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

and Grignard reagents following Reif's directions.[17]

TABLE I

$RCH(OH)CH{=}CHCH_3$[17,18]

Alcohol prepared	Bromide used	Halide, g.	Yield, %	B. p. of alcohol °C.,	at mm.
3-Penten-2-ol	Methyl	4000	30	121.6–123.6	760
2-Hepten-4-ol	*n*-Propyl	1400	46	92.8– 95.8	75
2-Octen-4-ol	*n*-Butyl	1200	51	93.9– 95.9	40
2,2-Dimethyl-4-hexen-3-ol	*t*-Butyl chloride	1000	3.4	73.4– 76.4	35

Preparation of $H_3CCHBrCH{=}CHCH_3$.[19]—The hydroxyl group of $RCH(OH)CH{=}CHCH_3$ is exceptionally labile. By shaking with constant-boiling hydrobromic acid at room temperature, bromides are formed which hydrolyze readily upon contact with water or even moist air. They must be washed very quickly or not at all.

Eight hundred g. of 3-penten-2-ol was shaken for twenty minutes with 1650 g. of hydrobromic acid (d. 1.48), then twice with 400 g. of acid for eight minutes each time. The product was separated, washed quickly with water and bicarbonate solution, dried over calcium chloride and distilled; 744 g. (54% yield) of 4-bromo-2-pentene was obtained; b. p. 70.2–72.2° (145 mm.) (b. p. 116.7–119.2° (760 mm.) with slight decomposition).[20]

Preparation of Alkenes.—Alkenes of structure RCH_2-$CH{=}CH_2$ were prepared in the customary manner from alkylmagnesium halides and allyl bromide in ethyl ether. To prepare $H_3CCHRCH{=}CHCH_3$, allyl bromide was replaced by 4-bromo-2-pentene. Before addition of the unsaturated bromide, the Grignard reagent was rapidly poured through a filter plate to remove small amounts of unreacted magnesium. After completion of the reaction, the ether was extracted from the product by repeated treatment with ice-cold, concentrated hydrochloric acid until the volume remained constant. The entire mixture was kept ice-cold during the extractions, which were carried out in the course of a few minutes. Excess halides were removed by allowing the crude hydrocarbon to stand with sodium methylate or ethylate in the respective alcohol (whichever would give those ethers most readily fractionated from the alkene expected). The alcoholic solution was then diluted with water, the product separated, washed again with ice-cold, concentrated hydrochloric acid as before, then with water and sodium carbonate solution, dried with calcium chloride and fractionated.

TABLE II

ALKENES[21]

Alkene prepared	Bromides use	Yield, %	B. p., °C.	d^{25}_4	n^{25}_D	*MR* Found	*MR* Calcd.
4-Methyl-2-pentene[22]	CH_3Br + 4-bromo-2-pentene	57	58.6–59.0	0.6685	1.3869 (25.3°)	29.62	29.44
5-Methyl-1-hexene[23]	*i*-C_4H_9Br + allyl bromide	21	85.5–86.0	.6895	1.3940 (24.9°)	34.05	34.06
4,4-Dimethyl-1-pentene[24]	*t*-C_4H_9Cl + allyl bromide	5	71.2–72.4	.6883	1.3909 (25.2°)	33.87	34.06
4-Methyl-2-heptene	*n*-C_3H_7Br + 4-bromo-2-pentene	27	113.8–114.1	.7188	1.4100	38.66	38.68
4-Methyl-2-octene[25]	*n*-C_4H_9Br + 4-bromo-2-pentene	28	137.3–137.9	.7286	1.4158 (24.8°)	43.45	43.30
4,5-Dimethyl-2-heptene[26]	*s*-C_4H_9Br + 4-bromo-2-pentene	8	135.0–136.1	.7431	1.4220 (24.8°)	43.15	43.30
4,6-Dimethyl-2-heptene[27]	*i*-C_4H_9Br + 4-bromo-2-pentene	36	129.5–130.1	.7239	1.4135	43.52	43.30
4,5,5-Trimethyl-2-hexene	*t*-C_4H_9Cl + 4-bromo-2-pentene	5	128.7–129.5	.7382	1.4198 (24.9°)	43.24	43.30
4-Cyclohexyl-2-pentene	Cyclohexyl bromide + 4-bromo-2-pentene	15	125.3–126.3 at 95 mm. (Siwoloboff: 195–196° at 760 mm., slight dec.)	.8322	1.4595	50.05	50.33

Preparation of 1,5-Alkadienes.—These compounds were prepared by reaction of 4-bromo-2-pentene with its own Grignard reagent (or magnesium alone) or with allylmagnesium bromide.[28] Thus, 85 g. of allyl bromide in 300 cc. of anhydrous ether was dropped, with stirring, onto six times the theoretical quantity of magnesium, moistened with 150 cc. of anhydrous ether, refluxed for half an hour, then run quickly through a filter plate and treated with 80 g. of 4-bromo-2-pentene. After working up the reaction mixture in the usual way, 28.8 g. of 4-methyl-1,5-hepta-

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also provided with a modified head, equipped with a condenser, similar to that of the Frey column shown by Fierz-David and Rufener, *Helv. Chim. Acta*, **17**, 1455 (1934). Distillation curves of all hydrocarbons were plotted and the principal cuts refractionated when the major portion of the product did not pass over within 0.5°.

Determinations of densities and refractive indices of hydrocarbons were carried out by John J. O'Brien using glass-stoppered pycnometers and a new, standardized Abbé refractometer. Densities are reduced to vacuum.

(17) Reif, *Ber.*, **39**, 1603 (1906); **41**, 2739 (1908).

(18) See Grignard, *Ann. chim. phys.*, **24**, 433 (1901). Von Auwers and Westermann, *Ber.*, **54**, 2993 (1921).

(19) Since the completion of this work, patents have been granted to the I. G. for a similar method of preparation of such halides, including 4-bromo-2-pentene; German Patent 508,891, 512,232, 513,364 and 553,279.

(20) Baudrenghien, *Bull. sci. acad. roy. Belg.*, **15**, 53 (1929); *Ber., soc. chim. Belg.*, **38**, 172 (1929), gives b. p. 117–120°.

(21) We obtained the following boiling points for a number of 1-alkenes previously described in the literature: 1-pentene, 30.0–30.1°; 1-hexene, 63.6–64.1°; 1-heptene, 94.0–94.4°; 1-nonene, 145.3–145.8°; 1-decene, 170.4–170.8°; allylcyclohexane, 154.0–154.4°: 4-methyl-1-pentene, 55.0–55.5°; 4-methyl-1-hexene, 86.8–87.3°.

(22) Gorski prepared this alkene by the action of alcoholic potassium hydroxide on 4-chloro-(or iodo)-2-methylpentane: b. p. 57–58.5°; d^{20}_4 0.6706; n^{20}_D 1.3883, and b. p. 57–59°; d^{20}_4 0.6703; n^{20}_D 1.3884. *J. Russ. Phys.-Chem. Soc.*, **42**, 1356 (1910); *Chem. Centr.*, **82**, I, 635 (1911). See van Risseghem, *Bull. soc. chim. Belg.*, **42**, 219 (1933); van Risseghem, Gredy and Piaux, *Compt. rend.*, **196**, 938 (1933), for dehydration of 4-methyl-2-pentanol. Schmitt and Boord prepared it by "nuclear synthesis," finding b. p. 57.7–58.5°: d^{20}_4 0.6709; n^{20}_D 1.3885, and b. p. 54.2–55.2°; d^{20}_4 0.6702; n^{20}_D 1.3881, THIS JOURNAL, **54**, 751 (1932).

(23) André, *Ann. chim. phys.*, [8] **29**, 554 (1913), gives b. p. 84–85°. Brooks and Humphrey, THIS JOURNAL, **40**, 834 (1918), give 85–86°, d^{15}_{15} 0.7160. Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930), give b. p. 84–86°, d^{20}_{20} 0.6956; Soday and Boord, *ibid.*, **55**, 3293 (1933), b. p. 84.7°; d^{20}_4 0.6936; n^{20}_D 1.3954; *MR* (found) 33.94.

(24) Whitmore and Homeyer, THIS JOURNAL, **55**, 4555 (1933), report b. p. 72.35°, d^{20}_4 0.6827; n^{20}_D 1.3911; *MR* (found) 34.15.

(25) Calcd.: C, 85.63; H, 14.37. Found: C, 85.28; H, 14.58.

(26) Calcd.: C, 85.63; H, 14.37. Found: C, 85.99; H, 14.34.

(27) Calcd.: C, 85.63; H, 14.37. Found: C, 85.69; H, 14.46.

(28) Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

diene[29] was obtained: 49% yield; b. p. 110.5–110.9°; d^{25}_{4} 0.7284; $n^{25.1}_{\mathrm{D}}$ 1.4213; *MR* (found) 38.37; *MR* (calcd.) 38.21.

By substituting 4-bromo-2-pentene for allyl bromide in a similar reaction, a 38% yield of 4,5-dimethyl-2,6-octadiene[30] was obtained: b. p. 152.9–153.8°; d^{25}_{4} 0.7611; $n^{25.1}_{\mathrm{D}}$ 1.4375; *MR* (found) 47.62; *MR* (calcd.) 47.45.

Dehydration of RCH(OH)CH=CHCH$_3$.[31]—The unsaturated alcohols of Table I were dehydrated by adding about one-half their weight of crystalline oxalic acid and slowly distilling them through a long column. The water layer was drawn off from the distillate, the remainder of which was returned to the flask, and the distillation repeated. The resulting hydrocarbon was dried and fractionated. Besides 1,3-pentadiene, b. p. 42.0–42.3°, and 2,4-heptadiene, b. p. 107.5–108.0°, which are already described in the literature,[32] we have prepared 2,4-octadiene[33] in 33% yield: b. p. 133.5–134.0°; d^{25}_{4} 0.7427; n^{25}_{D} 1.4542; *MR* (found) 40.19; *MR* (calcd.) 38.21; exaltation, 1.98.

2,2-Dimethyl-4-hexen-3-ol gave 2,2-dimethyl-3,4-hexadiene in 19% yield: b. p. 107.4–108.0°; d^{25}_{4} 0.7375; n^{25}_{D} 1.4425; *MR* (found) 39.55; *MR* (calcd.) 38.21; exaltation, 1.34.

Preparation of Alkynes—1-Hexadecyne was prepared in 65% yield, by Bourguel's alkyne synthesis,[34] from cetene dibromide and sodamide: b. p. 156–157° (15 mm.); m. p. 15°.[35] Boiling points of certain other alkynes which we prepared by Bourguel's methods,[34] formerly reported by him and by others, follow: 1-heptyne (from heptaldehyde), b. p. 100.4–100.8°; 2-heptyne (by-product from 3-heptyne), b. p. 111.5–113.0°; 3-heptyne (from 3-heptene), b. p. 105.3–106.7°; 1-octyne (from 2-octyne), b. p. 127.6–128.0°; 2-octyne (from 1-heptyne), b. p. 138.0–138.4°.

Summary

The preparation of alkenes from the Grignard reagent and unsaturated halides has been extended to the use of 4-bromo-2-pentene. A number of new hydrocarbons have been prepared, particularly 2-alkenes and 1,5-alkadienes.

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[29] Calcd.: C, 87.19; H, 12.81. Found: C, 87.09; H, 13.09.

[30] Calcd.: C, 86.87; H, 13.13. Found: C, 87.28; H, 13.10.

[31] 4-Heptanol, b. p. 154.5–156.0°, was similarly dehydrated to 3-heptene, b. p. 95.8–96.3°; 2,4-dimethyl-3-pentanol, b. p. 138.6–140.1°, to 2,4-dimethyl-2-pentene, b. p. 82.9–83.4°; and 5-nonanol, b. p. 195–197°, to 4-nonene, b. p. 147.5–148.1°. The alcohols were prepared in 60–80% yields from ethyl formate and the corresponding Grignard reagents.

[32] *Cf.*, for example, 1,3-pentadiene: b. p. 43°, von Auwers and Westermann, *Ber.*, **54**, 2993 (1921); b. p. 42°, Hofmann, *Ber.*, **14**, 665 (1881); b. p. 42.4–42.6° (766 mm.), Farmer and Warren, *J. Chem. Soc.* 3221 (1931); 2,4-heptadiene: b. p. 107°, von Auwers and Westermann, *loc. cit.*, etc.

[33] Calcd.: C, 87.19; H, 12.81. Found: C, 87.02; H, 12.67.

[34] Bourguel, *Ann. chim.*, [10] **3**, 191, 325 (1925).

[35] Krafft and Reuter, *Ber.*, **25**, 2245 (1892); m. p. 15°; b. p. 155° (15 mm.).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY]

Additions to Conjugated Systems in the Anthracene Series. II. The Behavior of Certain Anthranols

BY PERCY L. JULIAN AND WAYNE COLE[1]

Recently it was shown that methyleneanthrone (I) behaves toward phenylmagnesium bromide like a typical α,β-unsaturated ketone.[2] Since this appears to be the first authentic case on record of 1,6-addition of the Grignard reagent to a conjugated system of multiple linkages,[3] it appeared desirable to add more evidence for such an addition to that already adduced.

The structure of our addition product (II) was proved earlier by conversion with atmospheric oxygen into the peroxide (V) and the constitution of the latter by pyrolysis to anthraquinone and benzyl alcohol. This same peroxide has now been obtained in excellent yield by passing oxygen into the solution secured on catalytic reduction of benzalanthrone (III) in acetone. This proves conclusively the structure of our peroxide (V), especially since catalytic reduction of benzalanthrone in alcoholic solution was shown[2] to yield 10-benzylanthrone (IV), a substance different from the compound described in Beilstein,[4] but the structure of which has now been demonstrated by its conversion with phenylmagnesium bromide into 9-phenyl-10-benzylanthracene (VI), identical with the product secured by Barnett, Cook and Wiltshire[5] from phenylanthrone and benzylmagnesium chloride. Moreover, we have

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[1] Abstracted from the senior research of Wayne Cole at DePauw University, 1934–35.

[2] Julian and Magnani, THIS JOURNAL, **56**, 2174 (1934).

[3] Three other cases of 1,6-addition have been reported. Nakanishi [*Proc. Imp. Acad. Tokyo*, **9**, 394–7 (1933)] claimed 1,6-addition of phenylmagnesium bromide to benzanthrone, which findings do not agree with those recently reported by Allen [THIS JOURNAL, **57**, 740 (1935)]. Likewise Nakanishi claims 1,6-addition of phenylmagnesium bromide to benzalanthrone, an observation which the facts recorded in this paper do not support. Baeyer and Villiger [*Ber.*, **36**, 2793 (1903)] report 1,6-addition of methylmagnesium iodide to fuchsone, but give no proof for the structure of their product. This matter is now under investigation in this Laboratory.

[4] Bach, *Ber.*, **23**, 2529 (1890).

[5] Barnett, Cook and Wiltshire, *J. Chem. Soc.*, 1730 (1927).