

testine pool.² Specific activity findings suggested a precursor relationship between methostenol and cholesterol. Methostenol-4-C¹⁴ was prepared in order to subject this hypothesis to experimental test. Cholesterol-4-C¹⁴ (0.05 mC.) diluted with 2.0 g. of cholesterol served as starting material. Methostenol-4-C¹⁴ was prepared by first synthesizing 7-dehydrocholesterol-4-C¹⁴ according to the method of Hunziker and Müllner.⁴ Hydrogenation of 7-dehydrocholesterol-4-C¹⁴ in dioxane over Raney nickel⁵ afforded Δ^7 -cholestenol-4-C¹⁴. Methostenol-4-C¹⁴ then was prepared from Δ^7 -cholestenol-4-C¹⁴ by methods previously described.^{6,7} After repeated chromatography on silicic acid: Celite (2:1) columns, methostenol-4-C¹⁴, m.p. 143–5°, exhibited a specific activity of 9,650 c.p.m./mg. A solution of radioactive methostenol in Tween-80⁸ was fed by stomach tube to two male albino rats (A and B) of the Holtzman strain, weighing 155 and 110 gm., respectively. The former received 89,700 c.p.m. and was sacrificed 6 hours after administration of the meal and the latter received 134,000 c.p.m. and was sacrificed 24 hours after intubation. A control was prepared which consisted of the liver and small intestine of a similar rat to which was added 4,000 c.p.m. of methostenol-4-C¹⁴ and sufficient alcoholic KOH to saponify the mixture. At each time of sacrifice, liver-intestine pool, carcass, and feces were separately saponified with alcoholic KOH. The non-saponifiable fraction of each preparation was isolated with ether, taken to dryness and liver-intestine and carcass mixtures were chromatographed on silicic acid: Celite (2:1) columns (1.8 × 20 cm.) using an elution gradient of benzene:Skelly C (2:1) against a reservoir of Skelly C. Fractions were plated and radioactivity measured with a thin end window gas flow counter. Results of the recovery of radioactivity in the methostenol or cholesterol fractions are shown in Table I. Specific activity values for cholesterol were determined after several crystallizations from methanol and a purification through the dibromide.⁹ Melting points were 146–148°.

TABLE I

THE RADIOACTIVITY OF CERTAIN STEROLS ISOLATED AFTER THE INGESTION OF A METHOSTENOL-4-C¹⁴ MEAL BY THE RAT^a

Rat no.	Tissue	Recovery of C ¹⁴ in non-sap. fraction			Cholesterol specific activity c.p.m./mg.
		Total c.p.m.	Methostenol c.p.m.	Cholesterol c.p.m.	
Control	Liver-Int.	3,750	3630	120	0
A (6 hr.)	Liver-Int.	14,500	4900	6170	199
	Carcass	5,400	1760	3040	39.9
B (24 hr.)	Liver-Int.	4,024	1270	2530	116
	Carcass	3,840	630	2950	21.7

^a Control received 4,000 c.p.m.; rat A, 89,700 c.p.m.; rat B, 134,000 c.p.m.

(2) C. L. Lora and W. W. Wells, *Fed. Proc.*, **18**, 276 (1959).

(3) Nuclear-Chicago Corp.

(4) F. Hunziker and F. X. Müllner, *Helv. Chim. Acta*, **41**, 70 (1958).

(5) L. F. Fieser and J. E. Herz, *THIS JOURNAL*, **75**, 121 (1953).

(6) W. W. Wells and D. H. Neiderhiser, *ibid.*, **79**, 6569 (1957).

(7) D. H. Neiderhiser and W. W. Wells, *Arch. Biochem. & Biophys.*, **81**, 300 (1959).

(8) Polyoxyethylene sorbitan monooleate, Atlas Powder Co.

(9) E. Schwenk and N. T. Werthessen, *Arch. Biochem. Biophys.*, **40**, 334 (1952).

A large fraction of the recovered C¹⁴ was located in the saponifiable fraction of the feces (rat A, 28.6%; rat B, 85.7%) presumably as bile acids and their derivatives. The rapid conversion of methostenol to cholesterol places methostenol in the role of an active intermediate of cholesterol biosynthesis. The recent isolation and characterization of 4 α -methyl- Δ^8 -cholesten-3 β -ol from mice preputial gland tumors¹⁰ suggests the interesting possibility that this sterol could give rise to methostenol by the migration of the double bond at C-8 (9) to C-7, *in vivo*.

(10) A. A. Kandutsch and A. E. Russell, *THIS JOURNAL*, **81**, 4114 (1959).

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π -COMPLEXES OF THE TRANSITION METALS. XII. SYNTHESIS WITH ALKYL CHROMIUM AND NICKEL COMPOUNDS

Sir:

One-step syntheses of polynuclear benzenoid hydrocarbons, *i.e.*, naphthalenes, phenanthrenes and anthracenes, by cyclic condensation of disubstituted acetylenes on triarylchromium(III) compounds have been reported.¹ In these reactions it is clear that the aryl groups bonded to chromium have participated in the cyclizations and substituted hydrogen has been concurrently abstracted from them. Although diarylnickel(II) derivatives are quite capable of cyclizing acetylenes to the benzene ring system, they do not form polynuclear aromatic structures.² We conclude, therefore, that organochromium(III) is a powerful *hydrogen acceptor*. This conclusion, in experimental trial, has led to unique syntheses which we now report.

Triethylchromium(III) is prepared by the same general method employed in the synthesis of the corresponding phenyl derivative.³ In tetrahydrofuran this alkylchromium compound also cyclizes toluene to hexaphenylbenzene; but also, *it contributes an ethyl group* in a mixed condensation with toluene, yielding 1,2,3,4-tetraphenylbenzene, I, m.p. 187–189°. Thus, organochromium(III), in addition to providing a two-carbon atom fragment for condensation with two molecules of toluene, has further demonstrated its hydrogen acceptor capacity by dehydrogenation of the dihydrobenzene ring.

Diethylnickel in tetrahydrofuran also condenses toluene to hexaphenylbenzene and provides an ethyl group for a mixed condensation. However, the relatively weak hydrogen accepting characteristic of organonickel(II) is manifested by reaction termination at the *dihydro stage*, and 1,2,3,4-tetraphenyl-1,3-cyclohexadiene, II, m.p. 170–171° [*Anal.* Calcd. for C₃₀H₂₄: C, 93.71; H, 6.29.

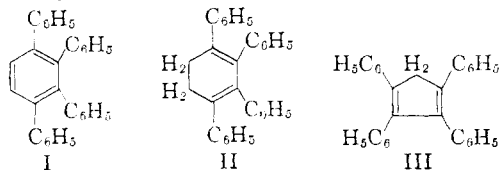
(1) H. Zeiss and W. Herwig, *THIS JOURNAL*, **80**, 2913 (1958); W. Herwig, W. Metlesics and H. Zeiss, *ibid.*, **81**, Dec. 5 (1959).

(2) M. Tsutsui and H. Zeiss, Abstracts, 134th Meeting, Amer. Chem. Soc., Chicago, Sept., 1958, p. 59-P.

(3) W. Herwig and H. Zeiss, *THIS JOURNAL*, **81**, 4798 (1959).

(4) Identification was made by physical and spectroscopic comparisons with authentic substance.

Found: C, 93.87; H, 6.07] is the product. This formulation is supported chemically by bromination of II with N-bromosuccinimide or bromine and dehydrobromination, and by dehydrogenation of II with palladium-charcoal, to 1,2,3,4-tetraphenylbenzene. The ultraviolet spectrum of II, having absorption maxima at 236 m μ , 268 m μ , and 326 m μ ($\epsilon = 15,600, 10,600$ and $12,100$) is also consistent with the cyclohexadiene structure. It is anticipated that the foregoing reaction will prove to be a general as well as a convenient method for preparing cyclohexadiene ring systems.



Mixed condensation between alkyl groups and acetylenes is shown, perhaps even more strikingly, by the reaction of trimethylchromium with toluene. In this example the organochromium(III) reagent contributes a methyl group, forming 1,2,3,4-tetraphenylcyclopentadiene, III, m.p. 176–178°,⁴ in addition to the normal product, hexaphenylbenzene. The oxidative potentialities of organochromium(III) are being examined in other areas of organic synthesis.

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ACTIVE PHOSPHORUS

Sir:

An early attempt to produce phosphorus atoms by a condensed discharge proved unsuccessful,¹ in view of the work of Winkler and co-workers²

(1) N. M. Gopshtein and S. Z. Roginskii, *J. Phys. Chem. (USSR)*, **7**, 587 (1936).

(2) D. A. Armstrong and C. A. Winkler, *J. Phys. Chem.*, **60**, 1100 (1956).

on the reactivity of active nitrogen it was felt that a comparative study with phosphorus might prove informative.

An apparatus similar to that used for nitrogen² was tried for phosphorus. Argon, as a carrier gas, was passed through a bulb containing phosphorus at a temperature from 25 to 100°. The flow rate of argon was about 50 micromole/sec. at a pressure of approximately 1 mm. in the reaction bulb. When only argon was allowed to flow through the discharge, no decomposition of reactants was observed. Similarly no reaction was observed when P₄ was allowed to mix with reactant with no discharge. A definite reaction was obtained between phosphorus, swept through the discharge with argon, and ethylene, propylene, butene-1, propane, methane, ammonia, and hydrazine. Phosphine was the major gaseous constituent produced in all cases. The reactions also were observed when a microwave discharge was used to generate the "active phosphorus."

Gas chromatographic analysis on the products of methane-active phosphorus reactions indicated at least six volatile products. Phosphine, methylphosphine and ethane were obtained in very small quantities. The ethane was approximately 2% of the phosphine fraction. A considerable amount of solid was deposited in the reaction zone during an experiment. This, along with red phosphorus, appears to be the solid phosphorus hydrides.

It also was found that with a new discharge tube and a clean-walled apparatus, a liquid was produced in relatively large quantities. It was shown not to be P₂H₄ from physical properties and elementary reactions.

Further work along with the identification of the "liquid" product is now being pursued.

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BOOK REVIEWS

Brandlehre und Chemischer Brandschutz. Eine Einführung in die Grundlagen. Zweite Ergänzte und Erweiterte Auflage. By LUDWIG SCHEICHL, Oberregierungsrat. Dr. Alfred Hüthig Verlag, Wilckenstrasse 3, Heidelberg, Germany. 1958. xiv + 424 pp. 16 × 23 cm. Price, DM 28.—.

This volume is not a scientific and technological treatment of ignition, combustion and explosions, as one would expect it to be if it were a technical book on "Brandlehre," but rather has as its main objective classifications and descriptions of materials in the technology of "Brand-schutz," i.e., of fire-proofing, fire-prevention, control and extinction. It would, therefore, have been more descriptive of the contributions of this book if the word "Brandlehre" had been omitted from the title. While technological aspects and classifications in "Chemischer Brandschutz" are well presented in the last two parts (Teil B and C) of the book, the first 207 pages, exclusive of 40 pages of classi-

fications and definitions pertaining to "Brandlehre" (pages 19–40 and 181–207) comprise good elementary, but unnecessary, reviews of well-known principles of physical chemistry. Pages 19 to 40 present interesting, but not actually fundamental, classifications of materials of combustion and definitions pertaining to ignition, flames, combustion and explosion. Pages 181 to 207 outline and classify burning processes and mechanisms, but the classifications are incomplete as are the descriptions of burning processes. It is true, however, that attention is called occasionally elsewhere in "Teil A" to applications of particular physico-chemical principles in combustion technology.

The actual fundamental principles comprising the science and technology of ignition, combustion and even fire-proofing and the control and extinguishing of combustion are merely mentioned briefly in spite of a great deal of the book being devoted to principles one might readily apply in this technology. It is interesting in view of the many