(1) H. Heusser, P. Th. Herzig, A. Fürst and Pl. A. Plattner, *Helv. Chim. Acta*, **33**, 1093 (1950).

(2) J. D. Chanley, THIS JOURNAL, **70**, 244 (1948).

(3) H. Ruschig, U. S. pat. 2,609,379, Sept. 2, 1952.

(4) C. M. Kagawa, E. G. Shipley and R. K. Meyer, *Proc. Soc. Exptl. Biol. and Med.*, **80**, 281 (1952).

(5) A. Grollman, *Endocrinology*, **29**, 855 (1941). We are indebted to F. J. Saunders, C. G. Van Arman and C. M. Kagawa of our Laboratories for the determination of biological activities.

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RECEIVED SEPTEMBER 24, 1953

MAGNETIC CATALYSIS OF A DECARBOXYLATION REACTION[1]

Sir:

There is now a considerable body of experimental evidence[2] that the rate of decarboxylation of C^{13} substituted carboxylic acids is appreciably higher that would be expected from the rate of decarboxylation of the C^{12}- and C^{14}-compounds on the basis of change of isotopic mass alone.

A possible cause of this apparent anomaly could lie in the nonzero nuclear spin and magnetic moment of C^{13}. Both C^{12} and C^{14} have zero values for these properties. A paramagnetic rare earth ion such as dysprosium at a distance of a few angströms from the C–C bond could cause an inhomogeneous magnetic field comparable to that caused by a C^{13} nucleus at one end of the bond.

We have now found such an acceleration of the rate of decarboxylation of (natural) phenylmalonic acid in aqueous solution at 45° in the presence of 0.5 *N* dysprosium ion.

The kinetics of the decarboxylation of phenylmalonic acid have been explored.[3] The conditions selected for the present experiments, *p*H 0.4–0.8, yield a first order reaction of un-ionized phenylmalonic acid to phenylacetic acid with a rate almost independent of *p*H. Experiments were carried out with phenylmalonic acid alone and in the presence of 0.5 *N* La^{3+}, Y^{3+} and Dy^{3+} as rare earth chlorides. The initial *p*H of the reaction mixtures was equalized by addition of standard hydrochloric acid. A dozen aliquots were withdrawn at intervals during the first 50% of reaction,

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(1) This work was assisted by the American Petroleum Institute through Research Project 50. The dysprosium was kindly made available to us by Dr. F. H. Spedding.

(2) P. E. Yankwich and E. C. Stivers, *J. Chem. Phys.*, **21**, 61 (1953).

(3) E. Gelles, accepted for publication, THIS JOURNAL.

the rare earth ions were precipitated as oxalates and the amount of reaction was then determined by titration with standard alkali.

0.5 N La^{3+} depresses the rate of decarboxylation by 10%. In the presence of the smaller Y^{3+} ion the rate of decarboxylation is equal within the experimental error of 4–5% to the rate of reaction in the absence of rare earth. On the basis of the salt effect of these diamagnetic ions the dysprosium ion, which is slightly larger than the yttrium ion, would be expected to give rise to a slightly slower rate of decarboxylation than that in the absence of rare earth or in the presence of Y^{3+}. In three sets of experiments the rate of reaction in the presence of 0.5 N Dy^{3+} was found to be 8, 10 and 13% faster than in the presence of 0.5 N Y^{3+}. The observed acceleration is tentatively attributed to the paramagnetic character of the dysprosium ion.

Investigations of the effect of paramagnetic ions on the decarboxylation of natural and isotopically substituted compounds are being continued.

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RECEIVED SEPTEMBER 28, 1953

SILICON TETRAFLUORIDE COMPLEX WITH ETHYLENEDIAMINE

Sir:

A recent report by C. J. Wilkins and D. K. Grant[1] of the preparation of two addition compounds of silicon tetrafluoride with one and with two molecules, respectively, of trimethylamine, has led us to add this note to the general subject of the coördinating power of the silicon halides. The fact that silicon assumes a coördination number of six in the fluosilicates, but is apparently unable to rise above four-coördination when chlorine atoms are employed as ligands, lends interest to the fact that in silicon tetrafluoride there is left sufficient room, as well as attractive force, about the silicon atom to accommodate one or even two molecules of trimethyl amine, with nitrogen the donor atom, as observed by Wilkins and Grant.

In following this general line of reasoning, we recently had prepared an addition compound of silicon tetrafluoride with ethylenediamine, the composition of which was determined by analysis and by molecular weight determinations as $SiF_4 \cdot CH_2NH_2NH_2CH_2$. No evidence of any other compound of the two reactants was obtained.

The ethylenediamine employed was twice redistilled from metallic sodium, and boiled within a range of 0.2°. The silicon tetrafluoride was prepared by thermal decomposition of precipitated barium fluosilicate, previously dried by heating at 200° for 3 hours in a vacuum of about 0.5 mm. The gas was preserved under pressure in a steel cylinder, and its properties agreed closely with the data given for pure silicon tetrafluoride by Jones, Kirby-Smith, Woltz and Nielson.[2]

The reaction of the vapors of anhydrous ethylenediamine, introduced into an evacuated flask to the limit of its vapor pressure at room temperature with gaseous silicon tetrafluoride, subsequently added, resulted in the formation of the white, solid complex and in a reduction of the pressure in the flask. More ethylenediamine was then admitted, followed by more silicon tetrafluoride. The quantity of liquid diamine added was measured by means of a buret; the tetrafluoride was measured in a gas buret over mercury. In one run, repetition of the procedure yielded 8 g. of a light, fine, white powder which was dried at 130°C. and 0.5 mm. for 3 hr. to free it of any excess diamine. At 0.2 mm. pressure the substance is sublimable about 225°. In other runs, smaller quantities were prepared. *Anal.* Fluoride, calcd., for $SiF_4 \cdot CH_2NH_2NH_2CH_2$ 46.35; found, 46.65%. Nitrogen, calcd., 17.08, found, 15.96%.

It is clear that in this compound a chelate structure is present, with ethylenediamine occupying two of the six coördination positions about the silicon atom. It is of interest that further addition of the diamine, even if coördinated in unidentate fashion, is apparently excluded by spatial considerations.

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RECEIVED SEPTEMBER 3, 1953

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[1] C. J. Wilkins and D. K. Grant, *J. Chem. Soc.*, 927 (1953).

[2] E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz and A. H. Nielson, *J. Chem. Phys.*, **19**, 242 (1951).

RATE OF THE ELECTRON-TRANSFER EXCHANGE REACTION BETWEEN MANGANATE AND PERMANGANATE IONS[1]

Sir:

We have successfully measured the rate of the isotopic exchange reaction between $MnO_4^=$ and MnO_4^-. Other investigators,[2,3,4] employing higher reactant and/or sodium hydroxide concentrations than we have used, had found complete exchange in contact times considerably longer than ours.

Using the separation procedure developed by Bonner and Potratz[4] of extracting MnO_4^- into a chloroform solution of triphenylsulfonium bromide, we have followed the exchange starting either with tagged $MnO_4^=$ or with tagged MnO_4^-. Separation methods involving the coprecipitation of MnO_4^- with tetraphenylarsonium perchlorate or perrhenate have also been used successfully. Reactions were started and stopped by the rapid ejection of solutions from automatic pipets into solutions being mechanically stirred.

Figure 1 shows three of our best exchange curves. In each of these runs the concentrations of $MnO_4^=$ and MnO_4^- were approximately equal; precise values for the concentrations of the individual reactants are not known however, because appreciable reduction of MnO_4^- to $MnO_4^=$ occurred. The dependence of the half-time of the exchange in 0.15 f NaOH at 1° on the total reactant concen-

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[1] This work was supported by the National Science Foundation under grant G-196.

[2] W. F. Libby, THIS JOURNAL, **62**, 1930 (1940).

[3] H. C. Hornig, G. L. Zimmerman and W. F. Libby, *ibid.*, **72**, 3808 (1950).

[4] N. A. Bonner and H. A. Potratz, *ibid.*, **73**, 1845 (1951).