

TABLE I

| Compd. no. | Compounds | Yield, % ^a | B. p., °C. | Mm. | n _D ²⁰ | M. p., °C. ^b | Empirical formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|------------|--|-----------------------|------------|-------|------------------------------|-------------------------|--|------------------|-----------------|--------------------|-------------------|
| I | 2- <i>o</i> -Toloxo-1,3-propanediol | 60 | 150-153 | 2.0 | 1.5391 | | C ₁₀ H ₁₄ O ₃ | 65.95 | 66.16 | 7.69 | 7.81 |
| II | 2- <i>m</i> -Toloxo-1,3-propanediol | 92 | | | | 66-67 | C ₁₀ H ₁₄ O ₃ | 65.95 | 66.22 | 7.69 | 7.81 |
| III | 2- <i>p</i> -Toloxo-1,3-propanediol | 68 | | | | 68-69 | C ₁₀ H ₁₄ O ₃ | 65.95 | 65.98 | 7.69 | 7.59 |
| IV | 2-Benzoyloxy-1,3-propanediol | 87 | 185-187 | 10.0 | | 38.5-40 | C ₁₀ H ₁₄ O ₃ | 65.95 | 65.88 | 7.69 | 7.59 |
| V | Ethyl <i>o</i> -toloxymalonate | 69 | 140-142 | 2.0 | | 49.5-50 | C ₁₄ H ₁₈ O ₆ | 63.15 | 62.75 | 6.77 | 6.77 |
| VI | Ethyl <i>p</i> -toloxymalonate | 65 | 110-114 | 0.1 | 1.4908 | | C ₁₄ H ₁₈ O ₆ | 63.15 | 63.32 | 6.77 | 6.81 |
| VII | 5-Benzoyloxy-2-phenyl- <i>m</i> -dioxane | 60 | | | | 75.5-76.5 | C ₁₇ H ₁₈ O ₃ | 75.55 | 75.85 | 6.71 | 7.01 |

^a Yields are based on material of reasonable purity and do not taken into account the recovery of starting materials.

^b M. p. data are for analytically pure samples.

The residual oil, which solidified on standing, was purified by crystallization from benzene-ligroin solution.

2-Benzoyloxy-1,3-propanediol (IV).—A solution of 32.5 g. (0.12 mole) of 5-benzoyloxy-2-phenyl-*m*-dioxane (VII), 170 ml. of ethanol, 60 ml. of water and 2.0 ml. of concentrated sulfuric acid was refluxed for two hours. Most of the ethanol was removed by distillation, the residue cooled and neutralized with sodium bicarbonate and the benzaldehyde steam distilled from the mixture. The aqueous solution of the diol was saturated with potassium carbonate and extracted with three 50-ml. portions of ether. After drying over magnesium sulfate, the ethereal solution was concentrated and the residual oil distilled under reduced pressure. The distillate solidified on cooling and was further purified by crystallization from benzene.

Table I summarizes the physical constants and analytical data for these compounds.

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The Reduction of 1,2-Isopropylidene-D-glucuronolactone with Lithium Aluminum Hydride¹

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In the synthesis of 6-C¹⁴-glucose described recently by Sowden,² the final step is the reduction of 6-C¹⁴-1,2-isopropylidene-D-glucuronolactone with sodium borohydride followed by acid hydrolysis of the resultant mixture to yield glucose. With the particular lot of ion exchange resin (Duolite A-4) available for our first experiments, some difficulty was experienced in complete removal of the borate ion. A modification of the reduction step was therefore developed, utilizing lithium aluminum hydride. Although this reagent has a disadvantage in that it requires anhydrous conditions for its action, it possesses two advantages: (1) an increased yield of glucose, (2) it is possible to isolate the intermediate 6-C¹⁴-1,2-isopropylidene-D-glucose in good yield.

Experimental

1,2-Isopropylidene-D-glucose.—The reaction vessel is a three-necked Grignard reaction flask into which are inserted a condenser and a dropping funnel, both protected with drying tubes. Stirring is performed with a magnetic stirrer, 8 ml. of a 1.6 *M* solution of lithium aluminum hydride (clear³) is added through the third opening in the flask

(1) This investigation was supported by grants from the National Heart Institute of the National Institutes of Health, U. S. Public Health Service, and the Helen Hay Whitney Foundation.

(2) J. C. Sowden, THIS JOURNAL, **74**, 4377 (1952); preliminary report, 119th Meeting, ACS, Milwaukee, April, 1952. I would like to express my gratitude to Dr. Sowden for his many valuable suggestions.

(3) W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 484.

followed by 10 ml. of anhydrous ether (stored over sodium) and the flask is stoppered; 1.08 g. of 1,2-isopropylidene-D-glucuronolactone is dissolved in 150 ml. of boiling anhydrous ether, the solution is allowed to cool, and is then added dropwise over a period of 30 minutes to the stirred lithium aluminum hydride solution. About 50 ml. more of ether is used to rinse in the last trace of lactone. The flask is placed in a water-bath at 50-60°, the solution is stirred and refluxed for 25 minutes, and is then cooled. Absolute alcohol is cautiously added at this point until the excess reagent is destroyed and then more rapidly with vigorous stirring until 25 ml. have been added. A clear, colorless solution should result. A solution of concentrated hydrochloric acid in alcohol is then added (4 parts concentrated hydrochloric acid to 10 parts absolute ethanol). The acid is added dropwise with stirring until a sample tested with phenolphthalein in alcohol shows that the mixture is barely acid (requires about 4 ml. of concentrated hydrochloric acid). The mixture should be essentially clear at this point. The solution is quickly cooled and is then poured into an iced mixture of 150 ml. of petroleum ether and 100 ml. of 0.01 *M* hydrochloric acid. The aqueous layer is separated and the ether layer is extracted once more with 100 ml. of 0.01 *M* hydrochloric acid. To deionize the solution, the combined aqueous extracts are passed through alternating layers of IR-120, H and IR-4B. In the isotope experiments where it is not desired to recover the resin, the two resins are mixed intimately before use—this being the most efficient procedure for maintenance of a neutral pH. The final resin layer is always the IR-120, H and the total volumes used are about 100 ml. of each resin (somewhat more in the case of the alternating layers). The neutral, colorless solution is concentrated at 50-55° *in vacuo* and yields 1.05 g. of slightly yellowish crystals, m. p. 153-157°. Recrystallization from ethyl acetate yields 0.70 g. of white crystals, melting at 161-162° and $[\alpha]_D^{25} -12.0^\circ$ (*c* 5.4, water). There was no depression of the melting point when the sample was mixed with an authentic specimen. A second crop was obtained upon the cautious addition of petroleum ether to the ethyl acetate mother liquors, 0.20 g., m. p. 158-160°, $[\alpha]_D^{25} -12.2^\circ$ (*c* 5.1, water).

D-Glucose.—The procedure described above for the reduction is followed up to, and including, the addition of alcohol to the reaction flask. The clear solution is then poured into a separatory funnel containing 200 ml. of water, 2 ml. of concentrated sulfuric acid, and 150 ml. of petroleum ether. The aqueous extract is removed and the ether layer washed once more with 50 ml. of 0.1 *M* sulfuric acid. The combined aqueous extracts are then heated for 1.5 hours on the steam-bath, and the colorless solution is cooled and treated with an excess of barium carbonate with shaking until the mixture is alkaline. The mixture is centrifuged and the precipitate is washed three times with water and finally with boiling water. Complete deionization is obtained by passing the solution through a 20-ml. layer of IR-120, H then 20 ml. of IR-4B and finally 10 ml. of IR-120, H. The combined eluate and washings are colorless, negative toward the naphthoresorcinol uronic acid test, and contain 0.85 g. of glucose according to a quantitative anthrone and reducing sugar analysis. The solution is concentrated, yielding a colorless sirup which is then treated with 4 ml. of 95% ethanol and seeded. After standing for one week, crystallization is complete, yielding 0.72 g. of anhydrous dextrose, m. p. 146°, $[\alpha]_D^{25} 52.3^\circ$, equilibrium in

water. No depression of the melting point was observed on mixing the sample with an authentic specimen.

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The Molecular Structure of Perfluorobutyne-2. Critical Marks for the Description of Electron Diffraction Curves

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A complete structure determination, rather highly precise because it is based mainly on microwave spectroscopic data and only partly on electron diffraction, has been achieved for trifluoromethyl-

including all interactions, for the following models, illustrating the indicated total range of models studied.

| Curve | F—F | C—C' | C'≡C'' | $\sigma_{\text{total}}^{\text{theoretical}}$ ^c |
|------------------|------|------|--------|---|
| A ^a | 2.15 | 1.46 | 1.21 | 1.007 |
| B ^{a,b} | 2.15 | 1.46 | 1.21 | 1.006 |
| C ^c | 2.15 | 1.43 | 1.20 | 1.009 |
| D ^d | 2.15 | 1.49 | 1.20 | 1.008 |
| E ^d | 2.13 | 1.47 | 1.20 | 1.013 |
| F ^d | 2.17 | 1.47 | 1.20 | 1.000 |
| G ^a | 2.15 | 1.47 | 1.20 | 1.008 |
| H ^a | 2.15 | 1.45 | 1.23 | 1.004 |
| I ^c | 2.15 | 1.49 | 1.14 | 1.011 |
| J ^c | 2.15 | 1.43 | 1.29 | 1.008 |
| K ^d | 2.13 | 1.37 | 1.26 | 1.013 |

Range 2.11–2.17 1.35–1.51 1.14–1.29 (C—F = 1.33)

^a Satisfactory curve. ^b Account taken of the effective slight shortening of C...C'' and C...F' expected to result from C—C≡C bendings. ^c Curve near the limit of acceptability, either within or without. ^d Completely unacceptable curve. ^e For 8 best (reasonably symmetrical and well-located) features; average deviation, Model B, 0.006 (for 22 best features, 0.019). Measurements by W. S.

acetylene.² The present electron diffraction study has led to almost identical bond angle and bond distance values for perfluorobutyne-2: see Table I. The sample³ was generously supplied by Professor Henne and the detailed techniques were those currently used in these laboratories.⁴

TABLE I

| | F ₃ C—C≡C—H ¹ | | F ₃ C—C≡C—CF ₃ | |
|---------|-------------------------------------|----------------|--------------------------------------|---------------------|
| | Value | Limit of error | Value | Limit of error |
| C—F, Å. | 1.335 | 0.01 | 1.340 | 0.020 ^a |
| C—C, Å. | 1.464 | .02 | 1.465 | .055 ^{a,b} |
| C≡C, Å. | 1.201 | .002 | 1.22 | .09 ^a |
| C—H, Å. | 1.056 | .005 | | |
| ∠F—C—F | 107.5° | 1.0° | 107.5° | 1.0° |

^a Including 1.0% estimated limit of scale error. ^b If C≡C were assumed to be precisely 1.22 Å., the limit of error for C—C would be reduced to 0.040 Å. but the other limits would be essentially unchanged.

About one hundred seventy-five theoretical intensity curves were calculated in order to cover the rigid-model shape-parameter problem completely and the temperature factor problem, with its considerable and uncertain dependence on possible instrumental effects as well as the low frequencies² and large amplitudes of C—C≡C bendings (estimated root-mean-square $\delta \angle \text{C—C}\equiv\text{C}$, 9.5°), in some detail. All the models were given D₃ symmetry, and when the long F...F terms were finally included for some of the curves, free internal rotation was assumed. The significant points regarding the theoretical curves illustrated in Fig. 1 are indicated by marks in the figure itself rather than by the usual tedious verbal description.

Such *critical marks* can be generally self-explanatory (Table II seems almost unnecessary, except by way of introduction), and they are convenient, terse, highly legible (aiding, not distracting, the eye), and reasonably precise (more so than ordinary verbal description, especially since they aren't affected by limitations of space); their use should

(2) J. N. Shoolery, R. G. Shulman, W. F. Sheehan, Jr., Verner Schomaker and Don M. Yost, *J. Chem. Phys.*, **19**, 1364 (1951).

(3) A. L. Henne and W. G. Finnegan, *THIS JOURNAL*, **71**, 298 (1949).

(4) See K. Hedberg and A. J. Stosick, *ibid.*, **74**, 954 (1952).

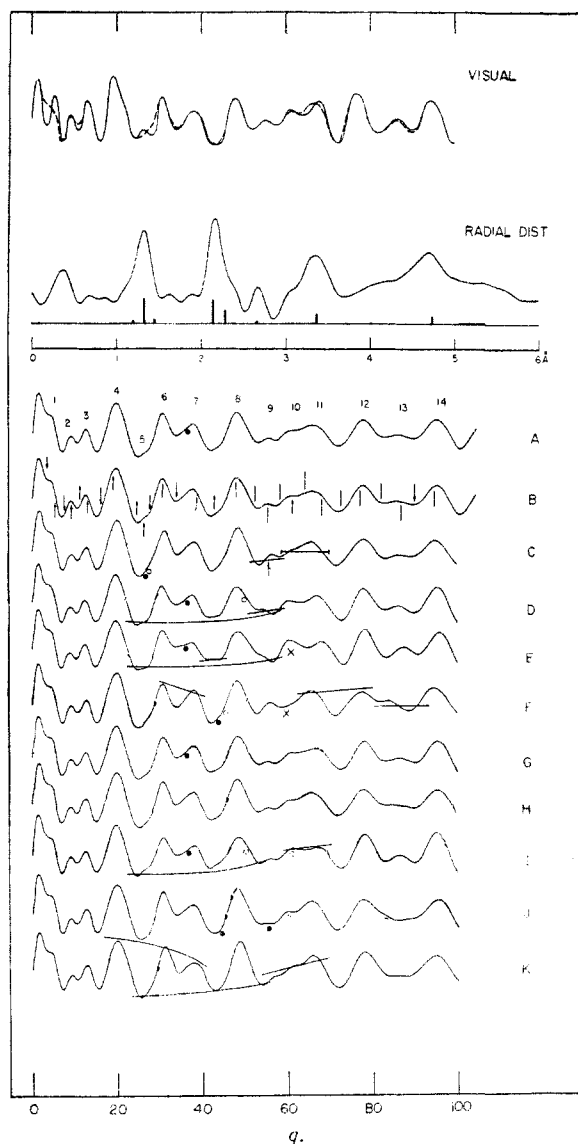


Fig. 1.—Electron diffraction curves for F₃C—C'≡C''—C'''F₃. Visual: Solid, W.S.; as modified by dashed additions, V.S. Both drawn with the help of differential comparisons with the best theoretical curve and photographs of trifluoromethylacetylene.¹ Radial distribution: Based on *solid* visual curve. Theoretical: Final curves

(1) U. S. Rubber Co. Predoctoral Fellow, 1950–1951. Present address: Shell Development Company, Emeryville, California.