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.

Cmpd.	Tautomers Config.	Description	S^* Calcd.	S^* 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.

(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
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA KENNETH S. PITZER
BERKELEY, CALIFORNIA CHARLES W. BECKETT

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°, $[\alpha]^{22}D$ −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,

(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).

but it was difficult to obtain consistent results because of the ready racemization of the acid in solution. The best sample had $[\alpha]^{26}D$ 2.4 ± 0.5° (0.0538 g. in 2 ml. of ethyl acetate, 2-dm. tube). It melted at the same temperature as the racemic acid and the mixed melting point was not depressed. Further studies of the racemization of the salt and the acid will be made and a full description of this work and of the synthesis of 1,4,5-trimethylphenanthrene, m. p. 62.6–63.0°, will be published soon.

THE OHIO STATE UNIVERSITY MELVIN S. NEWMAN
COLUMBUS 10, OHIO
NORTHWESTERN UNIVERSITY ALLEN S. HUSSEY
EVANSTON, ILLINOIS

RECEIVED MARCH 17, 1947

HYDROGEN CHLORIDE AS A CONDENSING AGENT

Sir:

Mr. S. H. McAllister has kindly pointed out to us an error in our paper "Hydrogen Chloride as a Condensing Agent", in THIS JOURNAL, **66**, 1309 (1944), in the statement that the alkylation of toluene with isopropyl chloride using hydrogen chloride as the catalyst resulted in the exclusive formation of the para substituted product. In a duplication of this experiment in the laboratories of the Shell Development Company by Mr. Edwin F. Bullard, it was found by infrared spectral analysis that the monosubstituted product contained 25% ortho, 22% meta, and 53% para. As we do not have the expensive equipment available in the industrial laboratory, our products were kindly analyzed by Mr. F. S. Mortimer of the above mentioned company with the following results: 31 ± 1% ortho, 27 ± 1% meta, and 42 ± 1% para. These analyses have been confirmed by Dr. R. V. Weigand at The Pennsylvania State College by raman spectra with the following results: 38% ortho, 25% meta, and 37% para.

This illustrates the need of caution in giving the ratio of isomers in a product when adequate methods of analysis are not available.

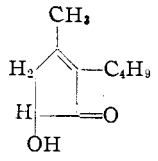
SCHOOL OF CHEMISTRY AND PHYSICS J. H. SIMONS
THE PENNSYLVANIA STATE COLLEGE HAROLD HART
STATE COLLEGE, PENNA.

RECEIVED MARCH 29, 1947

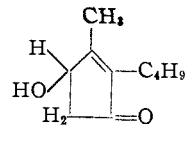
THE SYNTHESIS OF DIHYDROCINEROLONE

Sir:

In a previous communication[1] we reported the synthesis of 1-butyl-5-hydroxy-3-methyl-2-cyclopenten-1-one (I), the structure previously ascribed to dihydrocinerolone.[2] As the α-hydroxyketone (I) was not identical with the dihydro derivative



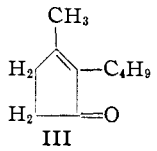
I



II

of natural cinerolone, the revised formula 2-butyl-4-hydroxy-3-methyl-2-cyclopenten-1-one (II) was suggested.

We have now synthesized the hydroxy ketone identical with dihydrocinerolone. The synthesis was accomplished by the bromination of dihydrocinerone (III) with the employment of N-bromo-



III

succinimide and subsequent hydrolysis of the bromo derivative.

Equimolecular quantities of dihydrocinerone and N-bromosuccinimide in carbon tetrachloride were heated under reflux for eighteen hours and, after removal of the insoluble succinimide and the solvent, the crude bromo derivative was hydrolyzed by refluxing with an aqueous suspension of calcium carbonate. This hydrolysis procedure has been employed for the conversion of chlorocinerone to cinerolone. The product had properties in agreement with those of dihydrocinerolone (Table I).

TABLE I

COMPARISON OF THE PROPERTIES OF DIHYDROCINEROLONES

Dihydrocinerolone	B. p. °C.	Mm.	n_D	Semicarbazone m.p., °C.	3,5-Dinitrobenzoate m. p., °C.
From cinerolone	115–117	1[2]	1.4958 (22°)[2]	185[2]	111
Synthetic	110–114	0.3	1.4955 (25°)	187	111

The slight difference in melting points of the semicarbazones is probably due to impurities in the natural materials (mixed m. p. 185–187°). A similar difference in the melting points of the 3,5-dinitrobenzoates was initially observed. However, after several recrystallizations the derivative from the natural material melted at the same point as that of the synthetic compound (mixed m. p. 111°).

The substitution of bromine into the 4-position of dihydrocinerone (III) is not unexpected, as Ziegler and co-workers[3] have shown that N-bromosuccinimide characteristically brominates in the allyl position. These results, then, support structure II for dihydrocinerolone.

The action of N-bromosuccinimide is being

(1) LaForge and Soloway, THIS JOURNAL, **69**, 186 (1947). In column 1, line 8, the position of the hydroxyl group in the name of the compound should read "5" in place of "4."

(2) LaForge and Barthel, *J. Org. Chem.*, **10**, 222 (1945).

(3) Ziegler and co-workers, *Ann.*, **551**, 80 (1942).