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Abstract

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2,4-DIMETHYLPENTADIENE-1,3 IN THE SYNTHESIS OF ALKANES WITH TWO QUATERNARY CARBON ATOMS SEPARATED BY A CH_2 GROUP (DITERTIARYALKYLMETHANES)

(Presented by Academician A. N. Nesmeyanov, December 21, 1956)

In our previous communications ([1,2]), a method was described for the synthesis of ethylenic hydrocarbons with a quaternary carbon atom, consisting in the reaction between alkylmagnesium bromides and unsaturated tertiary bromides of the allylic type; the latter are readily obtained by hydrobromination of diene hydrocarbons of branched structure with a conjugated system of double bonds.

Thus, for example, the hydrobromide of 2,4-dimethylpentadiene-1,3 (I; Hal = Br) served as the starting material in the synthesis of 2,4,4-trimethylalkenes-2 ([1])*:

$$CH_3{-}C(CH_3){=}CH{-}C(CH_3){=}CH_2 \xrightarrow{+HHal} CH_3{-}C(CH_3){=}CH{-}C(CH_3)_2{-}Hal \xrightarrow{+RMgBr} CH_3{-}C(CH_3){=}CH{-}$$

(I) (II)

In the present work, using the same 2,4-dimethylpentadiene-1,3 as the starting substance, we have developed a new convenient route for the synthesis of very difficultly accessible paraffinic hydrocarbons with two quaternary carbon atoms separated by a CH_2 group—ditertiaryalkylmethanes (in the literature only the first member of this series of hydrocarbons, 2,2,4,4-tetramethylpentane ([3]), has been described). The above-mentioned reaction constituted the first stage of this synthesis; moreover, the use, instead of the bromide, of the hydrochloride of 2,4-dimethylpentadiene-1,3 (I; Hal = Cl) made it possible to raise the yield of 2,4,4-trimethylalkenes-2 (II) from 30 to 45-50%, calculated on the initial diene.

Alkenes (II) (R = CH_3, C_2H_5, C_3H_7, C_4H_9), already containing one quaternary carbon atom, were then converted by the action of hydrochloric acid into

the corresponding tertiary chlorides, 2-chloro-2,4,4-trimethylalkanes (III; yield 90%), which were subsequently introduced into reaction with organomagnesium compounds in the presence of mercuric chloride (a catalyst used in the Grignard–Wurtz reaction between RMgBr and tertiary chlorides ([4,5])); the products of this last stage of the synthesis were alkanes with two quaternary

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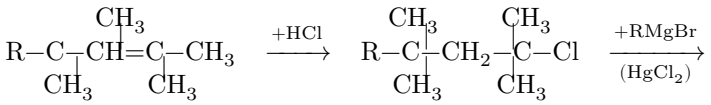
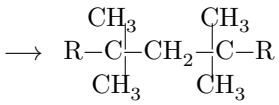
* By the same route from 3,5-dimethylheptadiene-2,4, 3,5-dimethyl-5-ethylalkenes-3 were obtained ([2]).

carbon atoms separated by a CH_2 group (IV; ditertiaryalkylmethanes:)



(II) (III)



(IV)

$$R = CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9$$

On reaction with organomagnesium compounds, the saturated tertiary chlorides (III) also eliminated hydrogen chloride, giving the starting alkenes (II) in 50–55% yield; these were again used for the synthesis of alkanes (IV). The alkenes (II) and alkanes (IV) were readily separated by distillation. The yield of alkanes was 15–25%, calculated on the tertiary chloride introduced into the reaction, and 30–50%, calculated on that consumed.

Experimental Part

Hydrochlorination of 2,4-dimethylpentadiene-1,3. The unsaturated monohydrochloride of 2,4-dimethylpentadiene-1,3 (I) was obtained by passing dry hydrogen chloride (to a gain in weight of 37 g) into the diene hydrocarbon cooled with snow and salt (96 g—1 mole; b.p. 92–93°/745 mm; n_D^{20} 1.4445; d_4^{20} 0.7375; literature data ([6]): b.p. 93–94°/755 mm; n_D^{20} 1.4448; d_4^{20} 0.7376). On distillation and on storage, the hydrochloride, like the hydrobromide ([1]), eliminated hydrogen halide and was converted to a considerable extent into the starting diene and its dimer. Therefore, for obtaining the alkenes (II), the dried, but undistilled, hydrochloride was used immediately after its preparation.

Synthesis of 2,4,4-trimethylalkenes-2 (II). To an ethereal solution of alkylmagnesium bromide (1.5 moles of alkyl bromide, 36 g of magnesium, and 300

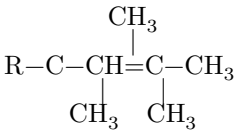
ml of absolute ether), with cooling by ice water, was gradually added an ethereal solution of the monohydrochloride of 2,4-dimethylpentadiene-1,3 (prepared from 1 mole of diene).

The reaction mixture was then heated for 5 hr; decomposition was carried out with dilute hydrochloric acid (2 N).

The yields of alkenes, calculated on the starting dimethylpentadiene, were 45-50%; their constants are given in Table 1.

Table 1

2,4,4-Trimethylalkenes-2



R	Name	b.p., °C/mm	n_D^{20}	d_4^{20}	Literature data ([3]): b.p., °C/mm	Literature data ([3]): n_D^{20}	Literature data ([3]): d_4^{20}
CH_3	2,4,4-Trimethylpentene-2	102-103/740	1.4131	0.7183	103-104/750	1.4130	0.7191
C_2H_5	2,4,4-Trimethylhexene-2	130-131/752	1.4261	0.7435	129-130/755	1.4264	0.7437
C_3H_7	2,4,4-Trimethylheptene-2	45-46/15	1.4310	0.7553	151-152/759	1.4307	0.7560
C_4H_9	2,4,4-Trimethyloctene-2	60-61/13	1.4360	0.7621	58.5-59/12	1.4366	0.7626

In all experiments, a dimer of 2,4-dimethylpentadiene-1,3 with b.p. 90°/10 mm was isolated from the higher-boiling fractions.

Hydrochlorination of 2,4,4-trimethylalkenes-2

The synthesized alkenes were saturated with hydrogen chloride while being cooled with snow and salt, and then shaken for 15-20 hours at room temperature with concentrated hydrochloric acid saturated, under cooling, with hydrogen

chloride. The resulting tertiary chlorides (III; 2-chloro-2,4,4-trimethylalkanes) were washed with water, dried over calcium chloride, and distilled in vacuo (yield 90%); their constants and analytical data are given in Table 2.

Table 2

2-Chloro-2,4,4-trimethylalkanes

Name	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % Cl
2-Chloro-2,4,4-trimethylpentane*	40–40.5/12	1.4308	0.8746	44.01	44.01	–	–	–	–	–	–
2-Chloro-2,4,4-trimethylhexane	55–56/10	1.4393	0.8768	48.78	48.63	66.60	11.53	21.75	66.44	11.77	21.79
2-Chloro-2,4,4-trimethylheptane	73–74/15	1.4448	0.8785	53.56	53.25	67.99	12.04	20.03	67.96	11.98	20.06
2-Chloro-2,4,4-trimethyloctane	90–90.5/12	1.4490	0.8865	57.74	57.86	69.46	12.17	18.85	69.26	12.15	18.59

* Literature data for 2-chloro-2,4,4-trimethylpentane ([3]): b.p. 53°/29 mm; n_D^{20} 1.431. The other chlorides have not been described in the literature.

Synthesis of ditertiaryalkylmethanes (IV) from tertiary chlorides (2-chloro-2,4,4-trimethylalkanes)

To an ethereal solution of the organomagnesium compound (1.1 mol of alkyl bromide, 24.3 g of magnesium, 220 ml of abs. ether) was added 4 g of cuprous chloride, and, after it had completely dissolved, the tertiary chloride (0.5 mol) was added very slowly (over 6 h) with constant stirring and cooling of the reaction mixture to 13–15°. Stirring was then continued for a further 5 h at room temperature and for 2 h at 30–35°; decomposition of the reaction mixture was carried out with dilute hydrochloric acid.

Table 3

Alkanes of the general structure
$R—C(CH_3)_2—CH_2—C(CH_3)_2—R$ (ditertiaryalkylmethanes)

R	Name	m.p.	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H
CH_3	2,2,4,4-Tetramethylpentane (*)	−65.2° (±2°)	120.7–121.3 (745)	1.4070	0.7198	43.75	43.76	—	—	—	—
C_2H_5	3,3,5,5-Tetramethylheptane	vitrifies below −70°	51/6	1.4309	0.7669	52.76	53.00	84.66	84.1534	15.35	
C_3H_7	4,4,6,6-Tetramethylnonane	vitrifies below −85°	84/9	1.4378	0.7813	62.05	62.23	84.64 84.57	15.15 14.96	84.70	15.30
C_4H_9	5,5,7,7-Tetramethylundecane	vitrifies below −95°	106/7	1.4420	0.7884	71.30	71.47	84.79 84.76	15.28 15.27	84.80	15.20

* Literature data for 2,2,4,4-tetramethylpentane ([3]) (obtained by the action of dimethylzinc on 2-chloro-2,4,4-trimethylpentane): m.p. −66.9; −67.1°; b.p. 122.3/760 mm; n_D^{20} 1.4069; d_4^{20} 0.7185. The other hydrocarbons have not been described in the literature.

(2 h). After distilling the ether from the washed and dried ethereal extract, the residue was boiled for 2 h with sodium, distilled from it, and subjected to fractional distillation on a column. A fraction of the starting 2,4,4-trimethylalkene-2 was collected (this fraction, whose yield in all cases was 50–55%, was subsequently used again for the synthesis of the corresponding alkane), together with a considerably higher-boiling alkane fraction—di-tert-alkylmethane. The yields of the alkanes ranged from 15% ($R = C_4H_9$) to 25% ($R = CH_3$), calculated on the tertiary chloride introduced into the reaction, or from 30 to 50%, calculated on the amount used; the constants and analytical data are given in Table 3.

The synthesized alkanes were studied by the method of combination light scattering.

Table 4 gives the spectra obtained, with intensities measured on a conventional visual scale in which the intensity of the frequency in the region 1440–1450 cm^{-1} is taken as equal to 10 units.

Table 4

Combination-scattering spectra of di-tert-alkylmethanes

Compound	Spectrum
2,2,4,4-Tetramethylpentane	217 (0.5), 262 (1; sh), 311-329 (1.5; sh), 349 (0.3), 376 (1), 420 (0.5), 498 (0), 556 (3), 645 (1), 678 (1.5), **734 (15)**, 769 (0.5), 812 (0.5), 862 (1.5), 875 (4), 918 (5), **930 (6)**, 996 (0.3), 1022 (0.3), 1076 (0.5), 1107 (1), 1144 (2.5), 1173 (2.5), 1196 (2.5), **1252 (12)**, 1325 (0.5), 1383 (1), **1443 (10)**, 1465 (2.5).
3,3,5,5-Tetramethylheptane	257 (0), 329 (1), 387 (1), 406 (0), 446 (0), 474-496 (2; dbl), 544 (2), 576 (1), 651 (0), 671 (0), **715 (9; sh)**, 776 (1.5), 833-840 (3; dbl), **930 (4; sh)**, 974 (1), 1012 (2.5), 1061 (2.5), 1133 (2.5; ph), 1170 (2.5), **1218 (4)**, 1227 (2), 1296 (1), 1323 (0.5), 1383(1), **1443 (10; sh)**, 1463(3).
4,4,6,6-Tetramethylnonane	240 (0.3), 291 (0.8; sh), 340 (1), 397 (0), 455 (0), 494 (1; dbl), 586 (0.5; sh), 627 (0), 687 (1), **735 (8; sh)**, 850 (1), 873 (2), 884 (0.5), 912 (0), **930 (3.5)**, 996 (0.6), 1040 (5), 1101 (1.5; sh/ph), 1138 (2), 1166 (2), **1204 (3.5; sh)**, 1223 (1.5), 1258 (1), **1304 (3; dbl/ph)**, 1350 (1), 1381 (1.5), **1443 (10; sh)**, 1461 (2).
5,5,7,7-Tetramethylundecane	224 (1; sh/ph), 320 (1.5; sh), 380 (0.1), 397 (0), 420 (0), 493 (0), 586 (1; sh), 675 (0.5), 695 (0), **735 (9; sh)**, 792(0.5), 822 (0), 854 (1.5), 875(2.5), 893 (2), 910 (2), 930 (2.5), 994 (0), 1056 (3), 1090 (3), 1138 (1.5; sh/ph), 1159 1.5; (sh/ph), **1198(4)**, 1241(1), 1264 (1), 1304 (4; sh), 1349(0.5; ph), 1380 (1.5), 1408 (0.5), **1450 (10; sh)**.

As is evident from the data presented, the spectra of all the synthesized di-tert-alkylmethanes contain a set of intense frequencies in the regions 700–750, 930, and 1200–1250 cm^{-1}, characteristic of complex branching in the chain ([7,8]), i.e., of hydrocarbons with a quaternary carbon atom.

Study of the spectra also showed that the alkanes do not contain alkene impurities—frequencies in the region of 1600 cm^{-1} were absent.

Synthesis of 3,3,5,5-tetramethylheptane from the ditertiary dichloride V (2,4-dichloro-2,4-dimethylpentane). The interaction of ethylmagnesium bromide (115 g of ethyl bromide, 24 g of magnesium, and 200 ml of abs. ether) with the ditertiary dichloride (V) (0.25 mole) in the presence of sublimate was carried out under the conditions described above for the reaction between $RMgBr$ and saturated tertiary monochlorides (III).

On distillation of the reaction products, 3,3,5,5-tetramethylheptane was isolated (in 5% yield, calculated on the dichloride) (b.p. 71–73°/12 mm; n_D^{20} 1.4307, d_4^{20} 0.7693), as well as 2,4-dimethylpentadiene-1,3 (b.p. 92–94°/750 mm; n_4^{20} 1.4440) and its dimer (b.p. 92°/12 mm).

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Note: Figure translations are in progress. See original paper for figures.