The reaction mixture was cooled and diluted with water (70 ml.). The product was extracted with petroleum ether (b.p. 30–60°) and the extract was washed with dilute hydrochloric acid, then water. The dried extract (magnesium sulfate) was evaporated to give an oil whose infrared spectrum (neat) shows absorption at 3.1, 5.8, and 8.42 μ, indicating the product to be a mixture of alcohol and formate (**30**).[24]

The crude product was reduced with lithium aluminum hydride in anhydrous ether in the usual way. The resulting product was analyzed by v.p.c. (TCEP, 128°) and showed to be a mixture of two components (retention times 31.5 and 39.8 min.), the minor of which was the original **28**. The two alcohols were separated by preparative v.p.c. (combined 5-ft. TCEP and 5-ft. Carbowax column). The new alcohol (retention time 23 min.) (*i.e.*, the axial alcohol **31**) had an infrared spectrum very different from that of **28** (retention time, 28 min.).

Oxidation of each alcohol (10 mg.) with 6 *N* chromic acid (0.1 ml.) in acetone (0.2 ml.) gave ketone **27**, identified by infrared and v.p.c. comparisons with authentic material (Carbowax, 111°, single peak at 11.5 min.).

Preparation and Properties of 2- and 3-Bromo-1-methylcyclohexanes

ELLIOT N. MARVELL AND HAROLD SEXTON[1]

Department of Chemistry, Oregon State University, Corvallis, Oregon

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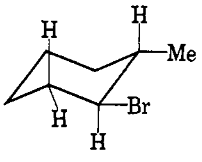
Samples of 2- and 3-bromo-1-methylcyclohexanes have been prepared by the Hunsdiecker method. Spectral methods showed these to be free of other position isomers, but to be mixtures of geometric isomers. Some attempts to prepare pure *cis* or *trans* isomers proved unsuccessful. The nature of the products obtained from a variety of methods of preparing such cycloalkyl bromides has been surveyed.

The considerable difficulties associated with the preparation of pure secondary bromides are well known.[2] Secondary cycloalkyl bromides, with their possibilities for geometric isomerism, provide a more complex problem than do aliphatic bromides. Recently Jensen and Gale[3] showed that cleavage of cycloalkylmercuric bromides under proper conditions can be achieved with complete retention of configuration, thereby providing an elegant mode of synthesis for geometrically uniform cycloalkyl bromides. The Hunsdiecker reaction has also been shown[3,4] to be useful for the preparation of unrearranged cycloalkyl bromides. Having need for pure samples of 2- and 3-bromo-1-methylcyclohexanes, we have studied the preparation of these substances in some detail. The results of this work are reported here.

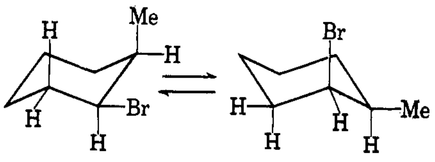
Identity and Purity.—Both 2-bromo-1-methylcyclohexane (I) and 3-bromo-1-methylcyclohexane (II) have been reported previously in the literature.[5] In no case, however, has unequivocal evidence been provided for identity and purity of these. Samples of I and II have been prepared now from the corresponding methylcyclohexanecarboxylic acids *via* the Hunsdiecker reaction. Satisfactory evidence for identity of I and II was provided in each case by (a) their mode of preparation, (b) their conversion *via* a Grignard reagent to 2- and 3-methylcyclohexanol, respectively, and thence to the relevant ketones which were identified by gas chromatography, and (c) the spectroscopic data discussed below. Both I and II were obtained as mixtures of *cis* and *trans* isomers when prepared in this way. A sample of I prepared from a nearly pure (m.p. 48–51°) *trans*-2-methylcyclohexanecarboxylic acid[6] was indistinguishable from a sample prepared from a liquid mixture of *cis* and *trans* isomers. The result parallels the observations of Eliel and Archarya.[4]

The n.m.r. spectrum of I is characterized by a very sharp doublet (J = 6.0 c.p.s.) at τ 8.90, and two low-field multiplets, one a clean sextet (doublets of a triplet, J = 10.5, 4.0 c.p.s.) centered at τ 6.32, the second an unresolved multiplet at τ 5.65. The ratio of the area under the 6.32 and 5.65 peaks to the rest of the spectrum is almost exactly 1:12. These data show that the product is a secondary bromide with one methyl group attached to a carbon bearing one hydrogen, and the chemical shift for the methyl group means the bromine atom must be attached to a carbon at least two carbons from the methyl. Excluded by this result alone are such rearrangement products as 1-bromo-1-methylcyclohexane, α-bromoethylcyclopentane, and 2-bromomethyl-1-methylcyclopentane. The presence of two peaks for the CHBr proton means that this is a mixture. Thus, the n.m.r. spectrum does not immediately eliminate II or mixtures of I and II as possibilities. Comparison of the spectrum with that of a sample ultimately identified as II shows (see below) that II cannot be present in I.

I is expected to be a mixture of *cis* and *trans* forms. The *trans* form (Ia) is conformationally uniform and its low-field CHBr proton is axial. From first-order analysis it should give rise to a sextet (doublets of a triplet) with $J_{a,a} > J_{a,e}$. Though nonuniform conformationally, the *cis* form Ib should have predominantly[7] an equatorial CHBr proton. Since $J_{a,e} \simeq$



Ia



Ib

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[1] National Science Foundation undergraduate participant in research during the summers of 1961 and 1962.

[2] J. Cason and J. S. Correia, *J. Org. Chem.*, **26**, 3645 (1961).

[3] F. R. Jensen and L. M. Gale, *J. Am. Chem. Soc.*, **82**, 148 (1960).

[4] E. L. Eliel and R. V. Acharya, *J. Org. Chem.*, **24**, 251 (1959).

[5] See for example (a) M. F. Shastakovskii, A. V. Bogdanov, and A. N. Volkov, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.*, 2184 (1962); (b) M. Murat, *Ann. Chem. Phys.*, **16**, 108 (1901); (c) M. Mousseron and R. Jacquier, *Bull. soc. chim. France*, [5]**18**, C80 (1951); (d) M. Mousseron, R. Granger, and J. Valette, *ibid.*, [5]**13**, 244 (1946); (e) M. Mousseron and R. Granger, *Compt. rend.*, **206**, 1486 (1938);

[6] A. Macbeth, J. A. Mills, and D. H. Simmonds, *J. Chem. Soc.*, 1011 (1949).

[7] Assuming the conformational equilibrium constant for Ib is similar to that of *cis*-4-bromo-1-methylcyclohexane,[8] the ratio of H_e to H_a should be near 9:1.

[8] F. R. Jensen and L. H. Gale, *J. Org. Chem.*, **25**, 2075 (1960).

[9] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp. 84–86.

$J_{e,e}$,[9] the dominant conformer of Ib should have a spectrum resembling an AX_3 quartet for the CHBr proton, the conformer of lesser importance a sextet (triplets of doublet). Generally the axial proton resonance should occur at a higher field than the equatorial.[10] Clearly the sextet at τ 6.32 is due to Ia. The peak at τ 5.65 which shows no discernible fine structure is assigned to the equatorial CHBr proton of Ib. On this basis, I consists of a mixture of 85 ± 5% and 15 ± 5% Ib. The somewhat unexpected observation that the equatorial methyls in Ia and Ib have identical chemical shifts is probably accounted for by their equivalent geometric relation to the neighboring axial or equatorial bromine.

The purity of I was established by spectroscopic means utilizing synthetic mixtures to check the limits of the method. The methyl protons of 1-bromo-1-methylcyclohexane (III) produce a very sharp singlet at τ 8.25 in the n.m.r. spectrum of that substance. As little as 1% of III in I can easily be detected, and no trace of this as a contaminant can be found from n.m.r. data. The n.m.r. spectrum of II shows a clean doublet due to the methyl protons at τ 9.10 and the limit of detectablity by this means lies about the 1% level. Again I is free from II by this test. This diagnosis is confirmed by infrared studies in the potassium bromide region. A very strong absorption band at 498 $cm.^{-1}$ characteristic of III is just barely visible in a thick-layer spectrum of I. There appears no inflection on the low frequency side of the 539-$cm.^{-1}$ band of I which could be due to the characteristic strong 523-$cm.^{-1}$ absorption of II. We conclude that the product of this Hunsdiecker reaction is at least 99.0% 2-bromo-1-methylcyclohexane, and the purity could be considerably better than that estimate which is definitely conservative.

The n.m.r. spectrum of the bromide (II) from the Hunsdiecker reaction of 3-methylcyclohexanecarboxylic acid shows a sharp doublet (J = 6.0 c.p.s.) at τ 9.10, a triplet of triplets[11] ($J_{a,a}$ = 11 c.p.s., $J_{a,e}$ = 4.0 c.p.s.) at 6.13, and an ill-resolved quintet (?) ($J_{e,a}$ = $J_{e,e}$ = 3.1 c.p.s.) at 5.50. Chemical shifts and coupling constants are consistent with a secondary cyclohexyl bromide having a methyl group on a carbon bearing a single proton, which is separated from the bromine-bearing carbon by at least one methylene group. The bromide consists of a mixture of *cis* and *trans* isomers, assignment being made on the basis of chemical shift and coupling constants similar to the one outlined in detail for I. Absence of a signal at τ 8.9 in the n.m.r. spectrum of II and lack of an inflection on the high frequency side of the 523-$cm.^{-1}$ band of II show that II is free of contamination by I. The level of detectability is in the region of 1%. The n.m.r. spectrum does not permit an accurate means for judging whether 4-bromo-1-methylcyclohexane (IV) is present in II. Fortunately the infrared spectrum makes this assessment possible, but not so accurately as in the earlier case. A relatively weak peak at 490 $cm.^{-1}$ in *trans*-IV is completely missing in a thick-layer spectrum of II. Therefore II from the Hunsdiecker process is at least 98% pure and consists of 60 ± 5% *cis* and 40 ± 5% *trans* isomers.

Attempts to prepare *cis* and *trans* isomers of I and II by cleavage of mercury salts failed. The 2-methylcyclohexylmercuric bromide obtained from the Hunsdiecker product was a liquid which failed to crystallize. Cleavage by the pyridine–bromide method[3] gave a 70:30 *trans–cis* mixture of I uncontaminated by other isomeric bromides. A solid mercury salt was obtained from a commercial sample of II. This melted at 88–90°, but was apparently not a pure geometric isomer for it gave a 60:40 *cis–trans* mixture of II.

Products from Other Methods.—Having established useful semiquantitative methods of analysis for the various methylcyclohexyl bromides, we have used these to survey the nature of the products obtained from a variety of preparative methods. Generally these were applied to the synthesis of I or IV, because commercial 3-methylcyclohexanol was difficult to purify.

Phosphorus tribromide has been widely used for the preparation of alkyl and cycloalkyl bromides from the corresponding alcohols. Eliel and Haber[12] have commented on the greater degree of rearrangement associated with that reagent as compared with phosphorus pentabromide. In light of their careful work with that latter reagent we did not investigate it further. The **Landauer and Rydon[13] method,** recently developed, has been successfully employed to prepare neopentyl iodide from neopentyl alcohol. Both this procedure and phosphorus tribromide have been used to convert 2- and 4-methylcyclohexanols (free of position isomers by gas chromatography) to bromides. As products obtained by either method were virtually identical, the comments will apply to both reactions. A series of preparations from 2-methylcyclohexanol gave mixtures of I, II, and III in which III was invariably the major constituent. The ratios of products varied quite widely, but III never constituted less than about 60% and normally made up *ca.* 80% of the product. A commercial sample labeled as practical grade I had a similar constitution. In view of the clean-cut synthesis of neopentyl iodide by Landauer and Rydon's method, the results noted here seem rather surprising. A possible explanation for the difference observed in these two cases is that a greater accumulation of positive charge at the substitution center occurs with the secondary alcohol leading to a higher degree of S_N1 character in the reaction of the cyclohexyl system.

Treatment of a 60:40 *trans–cis* mixture of 4-methylcyclohexanols gave a mixture of bromides containing 70–80% II and 20–30% IV. Though traces of I may be present, no evidence for the presence of bromides of rearranged carbon skeleton was noted. Since the n.m.r. spectrum showed bands due to equatorial CHBr protons only, the mixtures must be 70–80% *trans*-II and 20–30% *cis*-IV. This was indeed a surprising result since such a large degree of rearrangement of a secondary alcohol to a secondary bromide was quite unexpected. Furthermore the virtually exclusive formation of axial bromide would not have been predicted. It is interesting that Franzus and Hudson[14] have recently reported that treatment of 1,4-cyclohexanediol with phosphorus tribromide gives a mixture containing 68% 1,4-dibromide (30.4% *trans* and 37.6% *cis*) and 32% 1,3-dibromide (24.5% *trans* and 7.5%

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[10] See ref. 9, pp. 115–119.

[11] Each peak in this multiplet is further split by a secondary coupling (J ~ 0.5 c.p.s.) so that a very complex pattern is produced.

[12] E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24,** 143 (1959).

[13] S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

[14] B. Franzus and B. E. Hudson, Jr., *J. Org. Chem.* **28,** 2238 (1963).

cis). Though rearrangement occurs to a lesser extent apparently the axial isomer predominates in both bromides and to nearly 75% in the rearranged material. We conclude that while these reactions are very sensitive to conditions employed and thus the actual ratio of rearranged to unrearranged product obtained may vary quite widely the use of either phosphorus tribromide or Landauer and Rydon's method for the preparation of secondary bromides is not generally useful. It is also clear that previous workers[5] had in hand mixtures of bromides and not pure substances.

The **Cristol modification**[15] of the Hunsdiecker process was used for the preparation of II. In our hands it led inevitably to low yields because the product tended to decompose during distillation. Distilled bromide appeared to be mainly the expected II, though contamination by small amounts of I and IV was indicated by the infrared spectrum. Apparently traces of mercury salts in the product led to the decomposition and perhaps to the rearranged products as well. Since we made no serious attempt to find optimum conditions for the reaction, or for purification, we do not consider these results definitive with respect to the utility of this interesting method.

Displacement of tosylate using bromide ion in dimethylformamide[2] was tested with the tosylate of 2-methylcyclohexanol. Only traces of bromide were isolated, and an olefin, presumably 1-methylcyclohexene, was the major product. The bromide was not obtained in sufficient quantity to permit an analysis, and the method was not studied further since Eliel[12] also found the results discouraging.

We conclude that at present the only generally useful routes to cycloalkyl bromides involve either the Hunsdiecker reaction, or cleavage of the corresponding mercury salt where it is available. One useful route to the latter might well prove to be *via* formation of the chloride using phosphorus pentachloride in chloroform,[16] followed by conversion to the mercury salt.

Experimental[17]

1-Bromo-1-methylcyclohexane (III).—A 7.0-g. sample of 1-methylcyclohexanol (from methyl magnesium iodide and cyclohexanone), b.p. 72° (28 mm.), n^{20}D 1.4600, was shaken for 10 min. with a solution containing 75 ml. of 48% hydrobromic acid and 10.0 g. of anhydrous zinc bromide. The halide was decanted from the aqueous layer, washed with water, and dried over anhydrous potassium carbonate. Distillation, b.p. 65-66° (20 mm.), n^{20}D1.4886, gave a clear liquid in 55% yield. This bromide has been reported[18] to boil at 66° (22 mm.), n^{25}D 1.4868. Analysis[19] showed the product to contain at least 99% tertiary bromide. Infrared absorption occurs at 1452 s, 1380 m, 1250 s 1140 s, 1085 m, 965 m, 855 m, 765 s, 643 w, 556 m, 493 s, 433 w. The n.m.r. spectrum shows a 3H singlet at τ 8.25 and a series of unresolved peaks from *ca.* 7.7-8.8.

2-Bromo-1-methylcyclohexane (I). A. Hunsdiecker Method—The silver salt of 2-methylcyclohexanecarboxylic acid, dried to a constant weight (80.0 g.) over phosphorus pentoxide, was treated with 1 equiv. of bromine in 600 ml. of carbontetrachloride for 2 hr. at reflux. The silver bromide was removed by filtration and the solution was washed with sodium bisulfite solution, 10% potassium hydroxide, and water before drying over anhydrous sodium sulfate. The bromide was obtained as a light yellow liquid, 41 g. (73%). Careful fractional distillation with a concentric tube column gave 10.0 g. (18%) of a clear liquid, b.p. 59-60° (15 mm.), n^{20}D 1.4861, d^{20}_{20} 1.2595. The infrared spectrum showed absorption at 1455 s, 1382 m, 1264 m, 1190 s, 1078 m, 950 m, 906 m, 855 m, 779 m, 681 s, 610 w, 590 w, 569 w, 539 m, 472 w, 456 m, 423 w. N.m.r. showed an unresolved multiplet at τ 5.65, a sextet (J = 4, 10.5 c.p.s.) at 6.32, a doublet (J = 6 c.p.s.) at 8.90, and a complex series of peaks from *ca.* 7.5–9.1. A ratio of 1:12 was obtained for the area under the peaks at τ 5.65 and 6.32 compared with that under the remaining peaks. The product gave a single peak on analysis by gas chromatography.

Anal. Calcd. for $C_7H_{13}Br$: C, 47.47; H, 7.40. Found: C, 47.30; H, 7.51.

B. Cleavage of Mercury Salt.—The Grignard reagent from 8.0 g. of 2-bromo-1-methylcyclohexane (from Hunsdiecker) was treated with 16.5 g. of mercuric bromide. The reaction mixture was poured onto ice and acidified with 48% hydrogen bromide. The oily product was taken up in ether solution and dried; the solvent was removed. A straw-colored oil, n^{20}D 1.5565, remained which could not be induced to crystallize. The oil was cleaved by the pyridine–bromine method according to the directions of Jensen and Gale.[8] The bromide, n^{20}D 1.4850, shows infrared and n.m.r. spectra identical with those of the starting bromide except for enhancement of the multiplet at τ 5.65 and slight variations in relative intensities of infrared bands.

C. Landauer and Rydon's Method.—2-Methylcyclohexanol (25 g.) and 105 g. of triphenylphosphite–benzyl bromide salt were mixed and allowed to stand at 70° for 24 hr. in accord with the directions of Landauer and Rydon.[13] The product was distilled through a small Vigreux column: b.p. 50° (8 mm.), n^{25}D 1.4830. Presence of a strong band at 767 cm.$^{-1}$ and absence of absorption at 681 cm.$^{-1}$ indicated this to be mainly III. The n.m.r. spectrum shows a single sharp peak at τ 8.25.

D. Phosphorus Tribromide Method.—A sample of 2-methylcyclohexanol containing less than 3% 3-methylcyclohexanol (g.p.c.) was treated with the calculated amount of phosphorus tribromide at 0 to $-10°$. The mixture was allowed to stand overnight and the product was obtained by distillation. The crude product was washed in turn with cold concentrated sulfuric acid, water, sodium bicarbonate solution, and water, then dried over anhydrous potassium carbonate. The bromide was distilled through a 12-in. helice-packed column: b.p. 64° (19 mm.), n^{25}D 1.4868, yield 35–60%. Analysis by preferential hydrolysis[19] showed a minimum of 60% 1-bromo-1-methylcyclohexane, and the presence of infrared absorption at 767 and 680 cm.$^{-1}$ shows this to be a mixture of III and I.

E. Tosylate Replacement.—A 20-g. sample of 2-methylcyclohexanol was treated with 37 g. of *p*-toluenesulfonyl chloride in 75 ml. of dry pyridine at 0° for 16 hr. After the usual work-up, 37.3 g. of light yellow oil, n^{20}D 1.5133, showing absorption at 1350 and 1185 cm.$^{-1}$, was obtained. This tosylate was treated with 16.5 g. of sodium bromide in 200 ml. of dimethylformamide at 25° for 100 hr.[2] After being washed with 200 ml. of water and dried over anhydrous potassium carbonate, the residual oil was distilled at 19 mm. The major product, n^{20}D 1.4500, was recovered from the Dry Ice trap. A small amount of unchanged tosylate appeared in the residual material.

2-Methylcyclohexanecarboxylic Acid.—A sample of *o*-toluic acid, m.p. 102–104°, prepared either by carbonation of the Grignard reagent from *o*-bromotoluene or by oxidation of *o*-xylene,[20] was reduced according to the procedure of Macbeth, Mills, and Simmonds.[6] After recrystallization from water, the acid melted at 48–51°. A melting point of 51-52° for the *trans* isomer has been reported.[6] Larger batches of the mixed isomers were prepared by reduction of ethyl *o*-toluate over W-4 Raney nickel[21] in ethanol at 130° and 1700-p.s.i. initial hydrogen pressure. The ethyl 2-methylcyclohexanecarboxylate, b.p. 97–98° (10 mm.), n^{25}D 1.4720–1.4762, was hydrolyzed in ethanolic sodium hydroxide solution and the product was distilled: b.p. 120–122° (10 mm.), n^{25}D 1.4670. A boiling point of 133° (17 mm.) has been reported[22] for the mixture of geometric isomers.

3-Methylcyclohexanecarboxylic Acid.—Commercial *m*-toluic acid (Matheson Coleman and Bell), m.p. 110–112°, was reduced

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[15] S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

[16] For a discussion of this process, see H. L. Goering and F. H. McCarron, *J. Am. Chem. Soc.*, **80**, 2287 (1958); **78**, 2270 (1956).

[17] All melting points are uncorrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

[18] H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952).

[19] C. Walling, M. S. Karasch, and F. R. Mayo, *ibid.*, **61**, 2693 (1939).

[20] H. E. Zaugg and R. T. Rapala, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 820.

[21] A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).

[22] J. B. Culbertson, D. Butterfield, O. Kolewe, and R. Shaw, *J. Org. Chem.*, **27**, 729 (1962).

over platinum oxide catalyst in acetic acid at 100 atm. The reduced acid was obtained as a clear liquid, b.p. 134–136° (24 mm.), n^{20}_{D} 1.4568. An n^{25}_{D} 1.4566 has been reported[16] for a 74:26 *cis-trans* mixture. Larger batches were prepared more conveniently by reduction of the ethyl ester followed by hydrolysis of the ester by the procedure described for the 2-methylcyclohexanecarboxylic acid.

3-Bromo-1-methylcyclohexane (II). A. Hunsdiecker Method.—The silver salt of 3-methylcyclohexanecarboxylic acid was allowed to react with bromine according to the procedure described under I. The bromide, b.p. 56° (10 mm.), n^{25}_{D} 1.4844, was distilled through a 14-in. Vigreux column. It was obtained in 70% crude yield and 26% yield in pure form. Infrared absorption occurs at 1463 s, 1381 m, 1335 m, 1260 s, 1224 m, 1195 s, 1032 m, 945 m, 878 w, 692 s, 662 sh, 581 w, 524 s, 510 sh, 475 m, 438 w, 428 w, 406 w. The n.m.r. spectrum exhibits an ill-defined quintet (J = 3.5 c.p.s.) at τ 5.5, a broad multiplet (triplet of triplets, J = 4, 11 c.p.s.) at 6.13, a sharp doublet (J = 6 c.p.s.) at 9.10, and a series of peaks between 7.6 and 8.85.

Anal. Calcd. for $C_7H_{13}Br$: C, 47.47; H, 7.40. Found: C, 47.70; H, 7.45.

B. Cristol Modification.—A 3.72-g. sample of 3-methylcyclohexanecarboxylic acid was treated with mercuric oxide and bromine according to the procedure of Cristol and Firth.[15] The product showed a tendency to decompose during distillation, and a low yield 0.97 g. of bromide, b.p. *ca.* 45° (15 mm.), n^{20}_{D} 1.4909 was isolated. The infrared spectrum was identical with that from the Hunsdiecker reaction in the sodium chloride region, except for a small peak at 1720 and bands at 837 and 780 cm.$^{-1}$.

C. Cleavage of Mercury Salt.—A sample of 3-methylcyclohexylmercuric bromide was prepared according to the method described for the 2-isomer. After recrystallization from hexane–benzene, the salt melted at 88–90°. Cleavage of 7.3 g. of the mercury salt by the pyridine–bromine method[3] gave 84% of a clear liquid, b.p. *ca.* 55–60° (10 mm.), n^{20}_{D} 1.4860. Except for a lower intensity for the infrared band at 581 cm.$^{-1}$, the infrared and n.m.r. spectra of the Hunsdiecker and this product were identical.

Conversion to Ketones.—Dry oxygen was bubbled through a cold solution of Grignard reagent (from I or II) in ether for several hours.[23] The alcohol obtained (35–50% yield after distillation) was identified by g.p.c. using a 6-ft. type A column and comparison with internal standards. Since the separation of the two alcohols was incomplete, they were oxidized (dichromate) to the respective ketones and again checked for identity on a 6-ft. type A column. I gave 2-methylcyclohexanone and II gave 3-methylcyclohexanone.

4-Bromo-1-methylcyclohexane (IV). A. Cleavage of Mercury Salt.—A sample of the *trans* isomer was prepared by the method of Jensen and Gale.[3] The product, m.p. *ca.* 25°, showed an n.m.r. spectrum with a triplet of triplets (J = 4.0, 10.5 c.p.s.) at τ 6.18, a sharp doublet (J = 5.0 c.p.s.) at 9.16, and a series of ill-resolved peaks between 7.5–9.0.

B. Landauer and Rydon's Method.—A mixture containing 100 g. (0.58 mole) of benzyl bromide and 190 g. (0.61 mole) of triphenyl phosphite was heated at 155–160° for 5 days. The bronze-colored solid product was triturated with hexane, and the residual solid was dried *in vacuo*. A portion, 105 g., of the solid was mixed with 25 g. of 4-methylcyclohexanol and the mixture was allowed to stand at 70° for 24 hr. The volatile product was removed from the reaction mixture under reduced pressure, washed with dilute sodium hydroxide solution, and dried over anhydrous sodium sulfate. The bromide was distilled using a 24-in. concentric tube column: b.p. 49–51° (8 mm.), n^{25}_{D} 1.4810. Infrared absorption bands appear at 1462 s, 1384 w, 1359 w, 1310 w, 1254 s, 1245 s, 1190 s, 1105 w, 1030 m, 970 m, 950 m, 850 m, 702 m, 689 s. The n.m.r. spectrum consisted of a quintet (J = 4 c.p.s.) at τ 5.58, a sharp doublet (J = 6.0 c.p.s.) at 9.11, a second sharp doublet of lower intensity (J = 6.0 c.p.s.) at 9.13, and two poorly resolved multiplets between 7.9 and 8.7. A weak singlet τ at 2.25 and a series of peaks at 2.6–3.0 as well as absorption at 3320 cm.$^{-1}$ indicated contamination by phenol.

C. Phosphorus Tribromide Method.—A sample of 4-methylcyclohexanol, free from isomers by g.p.c. analysis, was treated with phosphorus tribromide according to the procedure described for I. The product was identical (except for the contamination by phenol) with that obtained by Landauer and Rydon's method.

Infrared Spectra.—All spectra in the sodium chloride region were run on neat samples in sandwich cells using a Perkin-Elmer Model 21. Spectra in the potassium bromide region were run on neat samples in a 0.05-mm. fixed cell using a Beckman IR-7.

N.m.r. Spectra[24]—All spectra were taken on a Varian A-60 proton magnetic resonance spectrometer using tetramethylsilane as an internal reference. Samples were run in varying concentrations in carbon tetrachloride solution.

Gas Chromatography.—Analysis by gas chromatography was made on a Perkin-Elmer Model 154 C instrument using helium as carrier gas. The alcohols were analyzed on a commercial type K column and the bromides on a 6 ft. × 0.25 in. column containing 15% trifluoromethylsilicone (Dow-Corning FS 1265) on Chromosorb.

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[23] M. T. Goebel and C. S. Marvel, *J. Am. Chem. Soc.*, **55**, 1693 (1933).

[24] We are indebted to the National Science Foundation for partial financial support toward the purchase of this instrument.

The Structure and Reactions of the 1:1 Adduct of Benzenesulfonyl Azide and Bicyclo[2.2.1]heptene

J. E. FRANZ, C. OSUCH, AND M. W. DIETRICH

Research Department, Organic Chemicals Division, Monsanto Company, St. Louis 77, Missouri

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Nuclear magnetic resonance and chemical evidence are presented which support an aziridine structure for the 1:1 adduct formed from benzenesulfonyl azide and bicyclo[2.2.1]heptene. Potassium thiophenate reacted smoothly with the adduct to afford 2-*endo*-thiophenoxy-3-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane which was readily converted to 2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane by Raney nickel treatment. Lithium aluminum hydride reduction of the adduct produced the 2-*exo*-sulfonamide directly. The reaction of the aziridine with thiophenol under acidic conditions followed by desulfurization yielded 7-benzenesulfonamidobicyclo[2.2.1]heptane as the major product. The n.m.r. spectrum of the aziridine prepared from 2,3-dideuteriobicyclo[2.2.1]-2-heptene and benzenesulfonyl azide conclusively established that rearrangement did not occur during this reaction and that carbonium ion intermediates were not involved. A mechanism analogous to epoxidation is proposed

In a preliminary communication[1] the reactions of various sulfonyl and phosphoryl azides with several olefins were reported. It was proposed that the 1:1 adduct formed from benzenesulfonyl azide and bicyclo[2.2.1]heptene is the aziridine (Ia) rather than the azetidine (Ib). One basis for this conclusion is the similarity in the nuclear magnetic resonance spectrum of I with that of 2,3-*exo*-epoxybicyclo[2.2.1]heptane. Although this correlation has been described[2] as being

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[1] J. E. Franz and C. Osuch, *Tetrahedron Letters*, 837 (1963).

[2] L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963), ref. 8.