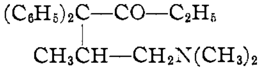
acid. The ketone was isolated as the sesquioxalate (m. p. 162–163°. *Anal.* Calcd. for $2C_{21}H_{27}ON \cdot 3H_2C_2O_4$: C, 64.86; H, 6.76; N, 3.15; $H_2C_2O_4$, 30.41; neut. equiv., 148. Found: C, 65.2; H, 6.66; N, 3.43, 3.39; $H_2C_2O_4$, 30.40; neut. equiv., 149). This was further characterized as the base (oil, b. p. 215° under 12 mm. *Anal.* Calcd. for $C_{21}H_{27}ON$: C, 81.50; H, 8.80; N, 4.53. Found: C, 81.50; H, 8.90; N, 4.54, 4.52), the hydrochloride (m. p. 189–191°. *Anal.* Calcd. for $C_{21}H_{27}ON \cdot HCl$: C, 72.92; H, 8.16; N, 4.05; Cl, 10.25. Found: C, 72.95; H, 8.14; N, 4.02, 4.08; Cl, 10.24), the picrate (m. p. 149–150°. *Anal.* Calcd. for $C_{21}H_{27}ON \cdot C_6H_3O_7N_3$: C, 60.22; H, 5.58; N, 10.41. Found: C, 59.95; H, 5.54; N, 10.55, 10.52) and the methiodide (m. p. 263–264°. *Anal.* Calcd. for $C_{22}H_{30}ONI$: C, 58.54; H, 6.70; N, 3.10; I, 28.11. Found: C, 58.45; H, 6.78; N, 3.06; I, 28.25, 28.35).



$$\begin{array}{l}(C_6H_5)_2C\text{—}CO\text{—}C_2H_5\\ \qquad\;\;|\\ \quad CH_3CH\text{—}CH_2N(CH_3)_2\end{array}$$

V

When the crude mixture obtained by the condensation of diphenylacetonitrile with 1-dimethylamino-2-chloropropane was treated with ethylmagnesium bromide, there was formed, among other products, another isomer of amidone, which has been designated as Isoamidone I. This was isolated as the binoxalate (m. p. 158–160°. *Anal.* Calcd. for $C_{21}H_{27}ON \cdot H_2C_2O_4$: C, 69.15; H, 7.32. Found: C, 69.20; H, 7.06). This was also characterized as the base (oil, b. p. 164–167° under 3 mm. *Anal.* Calcd. for $C_{21}H_{27}ON$: C, 81.50; H, 8.80; N, 4.53. Found: C, 81.35; H, 8.84; N, 4.76, 4.73), the hydrochloride (m. p. 172–173°. *Anal.* Calcd. for $C_{21}H_{27}ON \cdot HCl$: C, 72.92; H, 8.16; N, 4.05; Cl, 10.25. Found: C, 73.05; H, 8.21; N, 4.25, 4.22; Cl, 10.25) and the methiodide (m. p. 195–196°. *Anal.* Calcd. for $C_{22}H_{30}ONI$: C, 58.54; H, 6.70; I, 28.11. Found: C, 58.65; H, 6.85; I, 28.40, 28.50). From this, it appears that there is a third aminonitrile formed in the original condensation.

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RECEIVED MARCH 18, 1947

THE CATHODIC PROTIUM-TRITIUM SEPARATION FACTOR

Sir:

Protium–tritium separation factors of 13.4 and 14.7 were observed in the electrolysis at 20.0° of a 10% sodium hydroxide solution at a smooth platinum foil cathode using a current density of 0.1 amp./sq.cm. The alkaline solution contained approximately 10^{-11} atom fraction tritium and had a normal deuterium content. Protium–deuterium separation factors of 6–8 have been reported for smooth platinum cathodes in both acid and alkaline media.[1]

Tritium activity was measured using a counting gas mixture consisting of hydrogen, ethyl alcohol, and argon at 25, 20 and 20 mm. partial pressure at 25° in a glass envelope copper gauze cathode Geiger counter having an effective counting volume of about 200 cc. Approximately 2×10^{-3} mole of hydrogen was produced in an electrolytic run, the isotopic composition of the medium remaining practically constant. Under these conditions the isotope separation factor equals the tritium–protium concentration ratio in the alkaline solution divided by that for the cathode gas. Water vapor was stripped from the latter using a liquid air trap and traces of oxygen were removed by combustion over a glowing nichrome wire. The tritium activity of the alkaline solution was determined by quantitatively converting the hydrogen in 0.05-g. samples of solution to hydrogen gas over magnesium at 630° in an analytical train previously "seasoned" at this activity. Table I summarizes the pertinent data.

TABLE I

Hydrogen source		Tritium activity in counts per minute per mm. at 25° of hydrogen gas	Isotope separation factor
Alkali solution		574 (Average, 571)	
		568	
Cathode gas	Electrolysis 1	38.9	14.7
	Electrolysis 2	42.7	13.4

The equilibrium constant at 20.2° for the reaction

$$HT + H_2O \rightleftharpoons H_2 + HTO$$

has been reported to be 6.47 ± 0.12 by Black and Taylor.[2] Libby[3] calculated a value of 6.24 for this equilibrium at 20°. The protium–tritium ratio for the hydrogen gas in the electrolyses reported above is thus slightly more than twice that corresponding to thermodynamic equilibrium conditions prevailing at the electrode interface. A detailed description of the analytical techniques developed for this study will be reported elsewhere. This investigation was supported by a grant from the Research Corporation.

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[1] B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934); A. Eucken and K. Bratzler, *Z. physik. Chem.*, **A 174**, 269 (1935).

[2] J. F. Black and H. S. Taylor, *J. Chem. Phys.*, **11**, 395 (1943).

[3] W. F. Libby, *ibid.*, **11**, 101 (1943).

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MAXWELL LEIGH EIDINOFF

RECEIVED MARCH 8, 1947

TAUTOMERISM IN CYCLOHEXANE DERIVATIVES; REASSIGNMENT OF CONFIGURATION OF THE 1,3-DIMETHYLCYCLOHEXANES

Sir:

It is now established that cyclohexane has predominantly the chair configuration.[1] Except for

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[1] R. Rassmussen, *J. Chem. Phys.*, **11**, 249 (1943), and others there cited.

the work of Hassel,[2] however, the implications of this result with respect to cyclohexane derivatives have not been investigated. In the chair configuration, there are three hydrogen atoms above the carbon ring which together with the three equivalent hydrogens below the ring will be called polar (p). The other six hydrogens lie in an equatorial belt around the ring and will be called equatorial (e).

A monosubstituted cyclohexane can have the substituent either polar or equatorial. Since one form is converted to the other by mere distortion of bond angles (*i.e.*, passing through boat forms) they will be tautomers. For methylcyclohexane, the equatorial form is strain free, but the polar form involves steric interference. From comparison with similar interferences in the *n*-paraffins, this may be estimated to be about 2 kcal.

The possible configurational tautomers of the dimethylcyclohexanes are listed in Table I together with the estimated energy differences. Successive carbon atoms around the ring have their polar hydrogens alternately up and down. Thus *cis* 1,2, *trans* 1,3, and *cis* 1,4 have necessarily one polar and one equatorial methyl group. Correspondingly, *trans* 1,2, *cis* 1,3, and *trans* 1,4 can have both methyl groups equatorial or both polar, the former having much lower energy.

TABLE I

S^*, entropy contribution of tautomerism, optical isomerism and symmetry, cal./deg. mole.

	Tautomers		S^*	
Cmpd.	Config.	Description	Calcd.	Exptl.
cis 1,2	e, p p, e	Enantiomorphs	1.38[a]	0.83 ± 0.3
trans 1,2	e, e p, p	Energy diff. 3 kcal. *dl* isomers each with sym. no. 2	0.08	0.09 ± 0.3
cis 1,3	e, e p, p	Energy diff. 6 kcal.	0.00	0.06 ± 0.3[b]
trans 1,3	e, p p, e	Tautomers identical *dl* isomers	1.38	1.10 ± 0.3[c]
cis 1,4	e, p p, e	Identical	0.00	(.00)
trans 1,4	e, e p, p	Energy diff. 4 kcal. Sym. no. 2 each case	−1.36	−1.58 ± 0.3

[a] Greater interference to methyl rotation will reduce this value to agree with exptl. value. [b] For cmpd. previously labelled *trans*, b. p. 120.1°. [c] For cmpd. previously labelled *cis*, b. p. 124.5°.

Skita and Schneck[3] assigned the configuration of the dimethylcyclohexanes on the basis of higher b.p., refractive index, etc., for the *cis* isomer. However, in this case there is no real geometrical similarity associated with the *cis* name. It seems more likely that the presence or absence of a polar methyl in the low energy tautomer would determine the physical properties. Thus if Skita's assignment is correct for 1,2- and 1,4-dimethylcyclohexanes probably it should be reversed for the 1,3-dimethylcyclohexanes. This last conclusion is strongly supported by the experimental entropies of these substances.[4] While detailed calculations will be presented later, the principal differences between isomers arise from tautomerism, optical isomerism and symmetry. These entropy contributions are listed in Table I, which shows that agreement is obtained only when the assignment of *cis* and *trans* configuration is reversed for the 1,3 dimethylcyclohexanes.

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[2] O. Hassel, *Tids. Kjemi, Bergvesen Met.*, **3**, 32 (1943).

[3] A. Skita and A. Schneck, *Ber.*, **55B**, 144 (1922).

[4] Values for liquid from Oliver, Todd and Huffman, kindly communicated to us before publication. Vaporization data from Tables of Project 44 of the American Petroleum Institute.

PROJECT 44 OF THE AMERICAN PETROLEUM INSTITUTE
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RECEIVED FEBRUARY 24, 1947

OPTICAL ACTIVITY FROM A NEW TYPE OF STERIC HINDRANCE[1]

Sir:

We wish to report the synthesis and resolution of 4,5,8-trimethyl-1-phenanthrylacetic acid. The optical activity in this molecule in undoubtedly due to the fact that the methyl groups in the 4 and 5 positions are forced out of the plane of the phenanthrene nucleus,[2] as indicated in the figures.

The racemic acid was prepared by an eleven-step synthesis starting from 5,8-dimethyl-1-keto-1,2,3,4-tetrahydronaphthalene.[3] A Reformatsky reaction using ethyl α-bromopropionate, followed by dehydration, dehydrogenation, and hydrolysis afforded α-(5,8-dimethyl-1-naphthyl)-propionic acid. By two successive Arndt–Eistert reactions this was converted into γ-(5,8-dimethyl-1-naphthyl)-valeric acid, which on ring closure yielded 4,5,8-trimethyl-1-keto-1,2,3,4-tetrahydrophenanthrene. A Reformatsky reaction using ethyl bromoacetate, followed by dehydration, dehydrogenation, and hydrolysis resulted in the formation of the desired acid, m. p. 142.6–143.6°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found: C, 81.6, 81.9; H, 6.4, 6.4.

Resolution was effected by forming the brucine salt and recrystallization from ethyl acetate–ethyl alcohol solutions. Some difficulty was encountered because the salt racemizes in solution fairly easily and it crystallizes slowly. Hence we do not believe we have achieved maximum resolution. We obtained a number of fractions in the form of clusters of fine colorless needles, m. p. 126–128° after sintering at 122°, $[\alpha]^{22}\text{D}$ −33.3° (0.0907 g. in 2 ml. of ethyl acetate, 1-dm. tube).

Anal. Calcd. for $C_{42}H_{44}O_6N_2$: C, 75.0; H, 6.6; N, 4.2. Found: C, 74.4; H, 7.0; N, 4.0.

The free acid obtained from this salt in different experiments was either inactive or dextrorotatory,

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[1] The material herein presented is contained mostly in the Ph.D. thesis of Allen S. Hussey, Ohio State University, March, 1946. Further experiments on the resolution were made by Dr. Hussey at Northwestern University.

[2] See discussion, Newman, THIS JOURNAL, **62**, 2295 (1940).

[3] Ruzicka and Waldmann, *Helv. Chim. Acta*, **15**, 907 (1932).