TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	B. p. or m. p.	d^{25}_{25}	n^{25}_D	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found
II Ethyl *p*-methoxycinnamate	B. 132° (1 mm.)	....	....	69.88	69.82	6.84	7.06
III Ethyl β-(*p*-methoxyphenyl)-propionate	B. 103° (0.1)	1.0628	1.5016	69.19	69.17	7.72	7.72
IV β-(*p*-Methoxyphenyl)-propionic acid	M. 128–129°	....	....	65.04	64.83	6.07	6.08
V Ethyl β-(*p*-hydroxyphenyl)-propionate	B. 140° (0.2)	1.1083	1.5153	68.02	67.85	7.26	7.51
VI Ethyl β-(4-hydroxycyclohexyl)-propionate	B. 102–103° (0.2)	1.0309	1.5661	65.96	65.78	10.06	9.96
IX 2,4-Dinitrodiphenylhydrazone of β-(4-ketocyclohexyl)-propionic acid	M. 125–127°	....	....			N, 16.00	16.08
p-Methoxybenzylmalonic ester	B. 138° (0.1)	1.1055	1.4923	64.27	64.31	7.18	7.3

tral equivalent of the sample of keto acid was 174, corresponding to a calcd. molecular weight of 170.

The keto acid, VII, (2 g.) in 10 ml. of hot water was mixed with 2,4-dinitrophenylhydrazine (3 g.) in 15 ml. of hot water. The mixture was boiled under a reflux while 3–6 ml. of concd. hydrochloric acid was added. The solid which separated when the solution was cooled was then dissolved in hot dioxane and precipitated by the addition of hot water. The m. p. of the hydrazone was 125–127°. The hydrazone crystallized from ethanol showed a m. p. 90–94°. A hydrazone similarly prepared from the sample of the keto acid *ex* lignin had a m. p. of 90–93°. The mixed melting point was 90–94°. These hydrazones crystallized from ethanol are apparently derived from the ethyl ester of the keto acid, VIII.

Summary

The glycol 3-(4-hydroxycyclohexyl)-propanol-1 has been prepared by a series of reactions from anisaldehyde, and has been shown to be identical with the chief product of the hydrogenation of a sample of lignin derived from the hard wood aspen by the methanol process.

MADISON, WISCONSIN RECEIVED JULY 8, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 786]

An Electron Diffraction Investigation of the Structure of Propylene Bromide

BY VERNER SCHOMAKER AND D. P. STEVENSON

In a recent communication[1] we presented the results of an electron diffraction investigation of the structures of the racemic and *meso*-2,3-dibromobutanes. We report here the results of a similar investigation of propylene bromide.

The sample (b. p. 42° (15 mm.)) of propylene bromide used was fractionally distilled from a large batch prepared by Mr. Maurice Schlatter of these Laboratories. The electron diffraction apparatus and technique have been described by Brockway.[2] The wave length of the electrons (a_0 for gold = 4.070 Å.) was 0.0615 Å., and the camera distance was 10.85 cm. The gas jet was formed by the high temperature nozzle,[3] the temperature of the boiler being 90–110°. There was no indication of any decomposition of the propylene bromide.

Interpretation

The observed s_0 values $\left(s_0 = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}\right)$ for the twenty-four measurable features of the photographs are given in Table I together with the coefficients of the radial distributive function,[4,5] and the quantitative comparison with the simplified theoretical curves G and H of Fig. 1. The positions and designations of the observed features are indicated on the figure by numbered arrows.

The radial distribution function, curve A, shows a number of maxima of which only those at 2.85 and 4.62 Å. give accurate values for interatomic distances in the molecule, since it is only for these two peaks that the individual distribution curves for the maxima and minima are in agreement. These two distances undoubtedly correspond to the shorter non-bonded carbon–bromine and the

---

[1] D. P. Stevenson and Verner Schomaker, THIS JOURNAL, **61**, 3173 (1939).

[2] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[3] L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

[4] L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

[5] V. Schomaker, A. C. S. Meeting, Baltimore, Md., April, 1939.

TABLE I

Max.	Min.	C_n	s_0	$s_c{}^a$	$s_c{}^b$	$s_c/s_0{}^a$	$s_c/s_0{}^b$
	1	−3	1.83	2.22	2.22	(1.213)[c]	(1.213)
1		5	3.01	3.02	3.03	1.003	1.007
	2	−7	3.72	3.74	3.73	1.005	1.003
2		8	4.60	4.51	4.50	0.980	0.978
	3	−4	5.21	5.30	5.26	1.017	1.010
3		4	5.75	5.65	5.71	0.983	0.993
	4	−9	6.45	6.32	6.32	0.980	0.980
4		13	7.23	7.16	7.16	0.990	0.990
	5	−8	7.95	8.03	8.07	1.010	1.015
5		2	8.56	8.52	8.53	0.995	0.996
	6	−8	9.09	9.12	9.08	1.003	0.999
6		11	9.83	9.88	9.84	1.005	1.001
	7	−9	10.50	10.51	10.57	1.001	1.007
7		8	11.29	11.28	11.27	0.999	0.998
	8	−8	11.92	12.20	12.15	1.023	1.019
8		5	12.62	...	...	...	...
	9	−4	13.18	...	...	...	...
9		9	13.83	13.84	13.84	1.001	1.001
	10	−9	14.56	14.86	14.87	1.021	1.021
10		5	15.41	...	...	...	...
	11	−3	15.94	...	...	...	...
11		5	16.77	16.59	16.57	0.989	0.988
	12	−4	17.27	17.10	17.31	0.990	1.002
12		5	18.04	18.00	18.03	0.998	0.999
				Average 19 features		1.000 ± 0.010	1.000 ± 0.009

[a] C–Br = 1.91, ∠ C–C–Br = 110.5 (G). [b] C–Br = 1.93, ∠ C–C–Br = 109.5 (H). [c] Omitted from average.

bromine–bromine distances, since for a molecular model with tetrahedral angles and the C–C and C–Br distances equal to 1.54 and 1.91 Å., respectively, and a "*trans*" configuration with respect to the bromines, these distances are 2.82 and 4.57 Å. An increase of about 1° in the C–C–Br angles brings the calculated distances into agreement with those indicated by the radial distribution function.

Theoretical intensity curves were calculated for several molecular models suggested by the radial distribution function and our knowledge of the structures of the 2,3-dibromobutanes, by use of the formula

$$I(s) = \sum Z_i Z_j e^{-a_{ij}s^2} \frac{\sin l_{ij}s}{l_{ij}s} \qquad (1)$$

in which the various symbols have their usual significance.[2] Preliminary calculations showed that for $s \geqslant 6.5$ curves calculated by Equation 1 are indistinguishable from those calculated according to the more correct Equation 2. This may be seen by comparison of curves C (Equation 1) and I (Equation 2) of the figure. For s

$$I(s) = \sum \frac{Z_i - f_i)(Z_j - f_j)e^{-a_{ij}s^2}}{(Z - f)_{\mathrm{Br}}^2} \frac{\sin l_{ij}s}{l_{ij}s} \qquad (2)$$

< 6.5 the differences between the curves for Equations 1 and 2 are insignificant except that curve I does not show the unobserved peak at $s = 1.6$ shown by curve C. Inasmuch as the corrections introduced by the use of Equation 2 were found to be small, Equation 1 was used because of the simplification it introduces into the calculations.

Curves were first calculated for a model in which the bond angles were tetrahedral, the bond distances had their covalent values (C–H = 1.09 Å., C–C = 1.54 Å. and C–B = 1.91 Å.), and the configuration was "*trans*" with respect to the bromines as indicated by the radial distribution function. The a_{ij}'s were taken equal to zero for all distances except those involving hydrogen atoms and those dependent on the orientation about the 2,3 carbon–carbon bond. These curves are shown in the figure, B . . . . F, and the "libration-dependent a_{ij}'s" are given in the legend. Of these only curve E is in satisfactory agreement with the photographs. Curves C and D, corresponding to a rigid model and one with a librational amplitude of ± 14° about the *trans* configuration, respectively, are unsatisfactory because on them the fifth, eighth, tenth, and eleventh maxima are too pronounced. Curves B and F, which are for models with very large librational amplitude, are unsatisfactory because these same maxima do not appear on them. Quantitative comparison of curve E with the photographs gave ($\bar{s}_c/s_0$) = 1.010 ± 0.010, indicating that some of the distances in this model were too short. For this reason curves were calculated for the models described under G and H in the legend to the figure. The curves for these models showed the same behavior as those for the model of curves B . . . . F when the a_{ij}'s were varied, hence they are not given in the figure. Qualitatively curves G and H are indistinguishable from curve E but quantitative comparison of these curves with the photographs gives (s_c/s_0) = 1.000 ± 0.010. A curve calculated for a model with C–Br = 1.93 Å. and ∠ C–C–Br = 110.5° but otherwise similar to the models for curves E, G, and H was likewise satisfactory qualitatively but gave 0.990 ± 0.011 for ($\bar{s}_c/s_0$).

The results of our electron diffraction investigation of the structure of propylene bromide may be summarized as follows: C–Br = 1.92 ± 0.02 Å., ∠ C–C–Br = 110 ± 1° and a *trans* configuration with respect to the bromine atoms with $a_{\mathrm{Br-Br}}$ = 0.004 ± 0.002.

Discussion

The structure of propylene bromide presents no unusual features. The carbon–bromine distance, 1.92 ± 0.02 Å., is in good agreement with the value 1.91 ± 0.02 Å. found for this distance in ethyl,[6a] isopropyl,[6a] and *t*-butyl bromides,[6b] and in the bromomethanes,[6c] and the C–C–Br angle 110 ± 1° is like that found for the 2,3-dibromobutanes.[1]

The value found for a, 0.004 ± 0.002, corresponds to a librational amplitude of ± 19 ± 5°, which is, within the limits of error, equal to the value estimated for the 2,3-dibromobutanes, namely, 20°. This amplitude corresponds to a potential barrier, V_0 = 12 ± 5 kcal./mole, for a simple cosine potential function, $V = \frac{V_0}{2}(1 + \cos\phi)$. This value of V_0 is equal, within the limits of error, to the values found for ethylene bromide from an electron diffraction investigation,[7] $5 \leq V_0 \leq \infty$, and from the variation of the dipole movement in the gas,[8] V_0 = 8 ± 4 kcal./mole.

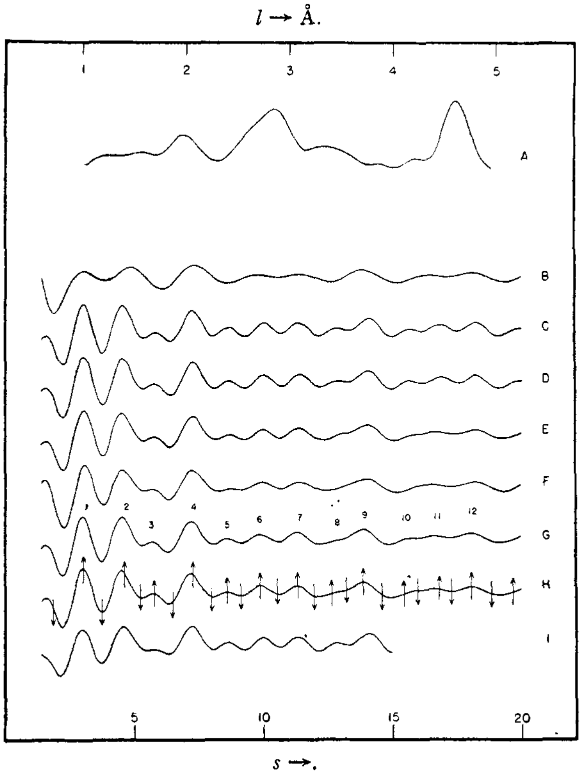

Fig. 1.—Curve A. Radial distribution curve. Curves B through I, theoretical intensity curves: B, angles tetrahedral, C–H = 1.09, C–C = 1.54, C–Br = 1.91, terms dependent on orientation about 2,3 C–C bond omitted, Equation 1; C, Curve B plus omitted terms, *trans* configuration; D, like curve C, but with $a_{\mathrm{Br-Br}} = 0$, $a_{\mathrm{C-Br}}$ = 0.015, $a_{\mathrm{H-Br}}$ = 0.009; E, like curve C, but with $a_{\mathrm{Br-Br}}$ = 0.004, $a_{\mathrm{C-Br}}$ = 0.028, $a_{\mathrm{H-Br}}$ = 0.016; F, like curve C, but with $a_{\mathrm{Br-Br}}$ = 0.010, $a_{\mathrm{C-Br}} > 0.1$, $a_{\mathrm{H-Br}} > 0.1$; G, ∠C–C–Br = 110.5, otherwise as E; H, C–Br = 1.93 Å., otherwise as E; I, like curve C but Equation 2.

Summary

From electron diffraction photographs of propylene bromide it has been found that C–Br = 1.92 ± 0.02 Å., ∠ C–C–Br = 110 ± 1° and that the molecule has a *trans* configuration with respect to the bromine atoms. The appearance of the photographs may be interpreted on the assumption that the molecule is essentially rigid except for a torsional oscillation with an amplitude of about 20°.

PASADENA, CALIFORNIA RECEIVED JULY 8, 1940

---

(6) (a) J. Y. Beach and D. P. Stevenson, THIS JOURNAL, **61**, 2643 (1939); (b) J. Y. Beach and D. P. Stevenson, *ibid.*, **60**, 475 (1938); (c) H. A. Levy and L. O. Brockway, *ibid.*, **59**, 1662 (1937).

(7) J. Y. Beach and A. Turkevich, *ibid.*, **61**, 303 (1939).

(8) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 635 (1939).