cis-3-hexene, there was obtained a 35.5% yield of pure *cis*-1,2-diethylcyclopropane (b.p. 93.5°, $n^{25}D$ 1.4035; *anal.* Calcd. for C_7H_{14}: C, 85.63; H, 14.37. Found: C, 85.89; H, 14.32). An analogous experiment with pure *trans*-3-hexene gave a 15.5% yield of pure *trans*-1,2-diethylcyclopropane (b.p. 86.5°, $n^{25}D$ 1.3982; *anal.* Found: C, 85.54; H, 14.49). In both reactions, vapor-phase chromatographic and infrared spectral analysis of the reaction mixtures showed only the presence of the starting olefin and the corresponding cyclopropane. Similar data from known mixtures of the olefins and cyclopropanes indicated that the analytical methods were capable of defining purity to at least 0.5%.

These results clearly establish the stereospecificity and discrimination in the reaction of an olefin with methylene iodide and zinc–copper couple. After this work was completed, a report[7] appeared stating that "methylene iodide and finely divided zinc–copper couple react with *cis*- and *trans*-butene to give *cis*-1,2-dimethylcyclopropane, *cis*-pentene and 2-methyl-2-butene, and *trans*-1,2-dimethylcyclopropane, *trans*-pentene and 2-methyl-2-butene, respectively. These reactions are comparable to that of diazomethane with *cis*- and *trans*-butene.[4]" Since experimental details were lacking in this brief account, we are unable to offer any explanation for these results, which apparently conflict with our own.

Studies of the methylene iodide/zinc–copper couple system, including the preparation of isotopically labeled cyclopropanes (from CD_2I_2 and $C^{14}H_2I_2$), are continuing.

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[7] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958). Reference 4 in the quotation refers to W. von E. Doering and P. M. LaFlamme, THIS JOURNAL, **78**, 5447 (1956).

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CALCIUM DIMETHYL, STRONTIUM DIMETHYL, AND BARIUM DIMETHYL

Sir:

We report the preparation and some properties of three new compounds, calcium dimethyl, $Ca(CH_3)_2$, strontium dimethyl, $Sr(CH_3)_2$, and barium dimethyl, $Ba(CH_3)_2$. Evidence of organo-compounds of these metals in solution had been known at least since 1905[1–4] but no such compound had been isolated and characterized, except for some complexes with organo-zinc compounds,[5–9] until the present work.

Calcium, strontium and barium, when rasped from bulk metal to a granular form, in an atmosphere of helium, react readily with methyl iodide in anhydrous pyridine. The solutions quickly become highly colored, and insoluble solids precipitate. These apparently are pyridine complexes containing both methyl and iodine attached to metal, of composition dependent on the conditions. Refluxing, followed by prolonged extraction of these solids with fresh pyridine, reduces the iodine content leaving ultimately the dimethyl metal compound as an insoluble residue. Pyridine separates readily from all three dimethyl compounds when the solids are evacuated at room temperature.

The dry solids were analyzed by hydrolysis of 10–100 mg. samples and then measurement of evolved methane and standard gravimetric determinations of both metal and iodine. Calcd. for $Ca(CH_3)_2$: Ca, 57.2; CH_3, 42.8. Found: Ca, 58.5, 57.8; CH_3, 42, 40; I, 1.9, 1.4, 1.7. Calcd. for $Sr(CH_3)_2$: Sr, 74.5; CH_3, 25.5. Found: Sr, 72.7, 74.2, 73.3; CH_3, 23, 22; I, 3.5, 3.2. Calcd. for $Ba(CH_3)_2$: Ba, 82.0; CH_3, 18.0. Found: Ba, 81.6, 78.8, 79.1; CH_3, 17, 18; I, 2.6, 2.5. Assuming the residual iodine, which seems impossible to remove even by very prolonged extraction, to be present as the metal iodide, the dimethyl compounds appear to be of better than 95% purity.

These compounds are all pale in color and might well be white but for the residual iodide. They undergo no visible change in vacuum below 400°, above which darkening occurs. All three hydrolyze very rapidly, and promptly become incandescent when exposed to oxygen or carbon dioxide.

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[1] E. Beckmann, *Ber.*, **38**, 904 (1905).

[2] H. Gilman and W. Schulze, THIS JOURNAL, **48**, 2463 (1926).

[3] Z. C. Glacet, *Bull. soc. chim. France*, **5**, 895 (1938).

[4] E. Kraus and A. v. Grosse, "Die chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1936, p. 123.

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[6] H. Gilman, R. Meals, G. O'Donnell, and L. Woods, THIS JOURNAL, **65**, 268 (1943).

[7] H. Gilman and L. Woods, *ibid.*, **67**, 520 (1945).

[8] H. Gilman, A. Haubein and L. Woods, *ibid.*, **67**, 922 (1945).

[9] H. Gilman and J. C. Bailie, *ibid.*, **65**, 267 (1943).

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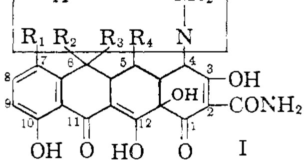
HYDROGENOLYSIS STUDIES IN THE TETRACYCLINE SERIES—6-DEOXYTETRACYCLINES

Sir:

Hydrogenolysis of tetracycline[1] under acidic conditions with palladium results in a mixture of products from which we have separated a new antimicrobial substance, *6-deoxytetracycline*, (Ia, m.p. of the hydrochloride, 245–246°, dec. *Anal.* Calcd. for $C_{22}H_{25}N_2O_7Cl$: C, 56.95; H, 5.38; N, 6.05. Found: C, 56.64; H, 5.50; N, 6.02). An analogous *6-deoxy compound* (Ib, m.p. of hydrochloride 250–251°, dec., *pK*′'s 3.4, 7.7, ~9.7 (H_2O).



I

Ia, $R_1 = R_3 = R_4 = H, R_2 = CH_3$
Ib, $R_1 = R_3 = H, R_2 = CH_3, R_4 = OH$

Anal. Calcd. for $C_{22}H_{25}N_2O_8Cl$: C, 54.93; H, 5.24; N, 5.82. Found: C, 54.86; H, 5.35; N, 5.75).

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[1] Tetracyn is the registered trade-mark of Chas. Pfizer & Co., Inc., for the antibiotic tetracycline.