to find what substances should be carefully studied, ordinary C. P. materials were used without further purification. The oxides used were shown to yield no carbon dioxide when treated with an acid. All the substances were dried overnight in a vacuum oven at 30° and kept in a vacuum desiccator until used. About 0.5 g. of the acid and 0.25 g. of the substance were ground together and placed in the reaction tube. The chemical method was used. The temperature of the bath was 115–116°. The results are given in Table III.

Summary

1. The temperatures have been determined at which a number of substituted malonic acids first begin to show evidence of decomposition when they are heated so that the temperature is increased at the rate of two degrees per minute.

2. The relationship is discussed between the composition, structure and the number of radicals present and the cracking temperatures so determined.

3. The results are of value in showing the effect of structure on the lability toward heat of a carbon to carbon bond in these compounds.

4. It is shown that certain contact substances lower the temperature at which this bond is broken by heat.

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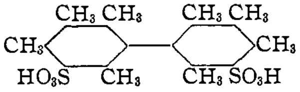
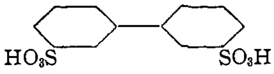
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Diphenyls. XXXIV.[1] Preparation and Properties of 2,2′,4,4′,5,5′,6,6′-Octamethyldiphenyl-3,3′-disulfonic Acid and Diphenyl-3,3′-disulfonic Acid

BY A. E. KNAUF[2] AND ROGER ADAMS

The resolution of 2,2′,4,4,′5,5′,6,6′-octamethyldiphenyl-3,3′-disulfonic acid (I) into optical antipodes has been accomplished. The active forms could not be racemized by any of the usual methods. On the other hand, attempts to resolve the corresponding diphenyl 3,3′-disulfonic acid (II) have been unavailing.


I


II

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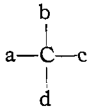
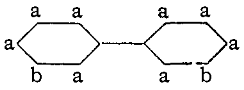
[1] For the previous paper in this field see VanArendonk, Becker and Adams, THIS JOURNAL, **55**, 4230 (1933). See also Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

[2] Submitted as a thesis for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

This pair of compounds illustrates more strikingly than do other recorded cases a peculiarity of the stereoisomerism in the diphenyl and related series, which has not hitherto been explicitly pointed out.

The theory of van't Hoff predicts that any compound of the type  $a-\overset{\displaystyle b}{\underset{\displaystyle d}{C}}-c$ should exist in two stereoisomeric forms—assuming that the substituents a, b, c, d are univalent radicals which are not in themselves optically active. It is of the very essence of this theory that the existence of the two isomers is in no wise dependent upon the specific properties of the individual radicals, but is conditioned solely by the fact that they are all four different from one another. Like considerations hold when van't Hoff's idea is applied to compounds containing more than one asymmetric carbon atom; they are equally applicable to cyclic and to open chain compounds; they account for the stereoisomerism in the allene and spiro series; and they apply also to molecular dissymmetry such as that observed among the inositols. Even the stereoisomerism attributed to elements other than carbon can be explained without change in this aspect of the van't Hoff theory. In all these cases, the number of stereoisomers depends upon the structure of the molecular skeleton, the number of univalent substituents of each particular kind, and the way in which the univalent substituents are distributed to satisfy the free valence of the skeleton. The specific properties of the univalent substituents themselves should be without effect on the number of isomeric forms.

But the stereoisomerism in the diphenyl and related series is not in accord with this widespread rule. The pair of substances cited above illustrates the impossibility of predicting the number of stereoisomeric forms of a compound defined only by the type formula III.



III

If (a) is the hydrogen atom there is one form; if (a) is the methyl radical there are two. In other words, the number of forms is not a type property of the molecule, but depends upon the specific nature of the univalent substituents.

It is thus evident that no mere extension of the van't Hoff theory (such as the one introduced by Werner) can account for the stereoisomerism in the diphenyl and other similar series. A new and independent assumption is indispensable. The various hypotheses hitherto suggested show that considerable freedom of choice in this field still exists. But to get along without some addition to the classical theory is formally impossible.[3]

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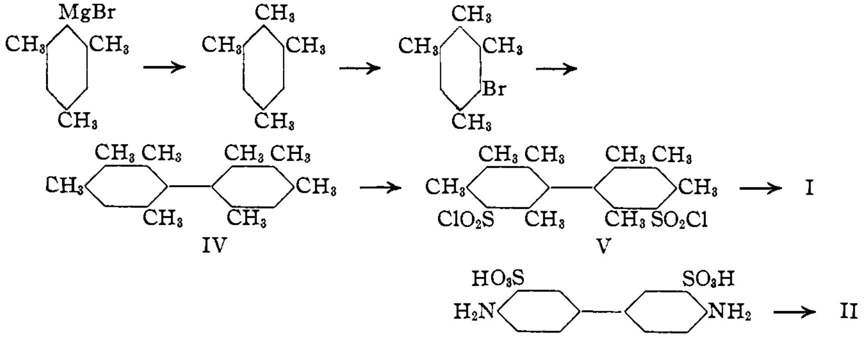
(3) The problem to obtain two compounds of the type described in this research was started over five years ago but owing to experimental difficulties, has just been completed. During this period Dr. J. K. Senior has continuously expressed his interest in this particular investigation. He was kind enough to present his views in writing and the authors have adopted them without essential change for the introductory paragraphs of this communication.

Experimental

Compounds I and II were prepared by the following series of reactions



During the course of the investigation the 3,3′-diaceto. and 3,3′-dichloroaceto derivatives of 2,2′,4,4′,5,5′,6,6′-octamethyldiphenyl were prepared but could not be successfully used.

2,2′,4,4′,5,5′,6,6′-Octamethyldiphenyl (Diisoduryl) (IV).[4]—In a 3-liter three-necked flask fitted with a mechanical stirrer, reflux condenser and 500-cc. dropping funnel were placed 24.3 g. of magnesium turnings, 70 g. of bromoisodurene,[5] 100 cc. of anhydrous ether and a few crystals of iodine. By warming the flask without stirring the reaction was started and allowed to proceed for a few minutes. Mechanical stirring was started and a solution of 143 g. of bromoisodurene in 400 g. of dry ether was added at such a rate that the ether refluxed steadily. The addition of the halide required about three hours, after which stirring was continued and the mixture heated on a steam cone for about twelve hours. The flask was then cooled and when the contents were at 10 °, 150 g. of finely powdered anhydrous cupric chloride was added as rapidly as the heat of the reaction permitted. To avoid loss of ether and to prevent hydration of the cupric chloride, the cupric chloride was placed in an Erlenmeyer flask which was connected by means of rubber tubing to the large end of an adapter. The small end of the adapter was attached to the flask containing the Grignard solution at the opening which previously held the dropping funnel. By properly inclining and shaking the Erlenmeyer flask the rate of flow of the powdered cupric chloride could be regulated. After addition of all of the solid, the ether was kept refluxing gently and vigorous stirring was continued for about twenty-four hours. At the end of this time the mixture was poured slowly into cracked ice and hydrochloric acid sufficient in amount to dissolve all of the solid (cuprous chloride). The ether layer was washed, and dried with anhydrous sodium sulfate. After removing the ether the remaining liquid was fractionally distilled under reduced pressure. The fraction boiling above 145° at 4 mm. was taken as crude diisoduryl. It solidified on cooling and was purified by crystallization from glacial acetic acid and washing the crystals with methyl alcohol; white crystals, m. p. 121–122°, yield 56 g. (21%).

Anal. Calcd. for $C_{20}H_{26}$: C, 90.15; H, 9.85. Found: C, 90.34; H, 10.07.

2,2′,4,4′,5,5′,6,6′-Octamethyldiphenyl-3,3′-disulfonyl Chloride (V).—Two grams of diisoduryl was added in small quantities with stirring to 10 g. of chlorosulfonic acid which

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(4) This substance was first made by W. M. Moyer as part of an earlier investigation.

(5) Isodurene was obtained by the procedure described by Smith and MacDougall, THIS JOURNAL, **51**, 3003 (1929), and was brominated by the method used by these authors for making bromomesitylene from mesitylene.

had been previously cooled to 0° by a freezing mixture of ice and salt. The diisoduryl dissolved completely and after the mixture had stood for one hour it was poured onto ice. After washing, the solid was dried in a desiccator containing sulfuric acid. Purification from benzene gave white crystals, m. p. 159–160°, yield 2.8 g. (77%).

Anal. Calcd. for $C_{20}H_{24}O_4S_2Cl_2$: Cl, 15.33. Found: Cl, 15.50.

Preparation and Resolution of 2,2′,4,4′,5,5′,6,6′-Octamethyldiphenyl-3,3′-disulfonic Acid (Diisoduryl Disulfonic Acid).—A mixture of 2.3 g. of V and a solution of 1 g. of sodium hydroxide in 150 cc. of water was boiled until solution was complete (about eight hours). The excess of sodium hydroxide was neutralized with dilute hydrochloric acid and the solution filtered free of solid material. The solution of sodium diisoduryl disulfonate was heated to boiling and added slowly to a solution of 4.1 g. of strychnine hydrochloride in 200 cc. of water. After standing for about twelve hours, the white crystals which had formed were filtered off and after drying first in an oven at 120° for four hours and then in an Abderhalden drier at 100° and 4 mm. pressure weighed 2.3 g. Evaporation of the mother liquor to a volume of 100 cc., followed by standing for twelve hours, yielded another crop of crystals which, when dried by the above method, weighed 2.2 g. Both fractions melted at 252–255° (with dec.). Further evaporation gave no crystals and when dry a dark brown rather gummy residue was obtained.

Rotation. 0.1786 g. of first fraction made up to 10 cc. in 80% methyl alcohol at 20° gave α_D $-0.25°$; $l = 1$; $[\alpha]^{20}_D$ $-14°$.

Anal. Calcd. for $C_{62}H_{70}O_{10}N_4S_2$: N, 5.12. Found: N, 5.03.

The amount of salt recovered amounted to approximately 85% of the theoretical quantity and since recrystallization of each fraction from water gave products with the same rotation, it became obvious that water was not a satisfactory solvent for resolution.

Resolution of Distrychnine Diisoduryl Disulfonate.—The two fractions were combined and 3 g. of material was dissolved in 400 cc. of boiling absolute alcohol. On standing for twelve hours, the solution deposited a considerable quantity of white crystals, 0.9 g. Evaporation of the mother liquor to 200 cc. followed by standing for twelve hours gave a further crop of crystals, 0.5 g. These fractions, both of which had a melting point of 252–255° dec., were combined.

The mother liquor was evaporated to dryness and 1.5 g. of light brown salt obtained, m. p., 248–251° dec.

Rotation. (Less soluble salt) 0.2680 g. made up to 10 cc. in 80% methyl alcohol at 20° gave α_D -0.57; $l = 1$; $[\alpha]^{20}_D$ $-21.3°$.

Recrystallization from absolute alcohol did not alter the melting point.

Anal. Calcd. for $C_{62}H_{70}O_{10}N_4S_2$: S, 5.85. Found: S, 5.70.

Rotation. (Less soluble salt) 0.3140 g. made up to 10 cc. in 80% methyl alcohol at 20° gave α_D $-0.68°$; $l = 1$; $[\alpha]^{20}_D$ $-21.6°$.

Rotation. (More soluble salt) 0.2905 g. made up to 10 cc. with 80% methyl alcohol at 20° gave α_D -0.30; $l = 1$; $[\alpha]^{20}_D$ $-10.3°$.

This fraction was not recrystallized.

Anal. Calcd. for $C_{62}H_{70}O_{10}N_4S_2$: S, 5.85. Found: S, 5.74.

l-Ammonium Diisoduryl Disulfonate.—A suspension of 0.6580 g. of less soluble strychnine salt in 15 cc. of dilute aqueous ammonia (1:15) was extracted four times with 10-cc. portions of chloroform and the rotation of the resulting aqueous solution determined.

Rotation. The volume of the tube used was 9.2 cc. and this contained theoretically 0.1697 g. of ammonium diisoduryl disulfonate, α_D -0.21; $l = 1$; $[\alpha]^{20}_D$ $-11.4°$.

Continued extractions with chloroform did not change the rotation.

Evaporation of 9.2 cc. of solution to dryness gave 0.1701 g. of salt (theoretical quantity 0.1697 g.). After drying in an Abderhalden dryer at 140° it was analyzed.

Anal. (Parr bomb) Calcd. for $C_{20}H_{32}O_6N_2S_2$: S, 13.91. Found: S, 13.74.

***d*-Ammonium Diisoduryl Disulfonate.**—This was prepared in a similar manner to the *l*-salt from 0.6668 g. of the more soluble strychnine salt.

Rotation. The volume of the tube used was 9.2 cc. and this contained theoretically 0.1720 g. of ammonium salt: α_D +0.21°; $l = 1$; $[\alpha]^{20}_D$ +11.2°.

Additional extractions did not change the rotation.

Evaporation of 9.2 cc. of this solution to dryness gave 0.1725 g. of ammonium salt (theoretical quantity 0.1720 g.).

Anal. Calcd. for $C_{20}H_{32}O_6N_2S_2$: S, 13.91. Found: S, 13.69.

Racemization Experiments.—Continued boiling of the ammonium salts of both *l* and *d* forms gave no change in rotation.

2,2′,4,4′,5,5′,6,6′-Octamethyl-3,3′-dichloroacetodiphenyl (Dichloroacetyldiisoduryl).—A mixture of 100 cc. of carbon disulfide, 2.6 g. of diisoduryl, and 7 g. of chloroacetyl chloride was cooled in a freezing mixture of ice and salt and 6 g. of anhydrous aluminum chloride was gradually added. After the mixture had been mechanically stirred for one hour, the carbon disulfide was removed by distillation and the aluminum chloride decomposed by adding ice and concentrated hydrochloric acid. The solid material which separated was filtered off and recrystallized from glacial acetic acid as white needles, m. p. 183–184°, yield 3.1 g. (74%).

Anal. Calcd. for $C_{24}H_{28}O_2Cl_2$: Cl, 16.93. Found: Cl, 16.95.

Attempts to replace the chlorines by dialkylamino groups or an amino gave ill-defined products. Attempts to oxidize to —COCOOH or —COOH groups were also unsuccessful.

2,2′,4,4′,5,5′,6,6′-Octamethyl-3,3′-diacetodiphenyl (Diacetyldiisoduryl).—A solution of 2.5 g. of diisoduryl and 2.5 cc. of acetyl chloride in 40 cc. of carbon disulfide was cooled in an ice-bath and 5 g. of anhydrous aluminum chloride was gradually added. After the mixture had stood for two hours, the carbon disulfide was removed by evaporation and the aluminum chloride decomposed by addition of ice and concentrated hydrochloric acid, m. p. 184°, yield, 2.8 g. (84%).

Anal. Calcd. for $C_{24}H_{30}O_2$: C, 82.28; H, 8.57. Found: C, 82.40; H, 8.82.

Attempts to oxidize the $COCH_3$'s to —COCHO by the method of Riley with selenium dioxide resulted in failure.

Diphenyl-3,3′-disulfonic Acid.—This acid was prepared from benzidine disulfonic acid[6] by a modification of the method of G. Schultz and W. Kohlhaus.[7] Sulfuric acid was used for the diazotization instead of hydrochloric acid. The potassium and barium salts of the diphenyl disulfonic acid were prepared for use in making the alkaloidal salts.

(*a*) **Brucine Salt.**—A solution of 11.8 g. of brucine in 61.5 cc. of 0.49 *N* hydrochloric acid and 40 cc. of water was prepared by boiling. This was added to a hot solution of 6.39 g. of dried potassium diphenyl disulfonate in 50 cc. of water. On cooling, a quantity of brucine salt crystallized which when dried at 110° weighed 15.5 g. (94% of the theoretical), m. p. 268–270° with softening at 244°.

Rotation. (Salt dried *in vacuo* at 110°) 0.3235 g. made up to 10 cc. in pyridine gave $\alpha_D = -0.82°$; $l = 1$; $[\alpha]^{29}_D$ −25.3°.

Recrystallization or fractionation from water or alcohol always gave products of identical rotation and melting point.

Anal. Calcd. for $C_{58}H_{62}O_{14}N_4S_2$: S, 5.81. Found: S, 5.71.

(*b*) **Strychnine Salt.**—This salt was made in a similar way to the brucine from 6.68 g. of strychnine in 20 cc. of *N* sulfuric acid and 200 cc. of water and 5.86 g. of dried

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[6] Griess and Dinsberg, *Ber.*, **22**, 2464 (1889).

[7] Schultz and Kohlhaus, *ibid.*, **39**, 3342 (1906).

barium diphenyl disulfonate in 100 cc. of water. On filtration and evaporation to dryness the salt was obtained.

It was purified from methyl alcohol and norite. All fractions gave the same rotation.

Rotation. (Dried *in vacuo* at 110°) 0.2363 g. made up to 10 cc. with pyridine gave α_D -0.71; $l = 1$; $[\alpha]_D^{\circ}$ $-30°$. Essentially the same rotation was observed at room temperature.

Anal. Calcd. for $C_{54}H_{54}O_{10}N_4S_2$: S, 6.52. Found: S, 6.41.

Attempts were also made to obtain the morphine, cinchonine, cinchonidine and quinine salts but in each case only oils were obtained.

Summary

Diisoduryl disulfonic acid has been resolved. Diphenyl 3,3'-disulfonic acid could not be resolved. These two compounds represent a pair which illustrate strikingly that the stereoisomerism in the diphenyl series cannot be defined by type formulas.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

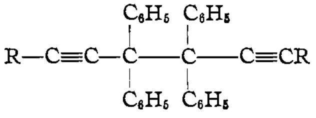
Rearrangements of Polyines. VI. Tetra-biphenyl-di-tertiary-butylethinylethane

BY JUNE CHIEN-YU TSAO AND C. S. MARVEL

It has been shown that hexa-substituted ethanes containing acetylenic groups on the central ethane carbon atoms readily undergo rearrangement to give more stable hydrocarbons.[1] The ease with which this rearrangement occurs appears to be dependent on the strength of the carbon-carbon single bond in the central ethane linkage.

$[R{-}C{\equiv}C]_3{-}CC{-}[C{\equiv}C{-}R]_3$

A



$$R{-}C{\equiv}C{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}C{\equiv}CR$$

B

None of the hexa-alkylethinylethanes (type A) undergo this rearrangement except under the influence of heat.[2] On the other hand all of the tetra-aryl dialkylethinylethanes (type B) which have been investigated[3] have changed to isomeric hydrocarbons at room temperature or below.

A remarkable increase in the degree of dissociation of hexaarylethanes[4] and of tetraaryldialkylethanes[5] has been observed when a biphenyl group has been introduced in place of a phenyl group in these molecules. This

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(1) See THIS JOURNAL, **55**, 3712 (1933), for the previous paper in this field.

(2) (a) Salzberg and Marvel, *ibid.*, **50**, 1737 (1928); (b) Ozanne and Marvel, *ibid.*, **52**, 5267 (1930); (c) Davis and Marvel, *ibid.*, **53**, 3840 (1931).

(3) (a) Stampfli and Marvel, *ibid.*, **53**, 4057 (1931); (b) Munro and Marvel, *ibid.*, **54**, 4445 (1932); (c) Harmon and Marvel, *ibid.*, **55**, 1716 (1933).

(4) Schlenk, Weickel and Herzenstein, *Ann.*, **372**, 1 (1910); *Ber.*, **43**, 1753 (1910).

(5) Conant and Schultz, THIS JOURNAL, **55**, 2098 (1933).