

low-boiling petroleum ether it was obtained as an amorphous powder, m. p. 83–91°, yield 19 g. (49%).

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.25; H, 6.62. Found: C, 84.62; H, 6.60.

9-Ethyl-10-phenylphenanthrene.—The carbinol (III, R = C_2H_5) (8 g.) was dissolved in acetic acid (40 cc.) and concentrated hydrobromic acid (22 cc.) added. After the mixture had been refluxed for a few hours, crystals started to separate. After twenty-two hours the crystals were collected and recrystallized from methyl alcohol as small plates, m. p. 161°; yield 4 g. (70%).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.56; H, 6.44. Found: C, 93.38; H, 6.35.

α -Bromopropiophenone was prepared in the same manner as the α -bromobutyrophenone. It was obtained in 90% yield as a yellow oil, b. p. 141° (18–20 mm.).

α -Phenoxypropiophenone was prepared in a manner analogous to that used in the case of α -phenoxybutyrophenone except that a slight excess of phenol and potassium carbonate was used. From 38 g. of α -bromopropiophenone 25 g. (62%) of colorless, silky needles was obtained, m. p. 79–80°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.55; H, 6.41.

1-Phenyl-1-(2-biphenyl)-2-phenoxypropanol-1 (III, R = CH_3) was prepared from 10 g. of α -phenoxypropiophenone by addition to an excess of 2-biphenylmagnesium iodide in a manner analogous to that used in the preparation of III (R = C_2H_5). No attempt was made to purify the crude product from the Grignard reaction. The ether was merely evaporated off and the residue used in the following reaction.

9-Methyl-10-phenylphenanthrene.—The crude carbinol was refluxed with hydrobromic and acetic acids for twenty-four hours. At the conclusion of this period the acid was neutralized and the product extracted with ether. The

ether was evaporated and the residue crystallized from ethanol, as colorless flat needles, m. p. 99–100°; yield 8.5 g. (72%, calculated from α -phenoxypropiophenone used).

Anal. Calcd. for $C_{21}H_{16}$: C, 93.99; H, 6.00. Found: C, 93.96; H, 6.17.

This hydrocarbon formed an orange picrate, m. p. 131–133°.

Desyl phenyl ether (II, R = C_6H_5) was prepared from desyl chloride⁶ in a manner analogous to that used in the preparation of α -phenoxybutyrophenone from α -bromobutyrophenone. From 11.5 g. of the desyl chloride 8.5 g. (59%) of desyl phenyl ether, m. p. 85° was obtained. The product described by Richard⁴ melted at 85.5°.

1,2-Diphenyl-1-(2-biphenyl)-2-phenoxyethanol-1 (III, R = C_6H_5) was prepared by the action of 2-biphenylmagnesium iodide on desyl phenyl ether. The reaction was carried out as described previously (III, R = CH_3 or C_2H_5). The carbinol was not purified.

9,10-Diphenylphenanthrene.—The impure carbinol was refluxed with a mixture of acetic and hydrobromic acids. The hydrocarbon crystallized from the reaction mixture and was recrystallized from acetic acid as long needles, m. p. 234°; yield 6 g. (62%).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.24; H, 5.50.

Summary

A convenient method for the preparation of α -phenoxy ketones has been devised.

By a suitable extension, the new type of ring closure has been used to prepare phenanthrene hydrocarbons with substituents in both the 9- and 10-positions.

(6) Ward, *Org. Syntheses*, **12**, 20 (1932).

DURHAM, N. C.

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Relations between Rotatory Power and Structure in the Sugar Group. XXXII. The Rotations of the Aldonic Gamma Lactones¹

BY C. S. HUDSON

The lactone rule of rotation² is a qualitative expression; it correlates the sign of rotation with the stereoconfiguration of the gamma lactone ring, but the magnitude of the rotation is not disclosed. The extensive data from which the rule was inferred have always seemed to preclude the possibility that the principle of optical superposition can hold in this group of lactones; thus, as one example, the specific rotations ($[\alpha]_D$ in

water) of the gamma lactones of D-ribonic (+18), D-arabonic (+72) and D-xylonic (+92) acids require by this principle that the value for D-lyxonic lactone be +146, but its observed value is +82. It has long seemed strange to me that superposition and also isrotation hold fairly closely among the alpha and beta forms of many sugars and glycosides, and among the aldonic amides, but have appeared to fail completely in the lactone group. Lately I have observed that the more extensive and more accurate data that are now available give good evidence that superposition and isrotation may hold, provided the

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(2) Hudson, *THIS JOURNAL*, **32**, 338 (1910).

TABLE I
THE EPIMERIC DIFFERENCE OF MOLECULAR ROTATION FOR THE TWO CONFIGURATIONAL CLASSES OF ALDONIC GAMMA LACTONES

Class A Lactones ($\neq R_4 \neq R_3$)

(Epimers of configurational type A)

Lactone	Mol. wt.	$[\alpha]_D$	$[M]_D$	Epimeric diff./2
d-Ribonic ^{3,3a}	148	+18	$A_1 + R_2 = +2660$	
d-Arabonic ^{3b}	148	+71.6	$A_1 - R_2 = +10600$	-3970
d-Galactonic ^{3b}	178	-77.4	$A_2 + R_2 = -13780$	
d-Talonic ^{3c}	178	-34.65	$A_2 - R_2 = -6170$	-3800
d-Manno-d-gala-heptonic ^{3d,4}	208	-74.2	$A_3 + R_2 = -15400$	
d-Manno-d-talo-heptonic ^{3e}	208	-35.7	$A_3 - R_2 = -7430$	-3980
d-Gluco-L-talo-octonic ^{3f}	238	+24.6	$A_4 + R_2 = +5850$	
d-Gluco-L-gala-octonic ^{3f}	238	+53.7	$A_4 - R_2 = +12780$	-3460

The data for the following four lactones seem less reliable than those for the preceding ones (see notes 3h and 3j).

L-Epifuconic ^{3g}	162	+36.7	$A_5 + R_2 = +5940$	
L-Fuconic ^{3h}	162	+78.3	$A_5 - R_2 = +12680$	-3370
β -L-Rhamno-hexonic ³ⁱ	192	+43.3	$A_6 + R_2 = +8310$	
α -L-Rhamno-hexonic ^{3j}	192	+83.8	$A_6 - R_2 = +16090$	-3890

Class B Lactones ($\neq R_4 \neq R_3$)

(Epimers of configurational type B)

Lactone	Mol. wt.	$[\alpha]_D$	$[M]_D$	Epimeric diff./2
d-Xylonic ^{3b}	148	+91.8	$A'_1 + R'_2 = +13590$	
d-Lyxonic ^{3k}	148	+82.4	$A'_1 - R'_2 = +12200$	+690
d-Gluconic ^{3b}	178	+68.0	$A'_2 + R'_2 = +12100$	
d-Mannonic ^{3b}	178	+51.5	$A'_2 - R'_2 = +9170$	+1460

lactones are divided into two types, according to their known configurations. The group of gamma lactones of the aldonic acids, beginning with the

(3) The rotations are taken from the following references: (3a) Fischer and Piloty, *Ber.*, **24**, 4214 (1891); (3b) Isbell and Frush, *Bur. Standards J. Research*, **11**, 649 (1933); (3c) Cretcher and Renfrew, *THIS JOURNAL*, **54**, 1590 (1932); (3d) Fischer and Passmore, *Ber.*, **23**, 2226 (1890); (3e) Isbell, *Bur. Standards J. Research*, **20**, 105 (1938); (3f) Hockett and Hudson, *THIS JOURNAL*, **60**, 622 (1938); (3g) Votoček and Kučerenko, *Coll. Czechoslov. Chem. Commun.*, **2**, 47 (1930); (3h) Mütter and Tollens, *Ber.*, **37**, 308 (1904) (two measurements differing by 8%); (3i) Fischer and Morrell, *ibid.*, **27**, 382 (1894); (3j) Fischer and Piloty, *ibid.*, **23**, 3102 (1890) (Jackson and Hudson, *THIS JOURNAL*, **56**, 2455 (1934), recently found +16,760 for this lactone but Fischer's value is used in the table pending a revision of the rotation of the lactone of the β -acid, for which only the quoted value, based upon one determination, is available); (3k) Fischer and Bromberg, *Ber.*, **29**, 581 (1896) (later measurements by Nef and co-workers give higher and lower values and the substance requires further study).

(4) Concerning the nomenclature see Hudson, *THIS JOURNAL*, **60**, 1537 (1938).

pentonic lactones, represents four types of configuration, which may be reduced to epimeric forms of two types, namely, the ribonic-arabonic and the xylonic-lyxonic types. *Within either of these types, the epimeric difference of rotation appears to be approximately a constant quantity.* This generalization is based upon the data of Table I. The R_2 symbols denote the portion of the molecular rotation that is due to carbon atom 2 and the A symbols designate the remainder of the rotation. The approach to constancy in the case of the lactones of Class A is close. The epimeric difference for lactones of Class B is opposite in sign to that for Class A, and it will require further data to determine whether lactones of Class B may show an epimeric difference

that will approach constancy as closely as do the values for substances of Class A, but the available data support the idea of constancy. It may be said in general that the obtaining of dependable data for lactones of Class B is much more difficult than for those of Class A; thus the present value for xylonic lactone ($[\alpha]_D = +91.8$)^{5b} is far larger than the value first found by Clowes and Tollens⁵ (+74.4) and it seems possible that different lactones were under observation.

Classification of Allonic Lactone.—The configuration of allonic lactone is that of a lactone of Class A; it is not included in the table because its epimer, altronic lactone, has never been crystallized. The specific rotation of the latter may be calculated from that of D-allonic lactone (-6.3 ,⁶ m. w. 178) as $(-6.3 + 7600/178) = +36$, where 7600 is the average value of $-2R_2$ from the first four pairs of lactones of the table. The calculated value is near the rotation (+35) reported by Levene and Jacobs⁷ for the amorphous D-altronic lactone; allonic and altronic lactones thus appear to belong in Class A. This conclusion is supported by the observation that the rotation of D-ribonic lactone is near the mean of the rotations of D-allonic and L-talonic lactones.

D-Allonic	$+R_5 + R_4 + R_3 + R_2 = -1120$
L-Talonic	$-R_5 + R_4 + R_3 + R_2 = +6170$
Average	$R_4 + R_3 + R_2 = +2525$
D-Ribonic (obsd.)	$R_4 + R_3 + R_2 = +2660$

Allonic lactone is an exception to the qualitative lactone rule of rotation in that its sign of rotation is negative instead of positive; the present quantitative comparisons indicate, however, that optical superposition holds for it and other lactones of Class A. It seems probable that higher carbon lactones of configurations similar to that of allonic lactone may also be found to be exceptions to the qualitative lactone rule but in agreement with the present quantitative views (*vide infra*).

Classification of D-Gulo-L-talo-heptonic Lactone.—The configuration of the lactone indicates that it is of the Class A type; the rotation of its epimer is not known. The relationship of its rotation ($[\alpha]^{20}_D + 25.5$, mol. wt. 208⁸) to that of talonic lactone is shown from the following comparison, which supports its allocation to Class A.

D-Gulo-L-talo-heptonic	$+R_6 - R_5 + R_4 + R_3 + R_2 = +5304$
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(5) Clowes and Tollens, *Ann.*, **310**, 176 (1899); cf. Nel, *ibid.*, **403**, 253 (1914).

(6) Austin and Humoller, *THIS JOURNAL*, **56**, 1154 (1934).

(7) Levene and Jacobs, *Ber.*, **43**, 3141 (1910).

(8) Isbell, *Bur. Standards J. Research*, **19**, 647 (1937).

L-Manno-L-talo-heptonic

$$-R_6 - R_5 + R_4 + R_3 + R_2 = +7430^{\text{3e}}$$

$$\text{Average } -R_5 + R_4 + R_3 + R_2 = +6367$$

L-Talonic (obsd.) $-R_5 + R_4 + R_3 + R_2 = +6170$

Calculations of the Rotations of Some Unknown Lactones of Class A.—The equations of the preceding paragraph yield the value $R_6 = -1063$ for heptonic lactones of Class A. This value appears to apply closely also to octonic lactones of Class A.

D-Gluco-L-gala-octonic^{3f}

$$R_7 + R_6 - R_5 + R_4 + R_3 - R_2 = +12780$$

D-Gala-L-gala-octonic⁹

$$R_7 - R_6 - R_5 + R_4 + R_3 - R_2 = +15400$$

$$\text{One-half of the difference} = R_6 = -1310$$

The two values of R_6 differ by an amount that corresponds to only one degree in specific rotation. Using the values $R_6 = -1063$ and $2R_2 = -7600$ (from the table, as previously explained) and the molecular rotation of D-allonic lactone (-1120) the following specific rotations of four unknown heptonic lactones of Class A may be calculated.

$$\text{D-Allo-D-allo-heptonic} = (-1120 - 1063)/208 = -10$$

$$\text{D-Allo-D-altro-heptonic} = -10 + 7600/208 = +26$$

$$\text{L-Talo-D-allo-heptonic} = (-1120 + 1063)/208 = 0$$

$$\text{L-Talo-D-altro-heptonic} = 0 + 7600/208 = +36$$

It is seen that the first and third of these lactones may prove to be exceptions to the qualitative lactone rule of rotation because of their similarity to allonic lactone in the important part of their configuration. From the value of $2R_2$ the specific rotations of the unknown epimers of the known D-gulo-L-talo-heptonic (+5304)⁶ and D-gala-L-gala-octonic (+15400)⁹ lactones, of Class A, may be calculated.

$$\text{D-Gulo-L-gala-heptonic} = (+5304 + 7600)/208 = +62$$

$$\text{D-Gala-L-talo-octonic} = (+15400 - 7600)/238 = +33$$

Three Lactones Possessing Unusual Properties.—L-Epirhammonic lactone is reported by Fischer¹⁰ to mutarotate so rapidly (-62 to -46 in twenty minutes and -5 in twenty-four hours) that one is led to believe, from present-day views, that the substance may be a delta rather than gamma lactone; further experimental study is obviously required. Its configuration places it in Class B.

The great speed of mutarotation of β -L-fucohexonic lactone,¹¹ the specific rotation of which

(9) Maclay, Hann and Hudson, *THIS JOURNAL*, **60**, 1036 (1938).

(10) Fischer and Herborn, *Ber.*, **29**, 1961 (1896); Fischer and Zach, *ibid.*, **45**, 3771 (1912).

(11) Votoček, *Coll. Czechoslov. Chem. Commun.*, **6**, 541 (1934).

changes from +69 to +45 in five hours, likewise indicates that the substance may be a delta lactone or a mixture of delta and gamma lactones; a reinvestigation of both the α - and β -L-fucohexonic lactones seems required. They possess the Class B configuration and experience has shown that the isolation of pure gamma lactones of this class requires careful control if the absence of delta lactones, crystalline free acids and their alkyl esters is to be assured.¹²

The optical behavior of D-gluco-D-ido-heptonic lactone appeared unique to Fischer¹³ when he discovered the substance. He reported that its initial specific rotation in water, twenty minutes after dissolving, was -80, which decreased and became nearly constant at -67.7 in twenty-four hours, but that "the mutarotation in this case is not caused by the partial transformation to acid, that occurs with many lactones, since the reaction of the solution remained neutral [*ganz neutral*] throughout the process." Philippe¹⁴ has confirmed this observation of Fischer, finding -82 for the rotation after three minutes, and -68 after six hours, the solution remaining neutral during the change. The cause of this unusual behavior remains hidden but its explanation appears to be required before it is possible to assign a rotatory value to this lactone.

(12) Nef, *Ann.*, **403**, 306 (1914); Isbell and Frush, ref. 3b.

(13) Fischer, *ibid.*, **270**, 64 (1892).

(14) Philippe, *Ann. chim. phys.*, **26**, 330 (1912).

During a conference at Princeton in January, 1939, the data here presented were discussed by Messrs. Walter Kauzmann and John Walter, Dr. Everett Gorin, Prof. H. Eyring, Prof. E. Pacsu and the author. The helpfulness of this conference to the author is gratefully acknowledged.

Summary

The aldonic gamma lactones are divided into two classes, in one of which the configurations are like the ribonic-arabonic pair of epimers (Class A) and in the other like the xyloxylyxonic pair (Class B). Lactones of Class A show an epimeric difference of molecular rotation that is nearly constant. Lactones of Class B, for which the data are not nearly so numerous or dependable as for Class A, show an indication of constancy of epimeric difference with a value that is different from that found for Class A. It seems possible in the case of lactones of Class A to extend the qualitative lactone rule of rotation to a quantitative comparison of rotations, because the constancy of epimeric difference, and certain other comparisons, indicate that optical superposition and isorotation hold fairly closely for lactones of Class A. The unusual characters of the mutarotations of epirhammonic, β -L-fucohexonic and D-gluco-D-ido-heptonic lactones are discussed, and the rotations of six lactones, now unknown, are calculated.

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The Action of Triphenylchloromethane on α -Methyl-D-mannopyranoside¹

BY A. J. WATTERS,² R. C. HOCKETT AND C. S. HUDSON

Recent publications³ have pointed out that polyalcohols containing only secondary hydroxyl groups may be etherified directly by triphenylchloromethane (trityl chloride) in pyridine solution, just as many simple secondary alcohols are etherified.⁴ The preparation of a ditryl uridine

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(2) Commonwealth Fellow, September, 1929-June, 1932.

(3) (a) Hockett and Hudson, *THIS JOURNAL*, **53**, 4456 (1931); (b) Hockett and Hudson, *ibid.*, **56**, 945 (1934); (c) Jackson, Hockett and Hudson, *ibid.*, **56**, 947 (1934).

(4) Helferich, Speidel and Toeldte, *Ber.*, **56**, 766 (1923); Josephson, *Ann.*, **493**, 175 (1932); Fairbourne and Cowdrey, *J. Chem. Soc.*, 129 (1929). We are also informed by Dr. N. M. Carter, Pacific Biological Station, Nanaimo, B. C., Canada, that α,α' -benzylidene glycerol forms a crystalline monotrityl ether; cf. Norris and Young, *THIS JOURNAL*, **52**, 754 (1930).

by Levene and Tipson⁵ provides an example, moreover, of the etherification of a coexistent primary and secondary group and further establishes the limitations of trityl chloride as an agent for analytical determination of the number of primary hydroxyls in compounds of unknown constitution.⁶ It remains unquestioned that the greater velocity with which this reagent attacks primary groups may be utilized advantageously in synthetic work.

The present investigation was undertaken to

(5) Levene and Tipson, *J. Biol. Chem.*, **105**, 419 (1934).

(6) Cf. Josephson, *Ann.*, **472**, 230 (1929); **493**, 174 (1932); *Ber.*, **62**, 313 (1929); Karrer, Schwarzenbach and Schöpp, *Helv. Chim. Acta*, **16**, 302 (1933); Vargha, *Nature*, **131**, 363 (1933).