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The Synthesis, Purification and Properties of Some Polyalkylcyclopropanes: Reduction of α,γ-Dibromides[1]

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Seven polyalkylcyclopropanes have been prepared and some of their common physical properties determined. In three of these cases, geometrical isomers were separated in good purity; in two other cases the separation was less complete. The effects of the structure in α,γ-dibromides on the nature of their debromination products have been investigated. Some generalizations concerning the chemical properties of cyclopropane hydrocarbons are made.

The literature on cyclopropane hydrocarbons is often confusing, and sometimes inaccurate. Only a few cyclopropane hydrocarbons have been purified rigorously, and some have even been identified incorrectly. In many cases no examination was made for olefinic or paraffinic impurities and, consequently, reactions due to impurities sometimes have been reported as typical of cyclopropane hydrocarbons. The separation and identification of individual geometrical isomers has been virtually ignored.

The primary purpose of the present work was to prepare some relatively pure polyalkylcyclopropane hydrocarbons, to study some of their physical properties and to separate, where possible, individual geometrical isomers. Infrared absorption spectra were determined on all of the compounds prepared, and some of these have been published as a part of a general study of such spectra.[2]

All of the cyclopropanes described in the present paper were produced by some modification of the Gustavson[3] method (reaction of an α,γ-dibromide with zinc). Many of these ring closures would have been impossible without the discovery by Lankelma[4] and his co-workers concerning the importance of maintaining a low temperature in this type of reaction. Prior to this innovation, the Gustavson reaction had been run at or near the reflux temperature of aqueous ethanol, and if the α,γ-dibromide contained even one bromine attached to a tertiary carbon atom, little or no cyclopropane was formed, dehydrohalogenation being the main process. Using the Lankelma modification, the present authors[5] prepared high-purity 1,1,2-trimethylcyclopropane on the enlarged laboratory scale by the reaction of 2,4-dibromo-2-methylpentane (a tertiary-secondary dibromide) with zinc. A second purpose of the present work was to investigate further the relationships of the structures of dibromides to the types of reduction products obtained when the low temperature procedure was used.

Table I presents the common physical properties of the cyclopropanes prepared in the present research, along with estimates of their purity. The first three purities were calculated by the general method of Rossini, *et al.*[6]; the others were arrived at by inspection of physical property data, such as boiling point and refractive index curves, since these would not crystallize, or the amount was too small.

Contrary to a common belief that cyclopropanes exhibit unsaturation to about the same degree as olefins, none of the alkylcyclopropanes prepared in this work would react with dilute aqueous permanganate solution or dilute non-aqueous bromine solutions at an appreciable rate. Indeed, exhaustive treatment with aqueous permanganate generally was used to free the cyclopropanes from olefinic impurities. Neither do the cyclopropanes peroxidize readily on contact with air, although all olefins do. Many of the unsaturated qualities attributed to the cyclopropane ring in the literature undoubtedly arose from the presence of unsuspected olefinic impurities.

The more highly alkylated cyclopropanes are hydrogenated less readily than the parent hydrocarbon. In this respect they closely resemble the highly alkylated derivatives of ethylene. Hydrogenolysis appears to be directed to the less substituted side of the cyclopropane ring.[5] In the present work it was found that hydrogenation of 1,1,2,2-tetramethylcyclopropane, in the same way as before,[5] at 250° and 137 atm. hydrogen pressure over nickel-on-kieselguhr catalyst gave a hydrogenolysis product containing 91% 2,2,3-trimethylbutane and only 9% of 2,4-dimethylpentane, as was expected.

The isomerization of cyclopropanes at high temperatures and in the presence of metals or metallic salts has been discussed already.[5]

Relationship of the Structures of Dibromides to their Debromination Products.—The nature and ratios of the products formed by the debromination of α,γ-dibromides with zinc vary markedly with the structure of the dibromide. The α,γ-dibromides

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[2] J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 3595 (1949).

[3] G. Gustavson, *J. prakt. Chem.*, **36**, 300 (1887).

[4] J. D. Bartleson, R. E. Burk and H. P. Lankelma, THIS JOURNAL, **68**, 2513 (1946).

[5] R. G. Kelso, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **74**, 287 (1952).

[6] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

TABLE I

PHYSICAL PROPERTIES OF CYCLOPROPANES PREPARED DURING THIS RESEARCH

Cyclopropane	B.p., °C. (760 mm.)	$n^{20}D$	d^{20}_4	F.p., °C.	Mole % purity
1,2-Dimethyl- (*trans*)	28.20	1.3710	0.6698	−149.82	99.5
(*cis*)	37.03	1.3830	.6941	−140.93	99.9
Lit.[8] (*trans*)	28.8–29.0 (759)	1.3713	.6769	......	..
(*cis*)	37.2–37.4 (756)	1.3822	.6928	......	..
1,1,2,2-Tetramethyl-	75.85	1.4009	.7186	− 80.75	99.9
Lit.[7]	74–75 (757)	1.3928	.7227	......	..
1,2,3-Trimethyl- (*trans*)	59.7	1.3873	.6979	......	95+
(*cis*)[a]	65–67	1.393–1.396	....	......	..
Lit.[9] (*cis–trans* mix.)	65–66 (748)	1.3942	.6942	......	..
1-Methyl-2-ethyl- (*trans*)	58.66	1.3846	.6935	Glass	97+
(*cis*)	67.01	1.3953	.7146	Glass	97+
Lit.[10] (*cis–trans* mix.)	64–65	1.3874	.6959	......	..
1-Methyl-2-(*n*)-propyl- (*trans*)	88.9	1.3976	.7155	Glass	95+
(*cis*)	96.6	1.4051	.7295	Glass	95+
Lit.[10] (*cis–trans* mix.)	92–93 (747)	1.4003	.7206	......	..
1,2-Dimethyl-3-ethyl- (*trans*)[b]	84–84.5	1.4004–1.4000	0.7244–0.7200	Glass	..
Lit.[4,c]	87 (732–739)	1.3980	....	......	..
(*cis*)	98.0	1.4122	.7462	Glass	95+
Lit.[4,c]	94 (732–739)	1.407	....	......	..
1,1,2,2,3,3-Hexamethyl-[d]	124–125	1.4291	.7685	+0.9	90+

[a] Amount of final sample was small and slightly unsaturated. [b] Probably a mixture of the *c,c,t* and *c,t,c* isomers. [c] Incorrectly identified, as will be shown in a later paper. Analysis on our product; calcd. for C_7H_{14}: C, 85.62; H, 14.38. Found: C, 85.45; H, 14.24 (for the *cis* isomer). Found: C, 85.40; H, 14.21 (for the *trans* isomer). [d] *Anal.* Calcd. for C_9H_{18}: C, 85.62; H, 14.38. Found: C, 85.40; H, 14.13.

may be divided into six types according to their peripheral structure, *i.e.*, the degree of substitution on the bromine-bearing carbon atoms: (1) primary-primary, (2) primary-secondary, (3) primary-tertiary, (4) secondary-secondary, (5) secondary-tertiary, (6) tertiary-tertiary. Types 1 and 6 are illustrated by 1,3-dibromopropane and 2,4-dibromo-2,4-dimethylpentane, respectively. The stability of the dibromides decreases in approximately the order mentioned (1 to 6).

Each of these types may be divided into three sub-types, differentiated only by the degree of substitution on the intermediate carbon atom (secondary, tertiary, quaternary). The ease of ring closure may not vary much among these sub-types, but the stability and ease of preparation of the dibromides varies widely among them. In general, the percentage yield of dibromides of a given type decrease as the sub-type is changed from secondary (*s*) to tertiary (*t*) to quaternary (*q*), whereas the quaternary dibromides rank higher in stability than the corresponding tertiary (*t*) ones.

Table II shows the α,γ-dibromides which were caused to react with zinc by the low temperature procedure and lists the yields of cyclopropanes, paraffins and olefins formed by the reactions. An example of the special type ($p,s(t)$) of primary-secondary dibromide which has a tertiary carbon situated between the bromine-bearing carbons is represented by 1,3-dibromo-2-methylpentane. All types which contain this special *t*-atom are of significance because there is a strong tendency toward the formation of α,β-dibromides by a rearrangement during the preparation of α,γ-dibromides. In this case (preparation of 1,3-dibromo-2-methylpentane by the action of phosphorus tribromide on the corresponding glycol) rearrangement was proved definitely by a fractionation of the product. Two dibromides (1,3-dibromo-2-methylpentane and 1,2-dibromo-2-methylpentane) were obtained in about 4:3 ratio; evidently, some of the secondary bromine had rearranged to the tertiary position. The 20% olefin found in the debromination product may have come from newly formed α,β-dibromide; however, reaction mechanisms whereby olefins can result from pure α,γ-dibromides already have been proposed.[5]

The three $s,s(s)$ types represented gave yields of 70 to 90% hydrocarbons which contained 60 to 90% cyclopropane, 0 to 10% paraffinic, and 10 to 30% olefinic products.

A special type ($s,s(t)$) of di-secondary dibromide is represented by two examples. In these cases no fractionation to remove the α,β-dibromide impurities could be accomplished, and the hydrocarbon products contained extraordinarily large amounts of olefins.

Another special type ($s,s(q)$) of di-secondary bromide which has a quaternary carbon between the bromine-bearing carbons is represented by 2,4-dibromo-3,3-dimethylpentane. Some of these (q)-types of dibromides are difficult,[11] or impossible,[12]

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(7) J. Baudrenghien, 2me Congreès national des sciences, *Compt. rend.*, Vol. II (1935), Brussels.

(8) J. Baudrenghien, *Bull. soc. chim. Belg.*, **38**, 172 (1929).

(9) N. D. Zelinsky and J. Zelikow, *Ber.*, **34**, 2856 (1901).

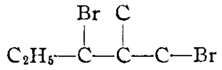
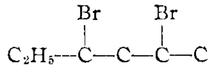
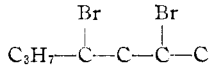
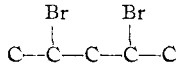
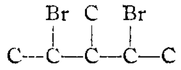
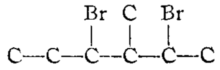
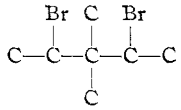
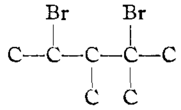
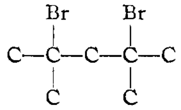
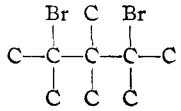
(10) R. Lespieau and R. L. Wakeman, *Bull. soc. chim.*, **51**, 384 (1932).

(11) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **70**, 946 (1948).

(12) B. R. Buchman, Calif. Institute Tech., private communication.

TABLE II

DEBROMINATION PRODUCTS OF α,γ-DIBROMIDES

Cyclopropane	Dibromide	Dibromide type	Hydrocarbon, % yield	Cyclopropane	Paraffin[a]	Olefin[b]	Ratio *t*:*c*
1-Methyl-2-ethyl-	 $C_2H_5{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}\overset{\text{C}}{\overset{\vert}{C}}{-}C{-}Br$	*p,s*(*t*)	74	78	2	20	6:7
1-Methyl-2-ethyl-	 $C_2H_5{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C$	*s,s*(*s*)	68	65	6	29	3:5
1-Methyl-2-(*n*)-propyl-	 $C_3H_7{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C$	*s,s*(*s*)	93	84	3	13	5:7
1,2-Dimethyl-	 $C{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C$	*s,s*(*s*)	85	90	None	10	2:3
1,2,3-Trimethyl-	 $C{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}\overset{\text{C}}{\overset{\vert}{C}}{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C$	*s,s*(*t*)	80–90	20–25	(?)	75–80	5:4
1,2-Dimethyl-3-ethyl-	 $C{-}C{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}\overset{\text{C}}{\overset{\vert}{C}}{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C$	*s,s*(*t*)	79	30	10	60	8:3[d]
1,1,2,3-Tetramethyl-[c]	 $C{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}\underset{\text{C}}{\underset{\vert}{\overset{\text{C}}{\overset{\vert}{C}}}}{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}C$	*s,s*(*q*)	33	(20)		60	(?)
1,1,2,3-Tetramethyl-[c]	 $C{-}\overset{\text{Br}}{\overset{\vert}{C}}{-}\underset{\text{C}}{\underset{\vert}{C}}{-}\underset{\text{C}}{\underset{\vert}{\overset{\text{Br}}{\overset{\vert}{C}}}}{-}C$	*s,t*(*t*)	70–83	3	27	70	1:1
1,1,2,2-Tetramethyl-	 $C{-}\underset{\text{C}}{\underset{\vert}{\overset{\text{Br}}{\overset{\vert}{C}}}}{-}C{-}\underset{\text{C}}{\underset{\vert}{\overset{\text{Br}}{\overset{\vert}{C}}}}{-}C$	*t,t*(*s*)	79[e]	65	17	18	..
1,1,2,2,3,3-Hexamethyl-	 $C{-}\underset{\text{C}}{\underset{\vert}{\overset{\text{Br}}{\overset{\vert}{C}}}}{-}\underset{\text{C}}{\underset{\vert}{\overset{\text{C}}{\overset{\vert}{C}}}}{-}\underset{\text{C}}{\underset{\vert}{\overset{\text{Br}}{\overset{\vert}{C}}}}{-}C$	*t,t*(*q*)	25[f]	21	21	58	..

[a] As determined by distillation and inspection of rectification diagrams. [b] As determined by titration by the procedure of A. W. Francis (*Ind. Eng. Chem.*, **18**, 821 (1926)). [c] Unpublished results of this Laboratory; amounts not sufficient to redistill or characterize. [d] Ratio of *c,t,c* and *c,c,t*, combined, to *c,c,c*. [e] From diene: all others from glycols. [f] Based on glycol; crude dibromide used.

to prepare by the action of phosphorus tribromide on the glycols. Because 1,1-dimethylcyclopropane and its homologs have been prepared in high purity from this special type of dibromide,[11] the large amount of olefin formed in the debromination of 2,4-dibromo-3,3-dimethylpentane (see Table II) cannot be explained simply; probably it resulted from a neopentyl-type rearrangement. The dibromide (2,4-dibromo-3,3-dimethylpentane) was not purified (attempted distillation yielded only tar), the crude being treated directly with zinc in *n*-propyl alcohol.

A secondary-tertiary dibromide, 2,4-dibromo-2,3-dimethylpentane (type *s,t*(*t*)), gave about a 75% yield of hydrocarbon product based on the conversion from the diene, through which intermediate the dibromide was made. The dibromide was not purified but was used as such, and again a large amount of olefin was obtained (see Table II).

2,4-Dibromo-2,4-dimethylpentane, the simplest possible dibromide of the *t,t*(*s*)-type, was prepared easily by addition of anhydrous hydrogen bromide to 2,4-dimethyl-1,3-pentadiene and was purified by crystallization; the yield of purified product was 80% from the diene. No attempt was made to distil the dibromide, for it has been reported to decompose readily.[13] It was debrominated by the low temperature method to yield 79% of hydrocarbons, of which 65% was 1,1,2,2-tetramethylcyclopropane (42% yield from intermediate diene) and the remaining 35% comprised about equal quantities of olefins and paraffins. Levina, Gladshtein and Akishin[14] have carried out the same series of reactions and obtained the cyclopropane in 60% yield (from diene). In the present work, this dibromide also was debrominated by reaction with zinc in formamide at 0°, and in refluxing ethanol. In the formamide solvent, there was obtained a 74% yield of C_7-hydrocarbons, 65% of which was good 1,1,2,2-tetramethylcyclopropane, but in the refluxing ethanol there was obtained only a 39% yield of hydrocarbons, none of which was the cyclopropane. This again emphasized the importance of temperature control in such reactions.

A *t,t*(*q*)-dibromide (the worst possible type from the standpoints of ease of preparation and reductive ring closure) is represented by 2,4-dibromo-2,3,3,4-tetramethylpentane. Debromination by the usual procedure gave a 25% yield (from glycol) of

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[13] A. Franke, *Monatsh.*, **34**, 1909 (1913).

[14] R. Y. Levina, B. M. Gladshtein and P. A. Akishin, *J. Gen. Chem.*, (*U.S.S.R.*), **19**, 1077 (1949).

hydrocarbon material comprising 58% of olefins and about equal quantities (21% each) of 1,1,2,2,3,3-hexamethylcyclopropane and paraffin(s).

Experimental

Production of Dibromides

At Low Temperatures.—The glycols, in all cases except those noted below, were converted to bromides by reaction with phosphorus tribromide at −20 to −5° by a procedure similar to that developed by Lankelma and co-workers.[4] Powerful stirring was a necessity because the glycols were quite viscous in this temperature range. Chloroform, methylene chloride and *n*-pentane were found to be solvents suitable for increasing the mobility of the reaction mixtures. The reaction mixtures were allowed to stand at room temperature for a week to ten days, during which time they separated into a dibromide layer and a heavy phosphorus acid layer. The entire mixture was then poured onto crushed ice, and the dibromide layer was separated and washed three or four times with an equal volume of ice-water. The crude, wet dibromide was then dried over anhydrous sodium sulfate.

At Room Temperature and from Solid Glycols.—It was found that 2-methyl-1,3-pentanediol would not form a dibromide at low temperature, so the initial reaction temperature of 35 to 45° was maintained during the addition of the phosphorus tribromide and a digestion period of two or three days. Solid glycols were either melted and phosphorus tribromide was added to lower the melting point sufficiently so that the reaction could be continued at 35 to 45°, or they were dissolved in *n*-pentane and brominated at lower temperatures.

By Gaseous Hydrobromination.—2,4-Dibromo-2,4-dimethylpentane was prepared by saturating 2,4-dimethyl-1,3-pentadiene with hydrogen bromide gas by the procedure described previously.[5] The yield of crude dibromide was practically quantitative and 80% of this (purified only by crystallization to a melting point of 8–9°) was used in the subsequent debromination step. The dibromide decomposed rapidly at room temperature; elemental analysis was meaningful, but could not be made with the customary accuracy: Calcd. for $C_7H_{14}Br_2$: Br, 61.95. Found: Br, 60.45. Apparently previous investigators[14] also found this dibromide unstable, as they did not isolate it, but used it in the crude state.

Table III

Properties of Dibromides Isolated

Compound	Yield,[a] %	B.p., °C.	Mm.	d^{20}_4	n^{20}_D
2,4-Dibromo-3-methylpentane	60	98	36	....	1.5100
Literature[9]	..	98	30	....	....
2,4-Dibromopentane	60	70	17	1.6302	1.4960
Literature[15]	..	71	17	1.6659	1.4987
2,4-Dibromohexane	65	75	10	1.5745	1.4984
Literature[10]	..	82	10	1.5756	1.4986
2,4-Dibromoheptane	87	99	12	....	1.4936
Literature[16]	..	100	12	1.495	1.4941
2,4-Dibromo-3-methylhexane[b]	57	85	4	1.5035	1.5003
Literature[4]	..	72	1	1.4504	1.4967
1,3-Dibromo-2-methylpentane[b]	38	86	9	1.5664	1.5023
Literature[17]	..	82	12	....	....

[a] Yield calculated from corresponding glycol. [b] Decomposes or isomerizes readily.

Purification and Properties of the Dibromides.—Most of the crude dibromides were distilled (at pressures as low as practical) to remove bromohydrins, olefinic monobromides and heavy residues. In some instances, dehydrohalogenation occurred during distillation and probably increased the amounts of olefinic bromides and heavy residues. When distillation was not practicable, the crude dibromide was used for the subsequent reaction, except in one case (above) in which (partial) purification by crystallization was feasible. The common physical properties and yields of all of the dibromides isolated in the present work are listed in Table III.

Sources.—The following glycols were obtained by purchase or gift: 2,4-pentanediol and 2,4-heptanediol (Carbide and Carbon), and 2-methyl-1,3-pentanediol (Celanese).

3-Methyl-2,4-pentanediol.—This diol was prepared (1) by hydrogenating 3-methyl-2,4-pentanedione which was synthesized by condensing sodio-acetylacetone with methyl iodide by a procedure which is an improvement over those previously reported in the literature[18,19] and (2) by hydrogenating 3-methyl-4-hydroxy-2-pentanone which was made by condensing methyl ethyl ketone and acetaldehyde.

(1) In a 5-liter, 3-neck flask, were placed 2.5 liters of absolute ether and 324 g. (6 moles) of sodium methoxide. Three moles (300 g.) of acetylacetone was added rapidly with vigorous stirring, giving fluffy, white sodio-acetylacetone. Six moles (852 g.) of methyl iodide was then added over a period of an hour, after which the reaction mixture was refluxed for two or three days. When the reaction was complete (no longer basic), the formed insoluble sodium iodide was removed by filtration and the ethereal filtrate was stripped of ether. The residue was vacuum distilled and gave 216 g. (1.9 moles) of 3-methyl-2,4-pentanedione, a 63% yield. A small amount (30 g.) of acetylacetone was recovered.

When methyl alcohol was substituted for the ether solvent, the yield of 3-methyl-2,4-pentanedione was decreased to 28%, and the amount of recovered acetylacetone increased to 50%. Methyl bromide, when substituted for methyl iodide, would not react under the same conditions. The use of ethanol solvent was undesirable for it dissolved some of the sodium iodide by-product (which reprecipitated during distillation), and it formed an azeotrope with both of the diones, giving mixtures separable only with difficulty.

The reduction of 3-methyl-2,4-pentanedione was accomplished readily at 70° with 102 to 137 atm. of hydrogen pressure over 5% by weight of Raney nickel catalyst in alcohol solvent; use of either a glass liner or stainless steel bomb as a container was necessary to prevent the formation of diketone–iron chelate compounds which poison nickel catalysts. The glycol was produced in 60% yield. A yield of 64% has been reported in hydrogenation of 3-ethyl-2,4-pentanedione by this procedure.[20]

(2) In a second procedure, which was essentially that used by Powell[21] in the synthesis of 3-methyl-4-hydroxy-2-heptanone, methyl ethyl ketone was condensed with acetaldehyde in the presence of sodium hydroxide to produce 3-methyl-4-hydroxy-2-pentanone.

The reaction mixture was neutralized with saturated tartaric acid solution, the resulting sodium tartrate was removed by filtration, and any aqueous layer was separated from the filtrate. The organic material was distilled up to about 85° to remove excess methyl ethyl ketone; the residue, when subjected to vacuum distillation, gave a 37% yield (from acetaldehyde) of 3-methyl-4-hydroxy-2-pentanone.

Anal. Calcd. for $C_6H_{12}O_2$: C, 64.60; H, 10.83. Found: C, 64.40; H, 10.81.

The ketol was hydrogenated under the same conditions as was the 3-methyl-2,4-pentanedione, and a 60% yield of 3-methyl-2,4-pentanediol was obtained after distillation under reduced pressure.

2,4-Hexanediol.—2,4-Hexanediol was prepared in 30% yield by the condensation of excess ethyl Grignard reagent with acetaldol.[22] The product was recovered from the aqueous layer of the hydrolysate by continuous ether extraction, stripped of ether, and fractionated under reduced pressure.

3-Methyl-2,4-hexanediol.—4-Methyl-5-hydroxy-3-hexanone was prepared in 47% yield by condensing diethyl ketone with acetaldehyde by the same procedure used (under

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Table IV

Properties of Intermediates Isolated

Compound	B.p., °C.	Mm.	$n^{20}\text{D}$	Yield, %	Basis of yield
3-Methyl-2,4-pentanediol	115	21	....	39	Acetylacetone
				33	Methyl ethyl ketone
Literature[25]	100	10	1.4440		
3-Methyl-2,4-hexanediol	116	17	1.4445	40	Diethyl ketone
Literature[4]	109	9	1.4450		
2,3,3,4-Tetramethyl-2,4-pentanediol	125	20	M.p. 74°	37	Diethyl methylmalonate
Literature[17]	113	11	M.p. 75–76°		
2,4-Hexanediol	83–85	2	1.439	30	Acetaldol
Literature[26]	210–211	750	....		
4-Methyl-5-hydroxy-3-hexanone	85	8	1.4365	47	Diethyl ketone
Literature[27]	84	10	....		
3-Methyl-4-hydroxy-2-pentanone	75	10	1.4320	37	Methyl ethyl ketone
Literature[25]	75	10	....		
3-Methyl-2,4-pentanedione	86	60	1.4455	63	Acetylacetone
Literature[28]	60–65	13	1.4437		
2,4-Dimethyl-1,3-pentadiene[a]	93.7–93.8	760	1.4412	73	Mesityl oxide
Literature[23]	93.0	760	1.4428		

[a] Other physical properties determined were: d^{20}_4 0.7369 (lit. 0.7368) and f.p. −116.0° (lit. −114.0°).

method 2 above) for 3-methyl-4-hydroxy-2-pentanone; the excellent yield was attributed to the fact that the acetaldehyde was distilled into the reaction mixture slowly. Hydrogenation to the glycol proceeded in about 85% yield.

2,3,3,4-Tetramethyl-2,4-pentanediol.—This glycol was prepared by alkylating methylmalonic ester with sodium methoxide and methyl iodide, and condensing the resultant dimethylmalonic ester with four equivalents of methyl Grignard reagent.

In a 5-liter flask, suitably equipped, was placed 4 moles of sodium methylate in 3 liters of methanol, and 680 g. of methylmalonic ester was added at a rate that caused a gentle reflux; 870 g. of methyl iodide was then added, dropwise. Reflux was maintained for two days by external heating, until the reaction mixture was neutral to litmus; then, unreacted methyl iodide (180 g.) and the methanol were removed by distillation. The residue (filtered) was distilled under vacuum to obtain 410 g. (a 55% yield) of dimethylmalonic ester, b.p. 66° (10 mm.), $n^{20}\text{D}$ 1.4160.

The reaction with methyl Grignard reagent was carried out in the customary manner to obtain a 68% yield of 2,3,3,4-tetramethyl-2,4-pentanediol after distillation under reduced pressure.

2,4,-Dimethyl-1,3-pentadiene.—This diolefin was prepared in 58–73% yields by condensation of methyl Grignard reagent with mesityl oxide, and slow distillation of the resulting crude carbinol, which dehydrated spontaneously. The experimental procedures were essentially those of Waterman and de Kok,[23] except that they used phthalic anhydride to promote the dehydration.

Cyclization Reactions

Low Temperature Procedure.—The reaction of the dibromides with zinc at about 0° were carried out by essentially the same procedure described by Lankelma, *et al.*,[4] and employed by the present authors.[5]

The Formamide Procedure.—In a 2-liter, 3-neck flask, suitably equipped, were placed 3 moles (196 g.) of zinc dust and 10 moles (960 g.) of formamide.[24] This was cooled to 0° and 2 moles (516 g.) of crude 2,4-dibromo-2,4-dimethylpentane was added over a period of 2 hours with stirring. The reaction mixture was allowed to warm to room temperature, and stirring was continued for about a day and a half. The crude hydrocarbon (b.p. 74–85°) was distilled from the mixture; it amounted to 151 g. or 77% based on dibromide. A small amount (48 g.) of high boiling organic liquid, not containing bromine, was separated from the solvent. Considered as a C_{14}-hydrocarbon (from coupling of allylic bromide by-products), it amounted to 24% yield, thus accounting for the remainder of the dibromide.

The "Original" Gustavson Procedure.—In an apparatus similar to the one used previously,[11] were placed 300 ml. of 85% ethanol and 90 g. (1.4 moles) of zinc dust. The alcohol was brought to gentle reflux and 200 g. (0.78 mole) of 2,4-dibromo-2,4-dimethylpentane was added over a period of a half-hour. The hydrocarbon product was removed by distilling it through a Vigreux column and was washed with ice-water and dried; only 30 g. or a 39% yield of hydrocarbon material was obtained, and contained none of the desired 1,1,2,2-tetramethylcyclopropane.

Purification and Distillations.—All of the alkylcyclopropanes described herein were treated exhaustively with saturated aqueous potassium permanganate to remove olefinic impurities. The hydrocarbons were distilled through either (1) a 15-plate column (0.5 in. × 40 in.) packed with $^1/_{16}$ in. stainless steel helices and equipped with a still-head of the type described by Turk and Matuszak[29] or (2) a Stedman column rated at 35 plates. The latter column was equipped with a Turk–Matuszak still-head, modified to allow electrically controlled take-off. Preliminary distillations were done on the 15-plate column; most final distillations were carried out on the Stedman column, but only after the hydrocarbons had been treated with permanganate, steam distilled, and dried over sodium sulfate. Silica gel was not used, as it had been found capable of decomposing cyclopropanes.[5]

A general utility column (1 in. × 36 in.) packed with $^3/_{16}$-in. glass helices was used for distillation of glycols, dibromides and other intermediates both at atmospheric and reduced pressures. Some sensitive dibromides were distilled at reduced pressures from a modified Claisen flask, only.

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