NOTES.

809. *Characterisation of Cyclic Compounds by Molecular Refractivities.*

By M. VAHRMAN.

WHEN incremental constants for carbon, hydrogen, and double bonds, such as those of Eisenlohr,[1] derived from Lorentz–Lorenz molecular refractivites for aliphatic compounds, are applied to cyclic hydrocarbons, the values obtained ($R_{\text{calc.}}$) are significantly different, in many cases, from those derived from M, d^{20}, and n_{D}^{20} ($R_{\text{obs.}}$). In the case of aromatic compounds, for example, $R_{\text{obs.}} - R_{\text{calc.}}$, although $0 \pm 0{\cdot}2$ for the benzene series, becomes about $+2{\cdot}5$ for the naphthalenes if the constant for an isolated double bond derived from the aliphatic series is used. This deviation (the exaltation) increases with degree of condensation of rings.

If the values for double bonds are omitted (which, in any case, probably have no validity outside the class from which they were derived), it has been found that $R_{\text{obs.}} - R_{\text{calc.}}$ can be used to characterise ring systems.

New constants for carbon and hydrogen were derived from the two homologous series of cyclohexanes and decalins, on the assumption that $R_{\text{obs.}} - R_{\text{calc.}} = 0$.

	$R_{\text{obs.}} - R_{\text{calc.}}$ Range	Mean	Standard deviation
Cyclohexanes [3] (38, from C_6H_{12} to $C_{13}H_{26}$)	$-0{\cdot}4$ to $+0{\cdot}4$	0	0·2
Benzenes [4] (16, from C_6H_6 to $C_{10}H_{14}$)	5·9 to 6·7	6·3	0·2
Decalins [5] (10, from $C_{10}H_{18}$ to $C_{17}H_{32}$)	$-0{\cdot}5$ to $+0{\cdot}5$	0	0·3
Octalins [5] (6, from $C_{10}H_{16}$ to $C_{17}H_{30}$)	2·1 to 2·8	2·5	0·2
Hexalins [5] (7, from $C_{10}H_{14}$ to $C_{15}H_{24}$)	4·1 to 5·0	4·6	0·3
Tetralins [5] (32, from $C_{10}H_{12}$ to $C_{15}H_{22}$)	6·5 to 7·2	6·8	0·2
Dialins [5] (7, from $C_{10}H_{10}$ to $C_{14}H_{18}$)	9·7 to 10·1	9·9	0·2
Naphthalenes [5] (9, from $C_{11}H_{10}$ to $C_{14}H_{16}$)	12·5 to 13·4	13·0	0·3

For 38 cyclohexanes up to $C_{13}H_{26}$ we have $C_{353}H_{706} = 1633{\cdot}338$, whence $CH_2 = 4{\cdot}627$. For 10 decalins up to $C_{17}H_{32}$ we have $C_{125}H_{230} = 553{\cdot}190$, whence $CH_{1{\cdot}84} = 4{\cdot}426$. Thus $C = 2{\cdot}11$, $H = 1{\cdot}26$, and $CH_2 = 4{\cdot}63$.

It is noteworthy that this value for CH_2 is the same as Eisenlohr's, as corrected by Bauer and Fajans.[2]

The constants for the series considered were then as tabulated. Of the data for 131

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[1] Eisenlohr, *Z. phys. Chem.*, 1910, **75**, 585.

[2] Bauer and Fajans in " Technique of Organic Chemistry," Interscience Publ., 1949, Vol. I, Pt. II, p. 1164.

[3] Rodd (ed.), " Chemistry of Carbon Compounds," Elsevier, 1953, Vol. IIA, p. 137.

[4] Ref. 3, Vol. IIIA, p. 101.

[5] " Elsevier's Encyclopædia of Organic Chemistry," 1948, Vol. 12B, pp. 1—344.

compounds originally considered, those for only 6 fell outside the ranges computed and were set aside.

To verify the values for the new atomic constants, $R_{\text{obs.}} - R_{\text{calc.}}$ was calculated for 30 higher n-alkyl homologues from C_{16} to C_{41} in the cyclohexane series, and for 8 from C_9 to C_{42} spaced over the benzene series, with the following results:

	$R_{\text{obs.}} - R_{\text{calc.}}$ Range	Mean	Standard deviation
Cyclohexanes [6] (30, from $C_{16}H_{32}$ to $C_{41}H_{82}$)	−0·05 to +0·19	−0·03	0·05
Benzenes [6] (8, from C_9H_{12} to $C_{42}H_{78}$)	6·27 to 6·34	6·30	0·02

Thus, the mean values of $R_{\text{obs.}} - R_{\text{calc.}}$ for these two series have been verified, with a narrower range of values and a smaller standard deviation for these higher homologues.

I thank A. C. Roy for help with the calculations.

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[*Received, February 22nd, 1960.*]

[6] " Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Inst., 1953.

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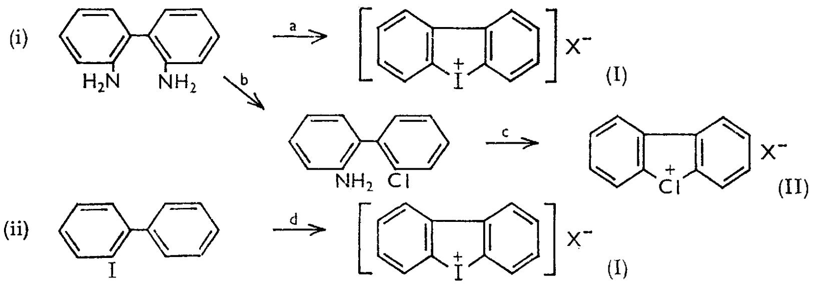
810. *2,2'-Biphenylenehalonium Salts.*

By DOUGLAS LLOYD and RONALD H. MCDOUGALL.

As we required large amounts of 2,2'-biphenylene-iodonium (I) and -chloronium salts (II), we studied the recorded methods (i) and (ii) for their preparation.[1]



a, HNO_2,KI; b, Sandmeyer reaction on monoacetyl derivative; c, HNO_2; d, AcOH, H_2SO_4.

Method (ii) has hitherto been used only for iodonium compounds, and we failed in attempts to use it for preparation of chloronium salts, presumably owing to the smaller tendency of chlorine than iodine to form multivalent oxygen derivatives, which are postulated as intermediates in the cyclisation.[2]

For method (i), 2,2'-diaminobiphenyl is got by reduction of 2,2'-dinitrobiphenyl. In our hands the best method of reduction was by tin and hydrochloric acid.[3] For 1 gram samples consistent results were obtained with hydrazine hydrate (best 10 mols. per nitro-group) and, as catalyst, either W-4 Raney nickel or 10% palladium–charcoal, but when

[1] Mascarelli *et al.*, *Atti R. Accad. Lincei*, 1907, **16**, II, 562; 1908, **17**, II, 580; *Gazzetta*, 1908, **38**, II, 619; Searle and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 1649; Rieger and Westheimer, *ibid.*, 1950, **72**, 28; Wasylewski, Brown, and Sandin, *ibid.*, 1950, **72**, 1038; Clauss, *Chem. Ber.*, 1955, **88**, 268; Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187; Sandin and Hay, *ibid.*, 1952, **74**, 274; Baker, Boarland, and McOmie, *J.*, 1954, 1476; Collette, McGreer, Crawford, Chubb, and Sandin, *J. Amer. Chem. Soc.*, 1956, **78**, 3819.

[2] Masson *et al.*, *Nature*, 1937, **139**, 150; *J.*, 1937, 1718; 1938, 1699.

larger batches were used benzocinnoline replaced much of the diamine (cf. Moore and Furst [3]); 5% palladium–charcoal gave only benzocinnoline 6-oxide.

Biphenyleneiodonium salts were prepared by both methods. The nitrate is more easily recrystallised than the iodide.

The ultraviolet spectra of biphenylene-iodonium and -chloronium salts resemble that of fluorene, although those of biphenyliodonium iodide and diphenylmethane are not alike. Presumably the rigidity of the cyclic halonium salts and of fluorene constrain them to take up similar conformations.

Experimental.—2,2′-Dinitrobiphenyl was prepared from *o*-chloronitrobenzene as described by Baker *et al.*[1] Yields averaged 58%. Kornblum and Kendall's method [4] gave greater yields but needed large volumes of solvent.

Reduction of 2,2′-dinitrobiphenyl. (*a*) 2,2′-Dinitrobiphenyl (20 g.) was heated on a water-bath with powdered tin (100 g.) and concentrated hydrochloric acid (200 ml.) until a clear solution resulted (*ca.* 2·5 hr.). The mixture was made alkaline with sodium hydroxide; ether-extraction gave the diamine (~80%), m. p. 78—79° (from ethanol), b. p. 155°/1·5 mm.

(*b*) 2,2′-Dinitrobiphenyl was dissolved in warm ethanol and hydrazine hydrate added, followed by a small amount of catalyst, in portions, until the reaction had subsided and the solution had become colourless. Further small amounts of catalyst were added to decompose excess of hydrazine. The solution was then boiled to remove dissolved gases, filtered hot, boiled with charcoal, filtered again, and cooled. The amine was isolated by pouring the mixture into very dilute aqueous sodium hydroxide. Best results were obtained with 1 g. of dinitrobiphenyl, 4 ml. of 100% hydrazine hydrate, and 10% palladium–charcoal or W-4 Raney nickel; both gave 74% yields of product, m. p. 78—79°. 5 g. of dinitrobiphenyl, 10 ml. of hydrazine hydrate, and Raney nickel once gave 85% of material of m. p. 77—78°.

Biphenyleneiodonium salts. The iodide is more easily recrystallised from aqueous dimethylformamide than from water. It was converted into the nitrate by reaction with silver nitrate. Yields were by method (i) 80% [as nitrate, m. p. 240° (from water)] and by method (ii) >90% (as sulphate, m. p. 283—284°).

Ultraviolet Spectra. Peaks were as follows: Biphenyleneiodonium nitrate 210, 252, 264, 274, 292 mμ (log ε 4·7; 4·17, 4·24, 4·18, 3·32). Diphenylenechloronium iodide 249, 257, 266 mμ (log ε 4·21, 4·31, 4·16) [cf. fluorene [5] 208, 265, 300 mμ (log ε 4·6, 4·28, 4·0)]. Biphenyliodonium iodide 325 mμ (log ε 2·65) [contrast diphenylmethane [6] 262 mμ (log ε 2·69)].

We are grateful to Dr. H. T. Openshaw and Mr. P. R. Baker of the Wellcome Research Laboratories, Beckenham, for recording some of the spectra. R. H. McD. is indebted to D.S.I.R. for a maintenance award.

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[*Received, March 1st,* 1960.]

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[3] Niementowski, *Ber.*, 1901, **34**, 3327; Macrae and Tucker, *J.*, 1933, 1520; cf. Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, 1932, **6**, 280; Balcom and Furst, *J. Amer. Chem. Soc.*, 1953, **75**, 4334; Dewar and Mole, *J.*, 1956, 2556; Moore and Furst, *J. Org. Chem.*, 1958, **23**, 1504.

[4] Kornblum and Kendall, *J. Amer. Chem. Soc.*, 1952, **74**, 5782.

[5] Menczel, *Z. phys. Chem.*, 1927, **125**, 161; Amer. Petroleum Inst. Res. Project 44, Catalog of U.V. Spectral Data. Serial No. 401.

[6] Orndorff, Gibbs, McNulty, and Shapiro, *J. Amer. Chem. Soc.*, 1927, **49**, 1541; 1928, **50**, 831.

811. *Glow-discharge Electrolysis of Liquid Sulphur Dioxide containing Water.*

By G. H. Cady, H. J. Emeléus, and B. Tittle.

Although numerous studies of the glow-discharge electrolysis of aqueous solutions have been made,[1] little is known of this phenomenon in non-aqueous sytems, apart from the recent synthesis of hydrazine by Hickling and Newns [2] by the electrolysis of liquid ammonia containing ammonium nitrate. The main difficulty with non-aqueous systems is to obtain adequate conduction and in the preliminary experiments on sulphur dioxide, which are described below, this was achieved by adding small amounts of water.

The first preliminary experiments were made with a cell in the form of a U-tube with a sintered glass plate separating the anode and the cathode compartment. The cathode was a platinum wire suspended with its end a few millimetres above liquid sulphur dioxide (*ca.* 30 ml.) to which about 0·50 g. of water had been added. The anode was a small platinum plate immersed in the solution, which was kept at −70°. Both sulphuric acid and sulphur were produced in the cathode solution, the yields being greater than would be expected from Faraday's law. The anode compartment contained a relatively small amount of sulphuric acid and no sulphur. The use of this cell was discontinued because of its high resistance and the rapid movement of solution from anode to cathode by electro-osmosis through the sintered plate.

Quantitative measurements were then made in a cell of 30 mm. internal diameter with an immersed platinum electrode (1·15 sq. cm.) and a platinum wire (0·25 mm. in diameter) suspended 3 mm. from the liquid surface. The phase above the liquid was sulphur dioxide vapour at a pressure of about 20 mm. The cell contained 15·5 ± 0·1 ml. of sulphur dioxide and a measured volume of water, and was kept at −71°. During electrolysis the current was maintained at 0·001 amp. by manual control of the output of a d.c. generator with a maximum output of 2000 v. As electrolysis occurred the resistance of the cell, including the 3 mm. gap, fell from a value in excess of 3×10^6 ohms to a minimum of about $1{\cdot}2 \times 10^6$ ohms. It then rose slowly to about $1{\cdot}9 \times 10^6$ ohms and finally increased sharply so that the required current (0·001 amp.) could not be maintained. The experiment was then terminated. The total number of faradays passed before termination was approximately proportional to the water added.

The products were studied by distilling away sulphur dioxide, adding water to the residue, and filtering off and weighing the sulphur. An aliquot part of the filtrate was titrated with base, and sulphate was determined as barium sulphate. In all cases the sulphate and hydrogen ion were nearly equivalent. A second aliquot part was warmed and titrated with potassium permanganate. Results are tabulated below. With two exceptions the runs were continued to a cell resistance of $2{\cdot}7 \times 10^6$ ohms or more.

Glow-discharge electrolysis of 15·5 ± 0·1 *ml. of liquid sulphur dioxide containing water; current* 0·001 *amp.*

Solute: ml. of H_2O	Total current passed (10^{-5} faraday)	H_2SO_4 produced (moles per faraday)	Sulphur liberated (g.-atoms per faraday)	Other reducing agents: $KMnO_4$ titration (g.-equiv. per faraday)	Ratio reached at end point of electrolysis: moles of H_2O added per mole of H_2SO_4 produced
		Cathode above solution			
0·010	2·3	6·5	5·0	0·63	3·7
0·050	9·5	6·7	4·8	0·17	4·3
0·100	22	6·9	4·7	0·14	3·7
0·100	6·9	7·9	4·3	1·4	Not reached
0·100	2·2	7·1	4·2	2·5	Not reached
		Anode above solution			
0·500	2·5	13·9	6·2	2·3	7·9
0·100	6·9	13·9	8·5	1·6	5·8

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[1] Cf. Davies and Hickling, *J.*, 1954, 711.

[2] Hickling and Newns, *Proc. Chem. Soc.*, 1959, 272.

The Table shows that the number of moles of sulphuric acid produced per faraday is, to the accuracy of the experiment, independent of the amount of water present and the stage the electrolysis has reached. The number of g.-atoms of sulphur produced per faraday at the end of the electrolysis, *i.e.*, when the resistance starts to rise rapidly, is also independent of the added water. The water-soluble reducing agent produced in the electrolysis tends to disappear as the electrolysis continues, probably because it is preferentially discharged at the electrodes.

The soluble reducing agent has not been identified: it could be a mixture of substances. A trace of hydrogen sulphide was present in the aqueous solution, as indicated by the odour. It is probable that sulphur was a secondary product since none was observed early in the electrolysis. The data for the suspended anode and cathode both show yields of sulphuric acid and sulphur in excess of those expected from Faraday's law. No oxygen was found among the reaction products, though very small amounts might not have been detected. Attack on the electrodes was very slight and the suspended wire lost only 0·0004 g. during the passage of $7{\cdot}5 \times 10^{-4}$ faradays of electricity. These experiments serve to illustrate the possibility of obtaining some quantitative data from a system such as this, in spite of its great complexity. They shed no light on the reaction mechanism, and the clue to this might be in the identification of the ionic and molecular species associated with the glow discharge.

One of the authors (B. T.) thanks the Department of Scientific and Industrial Research for a Maintenance Grant.

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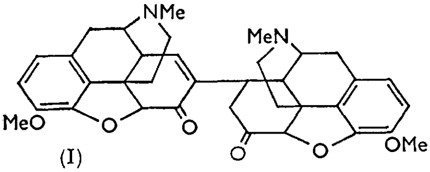
812. *Oxidation Products from Codeine.*

By IVOR BROWN and M. MARTIN-SMITH.

OXIDATION of codeine gives various products according to the reagent and the conditions.[1-3] We now report two further cases discovered during preparation of codeinone.

Substitution of manganese dioxide b * for " Attenburrow " manganese dioxide [5] in a previous procedure for the oxidation of codeine gave, in place of codeinone,[2] a 30% yield of 14-hydroxycodeinone. This direct allylic oxidation has analogies in the conversion of cyclohexene into cyclohexenone,[6] of cholesteryl acetate into 7-hydroxy- and 7-oxo-cholesteryl acetates,[6] and of vitamin A_1 into 3-hydroxy- and 3-oxo-retinene$_1$.[4]



(I)

A procedure using chromic oxide in acetic acid [3] gave, under certain conditions, not codeinone, but the dimer (I), known to result from condensation of neopinone and codeinone and from solutions of the anion (II) which generates a mixture of neopinone and codeinone *in situ*.[7] The dimer was isolated only when an excess of base was employed in the neutralisation of the acidic reaction mixture before isolation of the product. As codeinone itself

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* This term, to describe a commercial grade of manganese dioxide, is that used by Henbest, Jones, and Owen.[4]

[1] See, *inter alia*, Ach and Knorr, *Ber.*, 1903, **36**, 3067; Knorr and Hörlein, *Ber.*, 1907, **40**, 4889; Holmes and Lee, *J. Amer. Chem. Soc.*, 1947, **69**, 1996; Cahn and Robinson, *J.*, 1926, 908; Dieterle and Dickens, *Arch. Pharm.*, 1926, **264**, 257; G.P. 408,870, 1923; Rapoport and Reist, *J. Amer. Chem. Soc.*, 1955, **77**, 490.

[2] Highet and Wildman, *J. Amer. Chem. Soc.*, 1955, **77**, 4399.

[3] Findlay and Small, *J. Amer. Chem. Soc.*, 1950, **72**, 3247.

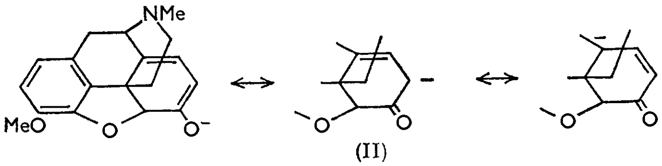
[4] Henbest, Jones, and Owen, *J.*, 1957, 4909.

[5] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.

[6] Meunier, Zwingelstein, and Jouanneteau, *Bull. Soc. Chim. biol.*, 1953, **35**, 495.

[7] Conroy, *J. Amer. Chem. Soc.*, 1955, **77**, 5960.

does not form this dimer on treatment with base, it may be that the codeinone produced exists in the reaction mixture as the dienol chromate ester which on treatment with excess of base liberates the dienolate anion (II) with consequent formation of the dimer.



(II)

To prepare the dimer it is only necessary to generate the anion (II) in an unambiguous manner [7] and in this work this was achieved by the mild alkaline hydrolysis of codeinone enol acetate.[8]

Experimental.—M. p.s were taken on a Kofler block.

14-*Hydroxycodeinone.* Codeine (1 g.) in chloroform (100 ml.) was shaken at room temperature with manganese dioxide b for 24 hr. After filtration, the manganese dioxide was extracted several times with hot chloroform, and the residue (0·48 g.) from the combined filtrates was crystallised from ethyl acetate, giving material (0·3 g.) which on sublimation had m. p. and mixed m. p. 279·5—280·5° and $[\alpha]_D$ −116° (*c* 0·92 in 10% acetic acid) {lit.,[9,10] m. p. 275°, $[\alpha]_D$ −111° (in 10% acetic acid)}, having the correct infrared spectrum (KCl disc). The oxime had m. p. 278° (decomp.) (lit.,[9] 279—280°) (Found: C, 65·6; H, 5·9; N, 8·5. Calc. for $C_{18}H_{20}N_2O_4$: C, 65·9; H, 6·1; N, 8·5%).

Dimer (I). (*a*) Codeine chromate (10 g.) was oxidised as previously reported [3] and the acid extract of the chilled ethereal solution (50 ml. of N-sulphuric acid) was poured into N-sodium hydroxide (165 ml.). The solution darkened and after removal of a small quantity of insoluble material (40 mg.) it was extracted with chloroform (25 ml.). Crystallisation of the oily residue therefrom yielded material (0·5 g.), m. p. 244° (from ethyl acetate), $[\alpha]_D$ −198·5° (*c* 0·9 in $CHCl_3$), $\lambda_{max.}$ 230, 281 mμ (ε 19,000, 3120) [lit.,[7] m. p. *ca.* 245° (decomp.), $\lambda_{max.}$ 230, 281 mμ (ε 18,100, 2860)] (Found: C, 72·4; H, 6·4. Calc. for $C_{36}H_{38}O_6N_2$: C, 72·7; H, 6·4%).

(*b*) Codeinone enol acetate [8] (0·5 g.) in methanol (10 ml.) was treated with a saturated solution of sodium carbonate (8 ml.), ethanol (50 ml.) being added to keep the whole in solution. After 5 min. on the steam-bath the solution was left for 1 hr. at room temperature. Dilution with water followed by extraction of the red solution with chloroform gave a residue (0·47 g.) which, crystallised from ethyl acetate had m. p. and mixed m. p. 244° (0·35 g.). The infrared spectra (KCl disc) confirmed the identity of the two specimens.

The authors thank Messrs. T. and H. Smith Ltd., for codeine, Mr. A. C. Currie of the Royal College of Science and Technology, Glasgow, for 14-hydroxycodeinone, Mr. J. M. L. Cameron and his staff for the microanalyses, and Dr. G. Eglinton and his colleagues for the infrared spectra. One of the authors (I. B.) acknowledges the tenure of a fellowship awarded by Glaxo Laboratories Ltd.

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[8] G.P. 902,257/1954; *Chem. Abs.*, 1956, **50**, 5043.

[9] Freund and Speyer, *J. prakt. Chem.*, 1916, **94**, 166.

[10] Lutz and Small, *J. Org. Chem.*, 1939, **4**, 220.