We are indebted to the Eli Lilly Company for a grant enabling one of us (M. S. N.) to take part in this work and for supplies of materials.

Summary

Molecular compounds containing from two to four molecules of desoxycholic acid have been prepared from certain polynuclear aromatic hydrocarbons, including the carcinogenically active methylcholanthrene and 1,2,5,6-dibenzanthracene. Since the sodium salts of these choleic acids are soluble in water, this provides a means of obtaining aqueous solutions containing carcinogenic hydrocarbons.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED JUNE 27, 1935

The Reactions of Titanium and Manganese with Hydrogen Peroxide in Basic Solution[1]

BY LYMAN E. PORTER AND GEORGE N. CADE, JR.

In the usual scheme of qualitative analysis for the common and the rarer metals, titanium appears in the iron division of the ammonium sulfide group.[2] The manganese is removed as the dioxide by boiling with nitric acid and potassium chlorate. Unless the ratio of titanium to manganese is very small, most of the former is left in solution with the iron, etc. The iron may then be precipitated by the use of sodium phosphate, hydrogen peroxide and sodium hydroxide, leaving the titanium in a soluble peroxidized form.[3] A similar action takes place when the phosphate is omitted. If, however, the manganese has not been previously removed, some or all of the titanium is precipitated during the process. This paper describes a study of this reaction.

Solutions of known and varying concentrations of manganese and titanium nitrates were made up. These were treated with excess hydrogen peroxide and with one normal sodium hydroxide until neutral and with 5 ml. in excess. A mahogany brown color appeared which was followed by the formation of a fine grayish-brown precipitate which was shown to contain all of the manganese. In the quantitative tests the titanium was determined in the solution after filtration, and its amount in the residue calculated by difference. Qualitative tests showed that both manganese and titanium appeared in the precipitate but that titanium was present in the filtrate only when the molar ratio of titanium to manganese exceeded approximately two. Excess peroxide was found present in all cases. Whenever the residue was dissolved in acid, the yellow or orange color of peroxidized titanium appeared, which is not the case when a mixture of $Ti(OH)_4$ and freshly precipitated manganese dioxide is similarly treated. This would indicate the presence of peroxidized titanium in the residue.

A series of quantitative tests was made in which the molar ratio of titanium to manganese in the original solutions varied between 2.2 and 8.4. The corresponding ratios in the resulting precipitates were found to vary between 1.8 and 4.8, indicating that no definite compound is formed, but that a greater amount of titanium is precipitated the larger its initial proportion. When the titanium and manganese solutions were not mixed until each had been treated separately with peroxide and sodium hydroxide, a similar result was obtained, the ratio of titanium to manganese in the residue being about half that obtained for corresponding concentrations in the previous series.

When the two metals were precipitated together by peroxide and sodium hydroxide, the ratio of titanium to manganese increased with lapse of time. In a series in which the original molecular ratio of titanium to manganese was 3.6, that in the residue increased steadily from 1.6 to 2.7 during the first twelve hours at 25°. At higher temperatures more titanium was precipitated. In both of these cases, it is probable that some $Ti(OH)_4$ was precipitated due to a partial decomposition of the peroxide, although an excess of the latter was always found in the filtrate. Furthermore, when the other factors were kept constant, the ratio of titanium to manganese in the residue decreased in general with increased concentration of hydrogen peroxide.

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(1) From a master's thesis submitted by G. N. Cade, Jr., in partial fulfilment of the requirements for a Master's degree at the University of Arkansas, 1935. Research Paper No. 390, Journal Series, University of Arkansas.

(2) A. A. Noyes, W. C. Bray and E. B. Spear, THIS JOURNAL, **30**, 481 (1908).

(3) P. E. Browning, G. S. Simpson and L. E. Porter, *Am. J. Sci.*, **42**, 106 (1916).

Summary

1. The impossibility of the separation of titanium from manganese by the use of hydrogen peroxide and sodium hydroxide is due to the adsorption and inclusion of the peroxidized titanium by the precipitated hydrous manganese dioxide. No definite compound is produced.

2. In the precipitation, more titanium appears in the residue as time passes, and at higher temperatures, due in part to partial decomposition of the peroxide and the precipitation of some tetravalent titanium.

3. Increasing the concentration of hydrogen peroxide reduces the amount of titanium in the precipitate.

FAYETTEVILLE, ARKANSAS RECEIVED MAY 17, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Preparation of Certain Alkenes, Alkadienes and Alkynes[1,2]

BY SAMUEL P. MULLIKEN, REGINALD L. WAKEMAN AND HAROLD T. GERRY[3]

The reaction $RMgX + CH_2{=}CHCH_2Br \longrightarrow RCH_2CH{=}CH_2$ is well known. Its discovery by Tiffeneau,[4] who applied it to certain aromatic compounds, dates almost from the birth of the Grignard reaction. Barbier and Grignard,[5] and later de Rességuier[6] adapted it to the synthesis of 6-methyl-1-heptene from isoamyl bromide. Von Braun, Deutsch and Schmatloch[7] recommended its use generally, preparing a number of open and closed chain unsaturated hydrocarbons and ethers. Brooks and Humphrey,[8] particularly, advocated it as a means of synthesizing pure alkenes. Kirrmann,[9] Wilkinson,[10] and others have developed it further. We have prepared a variety of alkenes in this manner.

This reaction has previously been applied to certain homologs of allyl bromide. Thus Prévost[11] has studied the products obtained from $RCH{=}CHCH_2Br$, containing $RCHBrCH{=}CH_2$ by rearrangement. Van Risseghem[12] has prepared 2-hexene, together with the other reaction products to be foreseen, by the action of crotyl bromide upon ethylmagnesium bromide. We have applied this synthesis to 4-bromo-2-pentene, thus preparing $CH_3CH{=}CHCHRCH_3$. It is not possible for $CH_3CHBrCH{=}CHCH_3$ to give rise to a mixture of isomeric bromides by synionic rearrangement,[13] since both end atoms of its "allylic system" are joined to identical hydrocarbon radicals, namely, methyl. The alkenes prepared from it should, therefore, possess the formula just given, free from isomers.

Lespieau[14] has prepared diallyl by the action of metallic magnesium upon allyl bromide. Other 1,5-alkadienes have been prepared similarly,[15] or obtained as by-products in the syntheses cited above.[11,12] We have prepared two 1,5-alkadienes from 4-bromo-2-pentene.

Experimental[16]

Preparation of $RCH(OH)CH{=}CHCH_3$.—These alcohols were prepared from crotonaldehyde

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[1] Abstract of a portion of a dissertation submitted by R. L. Wakeman to the Faculty of the Massachusetts Institute of Technology in partial fulfilment of the requirements for the degree of Doctor of Philosophy. June, 1930.

[2] This paper reviews the synthesis of certain unsaturates, including a number previously not described, used in developing a new procedure for the systematic identification of the hydrocarbons, intended to replace Genus IX, Vol. I of Mulliken, "A Method for the Identification of Pure Organic Compounds," John Wiley and Sons, 1908; see Mulliken and Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 275 (1935).

[3] We wish to acknowledge a generous grant to S. P. Mulliken from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences, largely by means of which the coöperation of H. T. Gerry was made possible.

[4] Tiffeneau, *Bull. soc. chim.*, **29**, 1157 (1903); *Compt. rend.*, **139**, 481 (1904).

[5] Barbier and Grignard, *Bull. soc. chim.*, **31**, 841 (1904).

[6] De Rességuier, *ibid.*, **15**, 182 (1914). *Cf.* André, *Ann. chim. phys.*, [8] **29**, 554 (1913).

[7] Von Braun, Deutsch and Schmatloch, *Ber.*, **45**, 1246 (1912). For allylcyclohexane, prepared by these authors, see also Zélinsky and Wychinska, *J. Russ. Phys.-Chem. Soc.*, **37**, 630 (1905); *Bull. soc. chim.*, **2**, 1122 (1907), and de Rességuier, *ibid.*, **7**, 431 (1910).

[8] Brooks and Humphrey, THIS JOURNAL, **40**, 822 (1918).

[9] Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926).

[10] Wilkinson, *J. Chem. Soc.*, 3057 (1931).

[11] Prévost, *Compt. rend.*, **187**, 946 (1928); *Bull. soc. chim.*, **49**, 1372 (1931); Prévost and Daujat, *ibid.*, **47**, 588 (1930).

[12] Van Risseghem, *Bull. soc. chim. Belg.*, **39**, 349 (1930).

[13] See, for example, Prévost and Kirrmann, *Bull. soc. chim.*, **49**, 226 (1931), and Hills, Kenyon and Phillips, *Chem. and Ind.*, **52**, 660T (1933).

[14] Lespieau, *Ann. chim. phys.*, [8] **27**, 149 (1912). See also Cortese, THIS JOURNAL, **51**, 2266 (1929).

[15] Prévost and Richard, *Bull. soc. chim.*, **49**, 1368 (1931).

[16] Thermometers were standardized and corrected for stem exposure (Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 222). Boiling points are corrected to 760 mm. by application of a factor of 0.1° per 2.7 mm., for pressures varying slightly therefrom. Fractionations were made through lagged Vigreux columns 50–60 cm. long, provided with prongs for a distance of 20–30 cm. (8–10 mm. between prongs). Most of the columns used were