ether was removed and the residue dried on a steam-bath at 0.05 mm. for an hour.

After preliminary experiments had shown that the product at this stage could not be catalytically hydrogenated, the residue was dissolved in 250 ml. of benzene and passed through a column of aluminum oxide. The column was then eluted with 110 ml. of benzene, and then with a mixture of 55 ml. of benzene and 55 ml. of ether. A small brown band of impurities remained at the top of the column. The solvent was removed from these eluates and the residue heated at 150° at 10 mm. for an hour. Ethyl (1-benzoyl-3-ethyl-4-piperidylidene)-cyanoacetate so obtained was an oil that weighed 65 g. (81%). A sample of this material evaporatively distilled at 0.05 mm. (jacket temperature, 215°) as a pale yellow oil with no apparent decomposition.

Anal. Calcd. for $C_{19}H_{22}O_3N_2$: C, 69.91; H, 6.80; C_2H_5O, 13.81. Found: C, 69.52; H, 6.91; C_2H_5O, 13.50.

The absorption spectrum of this ester, which was kindly determined by Mr. Carl Djerassi in this Laboratory, showed an absorption maximum at 219 mμ, the region in which α,β-unsaturated cyanoacetic esters are known to absorb.[15] The characteristic spectrum of the benzene nucleus also was noted.

Ethyl (1-Benzoyl-3-ethyl-4-piperidyl)-cyanoacetate (VIII).—A solution of 11 g. of VII in 50 ml. of absolute alcohol was shaken with hydrogen and 0.22 g. of Adams platinum oxide catalyst. The required amount of hydrogen was absorbed in about four hours. In this manner a total of 62 g. of VII was reduced. The combined alcohol solutions, after removal of the catalyst and evaporation of the solvent, left 58 g. (93%) of ethyl (1-benzoyl-3-ethyl-4-piperidyl)-cyanoacetate as a viscous pale yellow oil. A sample of this material evaporatively distilled at 0.03 mm. and a jacket temperature of 220°.

Anal. Calcd. for $C_{19}H_{24}O_3N_2$: C, 69.49; H, 7.37; C_2H_5O, 13.72. Found: C, 69.01; H, 7.63; C_2H_5O, 13.65.

Ethyl 3-Ethyl-4-piperidylacetate (Ethyl *dl*-Cincholoiponate (X)).—The clear reddish solution resulting from the addition of 19.5 g. of VIII to 200 ml. of concentrated hydrochloric acid was refluxed for twenty-four hours. On cooling the solution, benzoic acid crystallized out and was filtered off; the yield was practically quantitative. The aqueous filtrate then was evaporated to dryness under diminished pressure, 200 ml. of 10% alcoholic hydrogen chloride added, and the solution refluxed for twenty-four hours. The alcohol was removed under diminished pressure and the resulting salt mixture treated with chloroform, which dissolved the salt of the amino ester X but left 3.1 g. (calcd. 3.25 g.) of ammonium chloride undissolved. The chloroform solution was evaporated and the residue taken up in a mixture of 20 ml. of alcohol and 25 ml. of ether. This solution was cooled to 0° and treated with a cold 30% solution of sodium hydroxide, and the resulting sludge extracted four times with ether. After drying the ether solution over anhydrous sodium sulfate and distilling the ether, the residue was distilled. Redistillation gave 6.8 g. (57.5% from VIII) of ethyl 3-ethyl-4-piperidylacetate (X), b. p. 133–135° (11 mm.); $n^{20}{}_D$ 1.4672; $d^{20}{}_4$ 0.9910.

Anal. Calcd. for $C_{11}H_{21}O_2N$: C, 66.29; H, 10.62; C_2H_5O, 22.6. Found: C, 66.03; H, 10.84; C_2H_5O, 22.1.

A solution of X in dry ether when treated with dry hydrogen chloride gave a white, crystalline precipitate of ethyl 3-ethyl-4-piperidylacetate hydrochloride which, after recrystallization from a chloroform–ethyl acetate mixture, melted at 130–131° with previous softening.

Anal. Calcd. for $C_{11}H_{22}O_2NCl$: Cl, 15.04. Found: Cl, 15.25.

Summary

The C-alkylations of the potassium enolate of 1-benzoyl-3-carbethoxy-4-piperidone with ethyl iodide and benzyl chloride are described. Attempted alkylations with β-phenoxyethyl bromide and iodide were unsuccessful. γ-Phenoxypropyl bromide appeared from the analyses of the product to give 3-alkylation, but the chemical properties of this product are anomalous.

The conversion of the 1-benzoyl-3-alkyl-3-carbethoxy-4-piperidones, obtained from alkylations with ethyl iodide and benzyl chloride, to the 3-alkyl-4-piperidones is described.

The usefulness of the 3-alkyl-4-piperidones for the synthesis of 3,4-disubstituted piperidines is illustrated by the synthesis of ethyl 3-ethyl-4-piperidylacetate (*dl*-ethyl cincholoiponate).

MADISON, WISCONSIN RECEIVED FEBRUARY 15, 1946

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[15] Andrews, Cristol, Lindenbaum and Young, THIS JOURNAL, 67, 715 (1945).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Studies of 1,3-Dienes. II. Stereoisomerism of Bromides and Glycols Derived from 2,3-Dimethyl-1,3-butadiene[1]

BY ORVILLE J. SWEETING[2] AND JOHN R. JOHNSON

The addition of bromine to aliphatic 1,3-dienes is a well known reaction but with few exceptions the structure and configuration of the resulting bromides and the corresponding alcohols have not been definitely established. The older work in this field was not always interpreted correctly as the early investigators did not take cognizance of the marked tendency of the 1,2- and 1,4-dibromides to undergo anionotropic transformations (allylic rearrangements). Thus, the liquid and solid dibromide of 1,3-butadiene were believed at first to be the stereoisomeric *cis-* and *trans*-1,4-dibromo-2-butenes[3] but more recent studies have shown them to be the structurally isomeric 1,2- and 1,4-dibromides, which are quite readily interconverted.[4,5] 1,3-Cyclopentadiene is reported to yield three dibromides: a liquid 1,2-dibromide,[6] a liquid (*cis*) 1,4-dibromide, and a solid (*trans*) 1,4-dibromide.[7] The present paper deals

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[1] First paper, THIS JOURNAL, 63, 131 (1941).

[2] Present address, Department of Chemistry, Indiana University, Bloomington, Ind.

[3] Griner, *Compt. rend.*, 116, 723 (1893); 117, 553 (1894).

[4] Prévost, *Ann. chim.*, (10) 10, 113, 356 (1928); *Bull. soc. chim.*, (4) 43, 996 (1928).

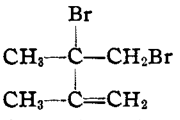
[5] Farmer, Lawrence and Thorpe, *J. Chem. Soc.*, 729 (1928).

[6] Farmer and Scott, *ibid.*, 174 (1929).

[7] Thiele, *Ann.*, 308, 333 (1899); see also, Blomquist and Mayes, *J. Org. Chem.*, 10, 134 (1945).

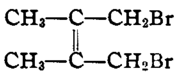
with the bromides formed from 2,3-dimethyl-1,3-butadiene and certain derivatives of them.

The addition of bromine to 2,3-dimethyl-1,3-butadiene could lead to two structurally isomeric dibromides, the 1,2-dibromide (I) and the 1,4-dibromide, and the latter can exist in a *cis*- or *trans* configuration (II, III)



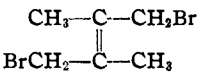
$$\begin{array}{l} \quad\ Br \\ \quad\ \ | \\ CH_3{-}C{-}CH_2Br \\ \quad\ \ | \\ CH_3{-}C{=}CH_2 \end{array}$$

dl-1,2-dibromide
I



$$\begin{array}{l} CH_3{-}C{-}CH_2Br \\ \quad\ \ \| \\ CH_3{-}C{-}CH_2Br \end{array}$$

cis-1,4-dibromide
II



$$\begin{array}{l} \qquad\quad CH_3{-}C{-}CH_2Br \\ \qquad\qquad\quad \| \\ BrCH_2{-}C{-}CH_3 \end{array}$$

trans-1,4-dibromide
III

As further addition of bromine could lead to the *meso*- and racemic forms of 1,2,3,4-tetrabromo-2,3-dimethylbutane, it is theoretically possible for this symmetrical 1,3-diene to yield five different bromine addition products having different physical properties, and the relative amounts of the individual bromides could vary widely with different experimental conditions.

In the present work three bromides were obtained from 2,3-dimethyl-1,3-butadiene: a liquid dibromide, b. p. 77.5–79.5° (5 mm.); a crystalline dibromide, m. p. 47–47.5°; and a solid tetrabromide, m. p. 138.5–139°. With some concession for minor discrepancies these products correspond to bromides that have been reported by previous investigators,[8–11] but there have not been sufficient data to establish fully their identity, particularly that of the liquid dibromide.

The addition of one mole of bromine to the diene in chloroform solution at temperatures from −20° to +30° gave 85–90% yields of a colorless dibromide, m. p. 47–47.5°, together with small quantities of the liquid dibromide and solid tetrabromide. In petroleum ether at 0° the reaction produced about 75% yields of the same crystalline dibromide, 4–5% of the liquid dibromide, and 6–8% of the same tetrabromide. Exploratory experiments indicated that the amount of liquid dibromide formed was not affected appreciably by the temperature of reaction, over the range from −80° to +50°. However, when the reaction was carried out slowly in very dilute chloroform solution, with strong ultraviolet illumination, the quantity of liquid dibromide rose to 55% of the theoretical and that of the solid dibromide fell to 10–15%.

The crystalline dibromide has been shown definitely by previous workers to be a 1,4-dibromo-2,3-dimethyl-2-butene, since it gives 80% of the calculated amount of bromoacetone upon ozonolysis and forms a 1,4-dibromo-2,3-dimethyl-2,3-butanediol by hydroxylation with permanganate.[9,10] The solid dibromide is quite volatile and sublimes readily at room temperature; when heated rapidly in small quantities it distils unchanged (b. p. 88.5–91° (5 mm.)) and resolidifies immediately in the cooled receiver. If distilled slowly the solid gives a liquid distillate, which on redistillation distils at 76–78° (5 mm.) and is indistinguishable from the liquid dibromide isolated directly from the addition of bromine to the diene. The pure crystalline dibromide remains unaltered over a period of several weeks at 20° but after a few months becomes discolored and undergoes partial liquefaction.

Macallum and Whitby[10] examined the behavior of the liquid and solid dibromide toward diethylamine (at 100°) but were unable in this way to establish the identity of the liquid bromide. Farmer, Lawrence and Scott[9] subjected the liquid dibromide to permanganate oxidation and to ozonolysis. Their extensive investigations failed to establish definitely the presence of a 1,2-dibromide and suggest that their liquid form was a mixture of the *cis*- and *trans*-1,4-dibromides. The previous investigators[9,10] have reported that the boiling points of the liquid and solid dibromide are practically identical but the present work has shown that two distinct fractions can be obtained by distillation through an efficient column: **liquid dibromide,** b. p. 77.5–79.5° (5 mm.) (previously reported, 105–110° (18 mm.),[10] 101–105° (15 mm.)[9]); **solid dibromide,** b. p. 88.5–91.5° (5 mm.), m. p. 47–47.5° (previously reported, 105–110° (18 mm.),[10] 103–105° (15 mm.)[9]). The *freshly distilled* liquid dibromide, b. p. 77.5–79.5° (5 mm.), appears to be essentially a pure individual but it rapidly undergoes isomerization. After standing for a short while the liquid will yield crystals of the solid dibromide when cooled to −30°.[12] All of our experiments were carried out with the freshly distilled liquid. Ozonolysis of a ten-gram sample gave 57% of the amount of bromoacetone calculated for a 1,4-dibromide and no formaldehyde could be detected, indicating the absence of any appreciable quantity of the 1,2-dibromide (I).

The liquid and solid dibromide reacted sluggishly with bromine and both gave the same solid tetrabromide, m. p. 137–138°, which was identical with the tetrabromide isolated directly from the addition of bromine to the diene. As the conditions of reaction were conducive to isomerization, this observation merely suggests that the product is derived from the more reactive isomer. Although metathetical reactions of allylic bromides usually do not afford unequivocal structure evidence, the reaction of the dibromides with potassium acetate was explored briefly. The solid

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[8] Kondakow, *J. prakt. Chem.*, (2) **62**, 166 (1900); Courtot, *Bull. soc. chim.*, (3) **35**, 969 (1906).

[9] Farmer, Lawrence and Scott, *J. Chem. Soc.*, 510 (1930).

[10] Macallum and Whitby, *Trans. Roy. Soc. Can.*, **22**, III, 33 (1928).

[11] Kogerman, *Sitzber. naturforsch. Ges. Univ. Tartu*, **41**, 249 (1934); *C. A.*, **29**, 3297 (1935).

[12] Kogerman[11] reported the isolation of "pure *cis*-1,4-dibromo-2,3-dimethyl-2-butene," m. p. 4.0–4.1°, by fractional crystallization of the liquid dibromide from ethanol at liquid air temperatures. The homogeneity of this dibromide was not established and the m. p. was determined with a small amount of material, from a cooling curve showing four arrests.

TABLE I

PROPERTIES OF DERIVATIVES OF 2,3-DIMETHYL-1,3-BUTADIENE

	B. p. or m. p., °C.	P^0	MR_D[a] (calcd.)	$\mu \times 10^{18}$[b]
Liquid 1,4-dibromide (*cis*)	b. 77.5–79.5 (5 mm.)	161	44.97	2.49
Solid 1,4-dibromide (*trans*)	m. 47–47.5	106	44.97	1.72
Liquid 1,4-diacetate (*cis*)	b. 108–111 (7 mm.)	189	51.22	2.58
Solid 1,4-diacetate (*trans*)	m. 38–39	125	51.22	1.90
Liquid 1,4-diol (*cis*)	b. 110–115 (5 mm.)	162	32.49	2.52
Solid 1,4-diol (*trans*)	m. 57–58	109	32.49	1.93
Solid 1,2,3,4-tetrabromide	m. 138.5–139	110	60.97	1.55
[1,4-Dibromo-2-butene (*trans*)][c]	m. 52–53	90	35.74	1.63

[a] Calculated from values given in Gilman's "Organic Chemistry," 2nd ed., 1943, John Wiley and Sons, New York, N. Y. [b] Calculated at 25°, using the relationship $\mu = 1.28 \times 10^{-20} \sqrt{T(P^0 - MR_D)}$. [c] The dipole moment of the solid 1,4-dibromide of 1,3-butadiene is included for comparison with that from 2,3-dimethylbutadiene.

dibromide was transformed readily into a crystalline diacetate, m. p. 38–39°, which produced on saponification a crystalline diol, m. p. 57–58° (*bis*-phenylurethan, m. p. 157–157.5°); the liquid dibromide gave a liquid diacetate, b. p. 108–111° (7 mm.), and a liquid diol, b. p. 110–115° (5 mm.) (*bis*-phenylurethan, m. p. 147–148°). The liquid diacetate is different from the known 1,2-diacetate (b. p. 92–102° (12 mm.))[13] and appears therefore to be one of the stereoisomeric 1,4-diacetates.

The solid and liquid diacetate took up bromine readily and from either compound there was obtained a liquid 1,4-diacetoxy-2,3-dibromo-2,3-dimethylbutane, b. p. 73–76° (7 mm.). The products were very similar and appeared also to be identical with the liquid dibromo-diacetoxy compound obtained by prolonged action of silver acetate on the crystalline tetrabromide of 2,3-dimethyl-1,3-butadiene. In the presence of platinum catalyst the isomeric diacetates absorbed one mole of hydrogen.

Dipole moment measurements show that the solid dibromide has a lower moment than does the liquid dibromide, and a similar relationship holds for the corresponding diacetates and diols (Table I). The physical and chemical evidence affords reasonable grounds for assigning the *trans*-configuration to the solid dibromide, and by analogy to the solid diacetate and solid diol. All of the evidence is consistent with the view that the liquid bromide (b. p. 77.5–79.5° (5 mm.)) is the *cis*-1,4-dibromide (II), and that the liquid diacetate and liquid diol derived from this dibromide are largely if not entirely the *cis*-isomers.

Experimental[14]

2,3-Dimethylbutadiene.—Anhydrous pinacol, pinacol hydrate, or pinacolone was dehydrated by rapid passage over activated alumina at 540–560°.[15] After drying the product over anhydrous calcium sulfate, it was fractionally distilled through a 15-cm. Widmer column and the fraction boiling at 69–70° at 741 mm. was collected; n^{25}_D 1.4310, d^{25}_4 0.72653.

Addition of Bromine to 2,3-Dimethylbutadiene.—Bromine was added to 2,3-dimethylbutadiene in chloroform or petroleum ether at several temperatures. Of sixteen runs made, three are reported in detail to illustrate the conditions used. Absorption of bromine was instantaneous, and some hydrogen bromide was always evolved.

(a) Forty-one grams (0.50 mole) of 2,3-dimethylbutadiene was dissolved in 200 ml. of chloroform and the mixture was cooled in an ice–salt mixture to −10°. Bromine (80.0 g., 0.50 mole) was dissolved in 150 ml. of chloroform and dropped into the flask over a period of five hours with vigorous stirring. After removal of most of the solvent, 105.0 g. of 1,4-dibromo-2,3-dimethyl-2-butene was isolated (87% yield). A sample melted at 47.0–47.5° after five recrystallizations from petroleum ether (b. p. 30–60°). The solid sublimes readily and the vapor is a strong lachrymator.

Anal. Calcd. for $C_6H_{10}Br_2$: Br, 66.08. Found: Br, 65.85.

Other runs similar to this were made at 20 to 30° and −20 to −10°, with essentially the same results. A small quantity of liquid dibromide and crystalline tetrabromide, m. p. 137–138°, could be obtained from the filtrates.

(b) Seventy-six grams (0.93 mole) of 2,3-dimethylbutadiene was dissolved in 200 ml. of petroleum ether (b. p. 30–60°). After the mixture had been cooled to −5°, 148 g. (0.93 mole) of bromine was dropped in with stirring at such a rate that the temperature remained below 0°. This required seven hours. After about half of the bromine had been added, colorless crystals began to separate; by the end of reaction, a thick slurry had formed. The solid, amounting to 25.5 g., was filtered off and found to be 1,2,3,4-tetrabromo-2,3-dimethylbutane; m. p. 138.5–139.0° after two recrystallizations from absolute ethanol. The tetrabromide is insoluble in petroleum ether, slightly soluble in diethyl ether, very soluble in chloroform and benzene.

Anal. Calcd. for $C_6H_{10}Br_4$: Br, 79.59. Found: Br, 78.90.

After having been cooled for twelve hours at −10°, the filtrate deposited crystals of the solid dibromide; weight, 145.5 g. (65% yield). The liquid filtrate was submitted to fractional distillation in a vacuum and gave 9.1 g. (4% yield) of a liquid dibromide, b. p. 67–75° (4 mm.), and an additional 21.5 g. (total yield, 75%) of the solid dibromide, b. p. 88.5–91.0° (5 mm.). The latter solidified in the receiver and was identical with the solid dibromide obtained previously.

(c) Eighty-nine grams (1.1 moles) of 2,3-dimethylbutadiene was dissolved in 650 ml. of chloroform. The mixture was cooled to −10° and 173 g. (1.1 moles) of bromine dissolved in 100 ml. of chloroform was added dropwise with stirring during two hours. Meanwhile the temperature slowly rose, but at no time exceeded 30°. The reaction mixture was illuminated with ultraviolet light from a mercury arc (in quartz) during the addition of bromine and during a subsequent eight-hour period of stirring at 25°. After the solvent had been removed at 25–28° in a vacuum, the residual oil was distilled under

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[13] Criegee, *Ann.*, **481**, 263 (1930).

[14] All temperatures were measured with thermometers previously compared with thermometers standardized by U. S. Bureau of Standards. Melting points were determined by the capillary tube method and all temperatures are uncorrected.

[15] Newton and Coburn, "Organic Syntheses," **22**, 40 (1942).

reduced pressure. Three fractions were collected: a 22.6 g. forerun; a liquid main fraction amounting to 129.0 g., b. p. 77–80° (5 mm.), (49% yield, calcd. as dibromide); and a third fraction of 26.7 g., b. p. 88–92° (5 mm.), (10% yield) which solidified in the receiver and proved to be the solid dibromide.

The main (liquid) fraction was carefully fractionated through a 30-cm. electrically heated column packed with glass helices. By this procedure was obtained 120.5 g. of nearly colorless, liquid dibromide, b. p. 77.5–79.5° (5 mm.) (46% yield); d^{25}_4 1.6695, n^{60}_D 1.5420, n^{25}_D 1.5558. It was exceedingly unpleasant to handle, since it was lachrymatory like the solid dibromide. On standing a few days in the light at room temperature, it became dark.

Anal. Calcd. for $C_6H_{10}Br_2$: Br, 66.08. Found: Br, 65.36.

A control experiment carried out under similar conditions, except that ultraviolet illumination was omitted, gave an 80% yield of the solid dibromide.

Ozonolysis of the Liquid (*cis*) Dibromide.—Ten grams of the freshly distilled liquid dibromide was dissolved in 200 ml. of petroleum ether (b. p. 0–30°) and ozonized oxygen was passed through the solution for ten hours (sufficient to furnish twice the calcd. amount of ozone). The temperature was maintained at about −70° by a Dry Ice–methanol freezing mixture. At the end of this time, the solution had acquired a brilliant blue color and colorless crystals had separated. The solution became yellow after standing for ten hours at −30°, and the ozonide became a dense yellow oil.

The ozonide was decomposed under reducing conditions in the customary manner[16] and the effluent gases were washed through two efficient gas washing bottles filled with water. No trace of formaldehyde was found by either the Fulton[17] or Eury[18] tests. Bromoacetone, amounting to 6.4 g. (57%), was collected at 40–43° (14 mm.) and was identified by forming the 2,4-dinitrophenylhydrazone, m. p. 122–123°. The latter was compared with the 2,4-dinitrophenylhydrazone prepared from an authentic sample of bromoacetone.[19] This compound, bright orange in color, melted sharply at 123.0–123.5° after several recrystallizations from an equal mixture of ethyl acetate and ethanol. Melting point of a mixture of these two phenylhydrazones was 121–123°.

Conversion of *trans*- to *cis*-1,4-Dibromo-2,3-dimethyl-2-butene.—A 25.0-g. sample of *trans*-1,4-dibromo-2,3-dimethyl-2-butene was placed in a small apparatus for vacuum distillation and heated slowly under reduced pressure. The distillate, 12.1 g. of a yellow-green oil, was collected over a period of fifteen hours, at a vapor temperature of 55–70° (5 mm.) (inaccurate owing to slow distillation rate) and a heating bath temperature of 120°. Fractionation of the lachrymatory oil gave a negligible amount of low boiling material and 11.1 g. of a nearly colorless dibromide, b. p. 76–78° (5 mm.), having properties identical with those of *cis*-1,4-dibromo-2,3-dimethyl-2-butene obtained directly from the diene.

Addition of Bromine to 1,4-Dibromo-2,3-dimethyl-2-butenes.—(a). Five grams (0.02 mole) of *cis*-1,4-dibromo-2,3-dimethyl-2-butene was dissolved in 100 ml. of petroleum ether (b. p. 60–70°) and refluxed for five hours with one equivalent of bromine (3.2 g.). Reaction occurred very slowly and the solution was not completely decolorized at the end of five hours. The brown precipitate was suction filtered, and on recrystallization from ethanol gave 6.4 g. (76% yield) of 1,2,3,4-tetrabromo-2,3-dimethylbutane, m. p. 137–138°. It was identified by mixed fusion under the microscope, using an authentic sample for comparison.

(b). Five grams (0.02 mole) of *trans*-1,4-dibromo-2,3-dimethyl-2-butene was dissolved in 150 ml. of petroleum ether (b. p. 60–70°) and was refluxed for six hours with one mole of bromine (3.2 g.). The color of the solution became lighter, but was not entirely discharged. Recrystallization of the product twice from boiling ethanol gave 5.0 g. (60% yield) of 1,2,3,4-tetrabromo-2,3-dimethylbutane, m. p. 137.5–138.0°. Identification was confirmed by mixed fusion under the microscope.

Reaction of 1,2,3,4-Tetrabromo-2,3-dimethylbutane with Silver Acetate.—A mixture of 15 g. of 1,2,3,4-tetrabromo-2,3-dimethylbutane with 25 g. of freshly prepared silver acetate in glacial acetic acid, stirred at 85–90° for fourteen hours, gave 2.5 g. of an oil, b. p. 72–75° (7 mm.). This material was colorless when freshly distilled, but became green within a few minutes and was badly discolored after standing for about five hours in the light at room temperature.

Anal. Calcd. for $C_{10}H_{16}O_4Br_2$: Br 44.41. Found: Br, 43.85.

The product is probably 1,4-diacetoxy-2,3-dibromo-2,3-dimethylbutane, since it appears to be identical with that obtained by adding bromine to either *cis*- or *trans*-1,4-diacetoxy-2,3-dimethyl-2-butene (see below). When anhydrous potassium acetate was used in a similar experiment the tetrabromide was recovered unchanged.

***trans*-1,4-Diacetoxy-2,3-dimethyl-2-butene.**—Sixty grams (0.61 mole) of freshly fused, finely pulverized potassium acetate was heated for ten hours at reflux temperature with 65 g. (0.27 mole) of *trans*-1,4-dibromo-2,3-dimethyl-2-butene in 550 ml. of absolute ethanol. Rapid precipitation of potassium bromide occurred, and at the end of the heating period 96% of the calcd. amount of potassium bromide was recovered by filtration. The filtrates were concentrated and the product was isolated by pouring onto crushed ice. The air-dried product weighed 35.8 g. (67%) and melted at 37–38°. A sample purified for dipole moment measurements, by reprecipitation twice from ethanol and dried for five days over phosphoric anhydride, melted at 38.5–39.0°.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.04; sapon. equiv., 100.1. Found: C, 59.83; H, 7.90; sapon. equiv. 99.0.

trans-1,4-Diacetoxy-2,3-dimethyl-2-butene is very soluble in the common organic solvents, and though not appreciably soluble in water at 0°, is very soluble in water at 20°.

***cis*-1,4-Diacetoxy-2,3-dimethyl-2-butene.**—By a procedure similar to the preceding one, 73.6 g. of potassium acetate and 60.5 g. (0.25 mole) of *cis*-1,4-dibromo-2,3-dimethyl-2-butene gave 48.5 g. (88%) of crude product which yielded 37.5 g. (75%) of a colorless fragrant oil on distillation, b. p. 108–111° (7 mm.) (138–144° (28 mm.)). No bromoacetate was found, and 92% of the calcd. amount of potassium bromide was recovered.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.04; sapon. equiv., 100.1. Found: C, 59.90; H, 7.95; sapon. equiv., 99.7.

cis-1,4-Diacetoxy-2,3-dimethyl-2-butene is very soluble in the common organic solvents and is quite soluble in water at room temperature (markedly less so at 0°). The refractive index was measured: n^{25}_D 1.4532, n^{60}_D 1.4416.

Addition of Bromine to *cis*- and *trans*-1,4-Diacetoxy-2,3-dimethyl-2-butenes.—(a) To a solution of 5.0 g. (0.025 mole) of *trans*-1,4-diacetoxy-2,3-dimethyl-2-butene in 100 ml. of carbon tetrachloride, 4.0 g. (0.025 mole) of bromine was added at −10°. The bromine was taken up very rapidly and the product was isolated by distillation. There was obtained 1.5 g. (17% yield) of a colorless liquid, b. p. 70–72° (7 mm.), which rapidly became green and turned black after several hours. This material seemed to be identical with that obtained by treatment of the tetrabromide with silver acetate.

Anal. Calcd. for $C_{10}H_{16}O_4Br_2$: Br, 44.41. Found: Br, 44.25.

(b) In like manner, *cis*-1,4-diacetoxy-2,3-dimethyl-2-butene rapidly reacted with bromine to give 1.4 g. (16%)

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[16] Noller and Adams, THIS JOURNAL, **48**, 1074 (1926).

[17] Fulton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 199 (1931).

[18] Eury, *Bull. sci. pharmacol.*, 85 (1904); *Suddeut. Apoth.-Ztg.*, 187 (1906); ("Merck Index," 5th Ed., Merck and Co., Rahway, 1940, p. 713).

[19] "Org. Syntheses," John Wiley and Sons, New York, 1943, Coll. Vol. II, p. 88.

of an oil, b. p. 74–76° (8 mm.) (130–132° (34 mm.)), apparently identical with that obtained from addition of bromine to the *trans* diacetate and from treatment of the tetrabromide with silver acetate. Distillation in a nitrogen atmosphere gave a colorless lachrymatory product, which discolored rapidly.

Anal. Calcd. for $C_{10}H_{16}O_4Br_2$: Br, 44.41. Found: Br, 44.10.

***trans*-2,3-Dimethyl-2-butene-1,4-diol.**—Ten grams (0.0500 mole) of *trans*-1,4-diacetoxy-2,3-dimethyl-2-butene and 31.5 g. (0.100 mole) of pulverized barium hydroxide octahydrate were stirred together in 50 ml. of ethanol under reflux for five hours. After precipitation of inorganic salts with carbon dioxide, the concentrated filtrates gave 2.7 g. (46%) of the diol, a white crystalline solid, m. p 57–58° after recrystallization from ethanol. The bis-phenylurethan, prepared by warming the diol with phenyl isocyanate and recrystallizing from chloroform, melted at 157.0–157.5°.

Anal. Calcd. for $C_{20}H_{22}O_4N_2$: C, 67.77; H, 6.26; N, 7.91. Found: C, 67.60; H, 6.20; N, 7.82.

***cis*-2,3-Dimethyl-2-butene-1,4-diol.**—By a procedure analogous to the foregoing, substituting potassium hydroxide in the saponification, the corresponding *cis*-1,4-diacetoxy-2,3-dimethyl-2-butene gave a liquid diol, b. p. 110–115° (5 mm.). The bis-phenylurethan melted at 147.0–148.0° after recrystallization from chloroform. A mixture of the two phenylurethans melted at 132–140°.

Anal. Calcd. for $C_{20}H_{22}O_4N_2$: C, 67.77; H, 6.26; N, 7.91. Found: C, 67.35; H, 6.16; N, 7.85.

2,3-Dibromo-2,3-dimethylbutane.—As this dibromo compound could be formed by addition of hydrogen bromide to 2,3-dimethylbutadiene, and its recorded melting points vary from 140 to 192°, a reference sample was prepared for comparison with the 1,4-dibromides obtained in the present work. The product from pinacol and aqueous hydrobromic acid[20] after careful drying and sublimation in a vacuum, melted at 177–177.5° in a *sealed tube*.

Anal. Calcd. for $C_6H_{12}Br_2$: Br, 65.50. Found: Br, 65.23.

The compound has a camphoric odor and sublimes quite readily.

Dipole Moment Measurements.—Thiophene-free benzene for use as solvent in the dipole moment measurements was dried for three days over calcium oxide, distilled over sodium, and stored over sodium wire. Physical constants were: b. p. 79.0–79.4° (745 mm.), n^{25}_{D} 1.4973, d^{25}_{D} 0.8725. Samples were weighed by difference from dropping bottles directly into the solvent and the dielectric constant was measured immediately, at several concentrations, each solution being diluted to prepare the succeeding one.

The apparatus used employs the heterodyne-beat method,[21] with an oscillator of 1.57 megacycles frequency. The measuring cell, of about 135 ml. volume, resembled that described by Smyth.[22] All measurements were made with the cell in a thermostat at 25.00 ± 0.06°.

Summary

The addition of bromine to 2,3-dimethylbutadiene has been reëxamined. Three geometrically isomeric pairs of compounds of the general formula, $A—CH_2—C(CH_3)=C(CH_3)—CH_2—A$, have been prepared in which A is —Br, $—OCOCH_3$, and —OH and the configurations have been correlated by measurement of the dipole moments.

The dipole moments of the solid tetrabromide, 1,2,3,4-tetrabromo-2,3-dimethylbutane, m. p. 138.5–139°, and of the crystalline 1,4-dibromide (*trans*) obtained from butadiene have been measured also.

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[20] Thiele, *Ber.*, **27**, 454 (1894).

[21] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., Inc., New York, N. Y., 1931; Le Fèvre, "Dipole Moments," Chemical Publishing Co., New York, N. Y., 1938.

[22] Smyth, THIS JOURNAL, **50**, 1547 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SOUTHWESTERN COLLEGE, WINFIELD, KANSAS]

Dielectric Constants of the Methanol–Water System from 5 to 55°[1]

BY PENROSE S. ALBRIGHT[2] AND LOUIS J. GOSTING[3]

It is desirable to have available accurate dielectric constant data for several liquids or solutions so they may be used as standards in different dielectric constant ranges as well as for many other purposes. Benzene and water are excellent standards for the low and high dielectric constant ranges, respectively. For the middle range, the lower aliphatic alcohols are one of the satisfactory groups of liquids for this purpose since they are quite easily purified, the lower members of the series are miscible with water in all proportions, and they have suitable dielectric constants.

Unfortunately, the data for the first member of this series, methanol, and its aqueous solution have been inconsistent. Jones and Davies[4] have summarized the data up to 1939 and have added their values for the dielectric constants of the methanol–water system at 20 and 25°. Their values, as do ours, differ considerably from the dielectric constant results for the methanol–water solutions, over a wide range of temperatures, as measured by Åkerlöf.[5]

It has been the purpose of this research to determine the dielectric constants of the methanol–water system in the temperature range 5 to 55°, using the equipment described below.

Experimental

Materials.—Conductivity water was prepared by three distillations. Tap water was first given an ordinary distillation. This distillate was distilled from a mixture of dilute sulfuric acid and potassium permanganate. The

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[1] Condensed from a thesis on file at Southwestern College, Winfield, Kansas.

[2] Present address: Department of Physics, University of Wichita, Wichita, Kansas.

[3] Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

[4] Jones and Davies, *Phil. Mag.*, **28**, 307 (1939).

[5] Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).