Highly purified samples of I (>99.8 mole %) and of II (>99.3 mole %) were prepared in the present work and their infrared spectra measured in the liquid state (see Table I).

TABLE I

FREQUENCIES OF SIGNIFICANT INFRARED ABSORPTION MAXIMA[a] OF METHYLENECYCLOBUTANE (I) AND 1-METHYLCYCLOBUTENE (II), IN cm.$^{-1}$

I—3083 (w,) 2990 (s), 1760 (m), 1680 (s) ,1423 (s), 1393 (w), 1251 (w), 1222 (w), 1199 (w), 1170 (m), 1075 (m), 1026 (w), 956 (w), 887 (s), 792 (w), 767 (w), 736 (w)

II—3325 (w), 3170 (w), 3050 (m), 2910 (s), 2721 (m), 2295 (w), 2165 (w), 2105 (w), 2025 (w), 1820 (w), 1761 (w), 1724 (m), 1640 (s), 1584 (m), 1437 (s), 1374 (m), 1276 (s), 1212 (w), 1188 (s), 1172 (s), 1088 (m), 1033 (m), 984 (s), 952 (s), 895 (m), 857 (s), 732 (s)

[a] Intensity: s, strong; m, medium; w, weak.

A previously published[12] spectrum of I in the liquid state contains not only the most prominent bands[13] of contaminating spiropentane (at 782, 990, 1051 and 1155 cm.$^{-1}$), but, as shown by comparison with the present data, even the medium intensity absorptions of the same impurity in the vicinity of 2015, 2310 and 2420 cm.$^{-1}$. A more recent spectrum,[14] measured on a purer specimen of I (but still containing some spiropentane, as indicated by a band of medium intensity in the vicinity of 990 cm.$^{-1}$), does not provide sufficient detail on the position of the absorption maxima.

Previously published data[12] on II include several bands, *e.g.*, at 804, 1110, 1130, 1345 and 1670 cm.$^{-1}$, which are absent in the present spectrum. The rather strong foreign band at 1670 cm.$^{-1}$ is obviously due to contaminating I.

The n.m.r. spectrum of II was also measured. It showed: (1) a doublet at 1.66 p.p.m. (J = 2 c.p.s.), due to the methyl group situated at the double bond; (2) a rather sharp line at 2.38 p.p.m., arising from the allylic hydrogens; and (3) a closely split signal centered at 5.60 p.p.m., due to the vinylic hydrogen. The relative intensities of the three signals were in the ratio 3:4:1, respectively.

Experimental

Methylenecyclobutane (I).—The commercially available I contained 16% of 2-methyl-1-butene and 4% of spiropentane as side products. I of about 99% purity was obtained by fractional distillation on a 70-plate spinning band column. The best portion of the distillate (>99.8 mole %) had b.p. 41.3° at 760 mm., n^{20}_{D} 1.4212.

Preparation of 1-Methylcyclobutene (II). Isomerization Procedure.—The alumina (Alcoa, grade F-1, 100 mesh) was pretreated at 300–320° under nitrogen for 24 hr., and employed immediately afterwards. In a typical catalyst preparation 12 g. of alumina was introduced into a three-necked flask equipped with a condenser, a dropping funnel, and a mechanical stirrer provided at its end with a semicircular impeller. The system, was purged with nitrogen, and the alumina was heated to 140°, at which point 2 g. of sodium was added. Mixing at 140° was continued for 20 min. and the black-colored catalyst obtained was cooled to 2–3° in an ice–water bath. A 50-g. sample of I was added in one portion to the flask; it is essential to use material freshly distilled over sodium, since samples not so treated deactivate the catalyst. The flow of nitrogen was reduced to a minimum and iced water circulated through the condenser. Stirring was continued for 2 hr., keeping the temperature below 5°. At the end of this period the supernatant liquid was quickly decanted into a precooled flask. The rest of the product, partly adsorbed on the catalyst, was recovered by distillation at 100 mm. into a Dry Ice–acetone trap. The total liquid weighed 47 g. (recovery, 94%) and contained 86% of II. Fractional distillation on the above column gave II, about 99% pure. The best portion of the distillate (>99.3%) had b.p. 37.3° at 760 mm., n^{20}_{D} 1.4081.

Analysis.—The purity of the olefin samples was determined by gas chromatography using silver nitrate–glycol[15] as the stationary phase. The infrared spectra were measured with a Model IR 7 Beckman spectrophotometer. A Varian A-60 spectrometer was employed for the measurement of the n.m.r. spectrum of II, using carbon tetrachloride as solvent and tetramethylsilane as the reference compound.

Acknowledgment.—Thanks are due to Mr. Ch. Greener and Mr. M. Lahmi for technical assistance. The authors are also indebted to Dr. S. Pinchas and Dr. Y. Shvo for the measurement of the infrared and n.m.r. spectra, respectively.

---

[12] F. F. Cleveland, M. J. Murray, and W. S. Gallaway, *J. Chem. Phys.*, **15**, 742 (1947).

[13] F. F. Cleveland, M. J. Murray, and W. S. Gallaway, *ibid.*, **16**, 158 (1948).

[14] D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4012 (1956).

[15] J. Shabtai, J. Herling, and E. Gil-Av, *J. Chromatog.*, **11**, 32 (1963); **8**, 349 (1962).

Preparation of 2-Bromo-3-methylbutane by the Radical Addition of Hydrogen Bromide to 2-Methyl-2-butene

WILLIAM J. BAILEY AND STEPHEN S. HIRSCH[1]

Department of Chemistry, University of Maryland, College Park Maryland

Received October 15, 1962

During the course of an investigation of the pyrolysis of olefins, a quantity of 2-bromo-3-methylbutane was desired. A search of the literature revealed that details concerning the synthesis and isolation of this structurally simple bromide were lacking.[2] Needless to say, this bromide has not been obtained in satisfactory yields from 3-methyl-2-butanol.[2] Although the peroxide-catalyzed addition of hydrogen bromide to 2-methyl-2-butene appeared to be the most suitable approach, the literature is filled with inconsistencies concerning the best conditions for, and the products obtained from, such an addition. In many instances products were merely detected but not isolated, the reactions were run on very small quantities of material, and no yields were reported. Low temperature,[3] no sol-

---

[1] American Chemical Society Petroleum Research Fund Fellow, 1959–1961; Celanese Fellow, 1961–1962; Goodyear Tire and Rubber Co. Fellow, 1962.

[2] For some of the problems involved in the preparation of 2-bromo-3-methylbutane from 2-methyl-2-butene, 3-methyl-2-butanol, or 3-methyl-1-butene see E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc. New York, N. Y., 1954 pp. 271–247 and pp. 367–411; A. Michael and N. Weiner, *J. Org. Chem.*, **5**, 395 (1940).

[3] A. Michael and N. Weiner, *ibid.*, **4**, 531 (1939).

[4] F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).

[5] F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, **7**, 491 (1942).

[6] W. E. Vaughan, F. F. Rust, and T. W. Evans, *ibid.*, **7**, 477 (1942).

vent,[3] much solvent,[4] exclusion of large amounts of oxygen,[5] irradiation with ultraviolet light,[6] addition of a co-catalyst,[7] strict exclusion of moisture,[4] and the presence of water,[2,8,9] were among the experimental conditions which have been attempted to effect abnormal addition of hydrogen bromide to various olefins. Although there are many examples of the reverse addition of hydrogen bromide to monosubstituted ethylenes in high yields, in the case of trisubstituted ethylenes where the competing ionic addition proceeds very readily, the yields are usually not as high. Thus, even though Kharasch and co-workers[8,10] claimed to have obtained high ratios of abnormal product by the peroxide-catalyzed addition of hydrogen bromide to isobutylene (87% isobutyl bromide) even in the presence of water, 2-methyl-2-butene formed only 64% of 2-bromo-3-methylbutane.[11] However, no attempt to isolate the product was reported.

We found that the addition of hydrogen bromide to 2-methyl-2-butene at room temperature, in very dilute pentane solution, under thoroughly dry conditions in the presence of benzoyl peroxide, worked very satisfactorily for the preparation of 2-bromo-3-methylbutane in a 55% yield. With two moles of olefin, an isomer ratio of 19:1 in favor of the anti-Markownikoff product was repeatedly obtained, in contrast to the less than 2:1 ratio previously reported,[11] while the over-all isolated yield approached the crude isomer preponderance of the earlier workers. Use of more concentrated solutions of olefin in pentane lowered the isomer ratio, but this may be rationalized when the reaction is used for preparative purposes, since the starting materials, are inexpensive, and the yield on a time basis can be increased.

Experimental

Until the addition of hydrogen bromide was completed all equipment and reagents were maintained thoroughly dry.[12] Glassware was dried at 140° overnight and vessels were allowed to cool with a Drierite-filled tube attached. A stirrer was fabricated from a 16-oz. polyethylene bottle by cutting it around in a continuous strip 0.25-in. wide and affixing this strip to a loop on the end of a glass rod and twisting through about twelve times. The ends of the strip were fastened by fabricating a "button" and "buttonhole" out of them. The stirrer was dried by storage in a large glass tube over magnesium perchlorate for several days. Commercial grade *n*-pentane was shaken repeatedly with concentrated sulfuric acid until the acid layer was colored only very slightly.

Into a 12-l., three-necked flask, equipped with a mercury-sealed stirrer and a straight-tube wide reflux condenser,[13] was distilled 7 l. of *n*-pentane directly from phosphorus pentoxide. Then 210 ml. (2.0 moles) of 2-methyl-2-butene (Phillips Petroleum Co., 99 mole % pure)[14] which had been dried over anhydrous sodium sulfate below 32° was pipetted from the desiccant into the reaction vessel. A 950-ml. Dry Ice condenser was affixed to the water condenser, and from a side arm, an inch from the top, a rubber tube led to a hood. Benzoyl peroxide, 22 g. (0.099 mole), which had been dried in a desiccator over magnesium perchlorate was added to the flask. Then hydrogen bromide, passed through a bubbler filled with paraffin oil and then a 36 × $^{5}/_{8}$ in. U-tube filled with magnesium perchlorate, was admitted to the flask over the liquid at a rate slightly faster than it could be absorbed with brisk stirring. Completeness of addition occurred within 1 to 1.5 hr., as evidenced by clouding of the solution and appearance of excess liquid hydrogen bromide dripping from the Dry Ice condenser.[15] After the condensers and gas inlet tube were replaced with an 18 × 1.25 in., helix-packed column, pentane was removed by distillation with stirring[16] until the volume was reduced to approximately 1 l., but the head temperature was not permitted to rise above 37°. The residual liquid was transferred to a 2-l. flask equipped with a thermometer extending into the liquid and more pentane was removed through a smaller column with stirring[16] until the flask temperature reached 55°, but with the head temperature maintained at or preferably below 37°.

The remaining liquid was distilled from the residual solids with stirring[16] without a column, under reduced pressure which was diminished in stages so that the flask temperature was maintained below 55° to prevent decomposition of the product. At the very end of the process the temperature was allowed to reach 60–65° under the best vacuum obtainable with a water aspirator. The receiver was packed in ice–salt and was connected to a Dry Ice condenser. The receiver was changed after the first half of the distillation so that the mole fraction of pentane would be low before the lower pressures were encountered. To hydrolyze the by-product *t*-amyl bromide the distillate was shaken vigorously in a 1-gal. jug for 2 hr. with 1 l. of water.[17] The organic layer was shaken for 2 min. with a small amount of concentrated hydrochloric acid. After the organic layer was cooled to 2°, it was briefly shaken with ice-cold water, then dilute, ice-cold sodium bicarbonate solution, and finally with two portions of ice–water. After the liquid was dried over calcium chloride, the pentane was removed through an 18 × $^{1}/_{3}$ in., helix-packed, vacuum-jacketed column with acetone at −60° circulated through the cold finger[18] with a high reflux ratio to cool the column, at approximately 550 mm., until the flask temperature reached 55°. This procedure was repeated at pressures of approximately 450, 350, 250, 150, 100, and 75 mm. until all the pentane was removed. After the acetone cooling was changed to conventional cold water cooling, distillation gave 165.6 g. (55%) of 2-bromo-3-methylbutane, b.p. 49.8–51.0° (75 mm.)[19]; $n^{20}\mathrm{D}$ 1.4445 [lit.[3] b.p. 115.3° (760 mm.); $n^{20}\mathrm{D}$ 1.4454]. The product can be stored in a thoroughly clean, ungreased, glass-stoppered bottle in the dark at 3–5° over a few lumps of anhydrous calcium chloride for long periods of time.

---

(7) W. E. Vaughan and F. F. Rust, British Patent 581,775 (October 24, 1946) [*Chem. Abstr.*, **41,** 3000b (1947)].

(8) M. S. Kharasch and W. M. Potts, *J. Am. Chem. Soc.*, **58**, 57 (1936).

(9) A. Johansson, *Arkiv. Kemi Mineral. Geol.*, **24A**, No. 30, 12 (1947).

(10) M. S. Kharasch and J. A. Hinckley, Jr., *J. Am. Chem. Soc.*, **56,** 1243 (1934).

(11) C. Walling, M. S. Kharasch, and F. R. Mayo, *ibid.*, **61**, 2693 (1939).

(12) All the standard methods for accomplishing this are not stated explicitly here, but it should be emphasized that precautions, at least comparable to those necessary for the preparation of a Grignard reagent, must be undertaken.

(13) Constrictions (bulbs, etc.) should be avoided in the water condenser so that refluxing liquid from the Dry Ice condenser will not cause water in narrow portions of the water jacket to freeze.

(14) This olefin also can be prepared by the method of Whitmore, *et al.* [F. C. Whitmore, C. S. Rowland, S. N. Wrenn, and G. W. Kilmer, *J. Am. Chem. Soc.*, **64**, 2970 (1942)]. The present authors found that a 54 × 1.5 in column packed with magnesium turnings (Grignard quality) was suitable for the preparation of 1 gal. of 2-methyl-2-butene, b.p. 39.0° (reported b.p. 39.5°), shown by vapor phase chromatography to be at least 99.6% pure.

(15) If there is any doubt as to the dryness of the system, the isomer ratio may be checked by vapor phase chromatography on a 2-m. di-*n*-decyl phthalate column (Perkin-Elmer Ax column) at 85°. The 2-bromo-3-methylbutane is eluted after the *t*-amyl bromide.

(16) At no point in the preparation should boiling stones be used as they appear to cause decomposition of the product.

(17) The chemical transformation of the by-product is undertaken to provide a greater boiling point spread. Mere conversion of the *t*-amyl bromide to *t*-amyl alcohol is not sufficient because the boiling point *vs.* pressure curves of the latter and 2-bromo-3-methylbutane approach each other as the pressure is lowered. (R. R. Dreisbach, "Pressure–Volume–Temperature Relationships of Organic Compounds," 3rd Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952).

(18) This temperature is easily reached by circulating acetone by means of a small pump through about 2–3 ft. of coiled, 0.25-in. copper refrigeration tubing immersed in a Dry Ice–acetone bath. Thick-walled rubber tubing wrapped with glass wool is used to complete the circuit. If −60° cannot be reached, a slightly higher temperature would probably do no harm.

(19) The reference quoted[17] may be used to advantage here to construct a curve relating boiling point to pressure in the event a pressure of exactly 75 mm. is not achieved. A pressure near this value should be used. If the pressure is too high, the product may decompose; if too low, the *t*-amyl chloride will be difficult to condense. The receiver is best kept in a Dry Ice bath. The material produced in this preparation was shown by vapor phase chromatography to be at least 99% pure.