This amine is quite stable in contrast to phenyl-β-naphtholaminomethane. This lends weight to the theory that the tautomerism of the hydroxyl group in the latter compound contributes to its instability.

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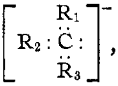
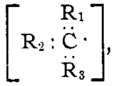
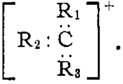
The Spatial Configuration of the Valences in Tricovalent Carbon Compounds[1]

BY EVERETT S. WALLIS AND FREDERIC H. ADAMS

The tetrahedral configuration of the valences of quadricovalent carbon has been generally accepted since the classical researches of van't Hoff and Le Bel. However, the spatial arrangement of the groups in compounds containing a tricovalent carbon atom has not been definitely proved. For the sake of clearness in discussion all tricovalent carbon compounds may be divided into three classes: (1) "carbanions"[2]  $\left[R_2:\overset{\overset{R_1}{\cdot\cdot}}{\underset{\underset{R_3}{\cdot\cdot}}{C}}:\right]^-$, (2) free radicals  $\left[R_2:\overset{\overset{R_1}{\cdot\cdot}}{\underset{\underset{R_3}{\cdot\cdot}}{C}}\cdot\right]$, and (3) carbonium ions  $\left[R_2:\overset{\overset{R_1}{\cdot\cdot}}{\underset{\underset{R_3}{\cdot\cdot}}{C}}\right]^+$. Much interest is attached to the possibility of the existence of a non-planar configuration in these compounds. If such a spatial arrangement be true, asymmetry would be possible when the three aryl groups around the central carbon atom are different. A study of the behavior of such compounds toward polarized light would also enable us to determine the degree of stability of the antimeric configurations. It is hardly possible experimentally to resolve such substances directly into *dextro* and *levo* forms. It would be necessary to prepare the corresponding quadricovalent compound in its enantiomorphic modifications, and then to determine whether the rotatory power of such compounds is retained or lost upon transition into the tricovalent state, and return to the quadricovalent condition. If optical activity of the final product is retained, it would necessarily imply that the tricovalent molecule from which it was formed was also optically active. An asymmetric spatial configuration would therefore be experimentally demonstrated. If, however, on assuming the tricovalent state the substituted groups move into the plane of the central carbon atom,

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[1] This paper is based upon a thesis submitted by Frederic H. Adams to the Faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Communicated in the form of two papers to the Division of Organic Chemistry at the 83rd and 85th meetings of the American Chemical Society held at New Orleans, La., March 28 to April 1, 1932, and at Washington, D. C., March 26 to 31, 1933, respectively.

[2] The above word is here proposed for a negatively charged carbon ion in contrast to the term "carbonium," which indicates a positively charged ion.

or acquire any other arrangement[3] which prevents the maintenance of asymmetry, then enantiomorphic modifications cannot exist and the preparation of these substances in optically active form is impossible. Previous attempts by several investigators[4] to settle this question failed because they were unable to obtain the necessary starting materials in optically active form. However, the resolution[5] of phenylbiphenyl-α-naphthylmethylthioglycolic acid has made it possible to obtain the optically active triarylmethane derivatives which are necessary for this polarimetric investigation.

It was the aim of these investigations to test more thoroughly this method of resolution, to prepare if possible other asymmetric carbinols in their optically active modifications, and to study the behavior of these compounds and their derivatives toward polarized light when they are made to undergo chemical change to the tricovalent state. Furthermore, a study has been made of the optical stability of certain asymmetric groups during reactions in which they apparently go through the free radical stage, notably in the Kolbe synthesis by electrolysis of the potassium salts of fatty acids, and in the Wurtz reaction.

Attention was first directed toward the resolution of aliphatic and mixed aliphatic–aromatic carbinols by means of their thioglycolic acid derivatives. In all cases these were unsuccessful. One illustration follows.

Methylethylphenylcarbinol was converted into its chloride, and the latter compound was made to react with thioglycolic acid according to the equation

$$(CH_3)(C_2H_5)(C_6H_5)CCl + HSCH_2COOH \longrightarrow \underset{(I)}{(CH_3)(C_2H_5)(C_6H_5)CSCH_2COOH} + HCl$$

The resulting compound (I), m. p. 137–138°, was found to combine with brucine and other alkaloids, but such salts showed a tendency to decompose into unsaturated hydrocarbons and alkaloid thioglycolates. No resolution was effected.

Investigations were therefore directed to the further applicability of this method of resolution to methane derivatives of the true aryl type. In such compounds decomposition reactions of the above type would be avoided. It was also thought to be of scientific interest to resolve if possible a triarylmethane derivative in which two of the aryl groups are bound together to form a heterocyclic ring. A comparison of the spatial stability of such a

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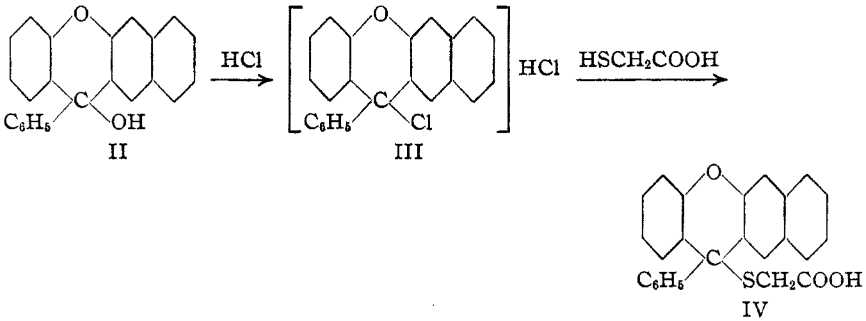
(3) Researches of this kind are well suited to clarify the question of the benzenoid or quinonoid constitution of these tricovalent compounds when they contain aryl groups. The question whether such substances can assume the quinonoid state and at the same time maintain an asymmetric configuration has previously been discussed [Wallis, THIS JOURNAL, **53**, 2253 (1931)].

(4) Schmidlin and Garcia-Banùs, *Ber.*, **45**, 3188 (1912); Meisenheimer and Neresheimer, *Ann.*, **423**, 105 (1921); Karagunis, Ph.D. Dissertation, Freiburg, 1926; H. Krauss, Ph.D. Dissertation, Munich, 1927.

(5) (a) Wallis, *Proc. Nat. Acad. Sci.*, **16**, 215 (1930); (b) Wallis, THIS JOURNAL, **53**, 2253 (1931); (c) **54**, 1693 (1932).

compound with that of phenylbiphenyl-α-naphthylmethylthioglycolic acid, in which the substituents are simple aryl groups, might give us an indication of the strain set up in the molecule by the "internuclear" bridge, and also the amount of distortion from the normal tetrahedral grouping.

Accordingly 12-phenyl-12-β-benzoxanthenol (II) was prepared and converted into its orange-red chloride–hydrochloride (III) according to the method of Gomberg and Schoepfle.[6] The latter compound in benzene solution reacted with thioglycolic acid to give a good yield of 12-phenyl-12-β-benzoxanthenethioglycolic acid (IV), a colorless crystalline solid melting at 187–188°.



Resolution of this acid by fractional crystallization of its brucine salt gave a *levo* modification $[\alpha]_D^{20}$ −48.5° in acetone. From the mother liquors were obtained samples of mixed *dextro* acid of varying rotations up to $[\alpha]_D^{20}$ +28.9°.

This compound (IV) was found to be much more easily racemized than phenylbiphenyl-α-naphthylmethylthioglycolic acid.

It was also found to turn orange slowly when exposed to diffuse light and rapidly when exposed to sunlight. Mineral acids, such as concentrated hydrochloric acid or sulfuric acid, dissolve it with the formation of deep orange-colored solutions. In fact this color was observed when any compound containing the 12-phenyl-β-benzoxanthenyl radical was treated with concentrated mineral acid. These reactions were always accompanied by racemization.

The Spatial Configuration of the Valences in Tricovalent Carbanions.— The work of Kuhn and Albrecht, and of Shriner and Young[7] on the sodium salts of optically active secondary nitroparaffins has shown that in all probability optically active anions of the type $\left[R_2 : \overset{R_1}{\underset{\cdot\cdot}{C}} : NO_2\right]^-$ are capable of existence. It must be pointed out, however, that the alternative formula for

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[6] Gomberg and Schoepfle, THIS JOURNAL, **39**, 1652 (1917).

[7] Kuhn and Albrecht, *Ber.*, **60**, 1297 (1927); Shriner and Young, THIS JOURNAL, **52**, 3332 (1930).

such ions, $\left[\begin{array}{ccccc} & & R_1 & & \\ R_2 & : & \ddot{C}:\ddot{N} & : & \underset{..}{\ddot{O}}: \\ & & \underset{\cdot\cdot}{:O:} & & \end{array}\right]^-$, has not yet been definitely disproved. A study of the spatial configuration of an anion of the type $\left[\begin{array}{c} R_1 \\ R_2:\underset{\cdot\cdot}{\ddot{C}}: \\ R_3 \end{array}\right]^-$ in which R_1, R_2 and R_3 are different aryl groups should therefore be of interest, for in this case no such alternative formula is likely, and the presence of optical activity can only be explained by the asymmetric non-planar arrangement of the three substituent groups and the electron pair.

The salt-like nature of the sodium compounds of triphenylmethyl and its analogs in ether solution has been demonstrated by Schlenk and Marcus.[8] Kraus and his co-workers[9] have prepared these organo-metallic compounds by the action of sodium on triarylchloromethanes in liquid ammonia, and have shown by conductivity measurements that the C–Na bond in this solvent is ionic and not covalent.

As has been noted,[10] *l*-12-phenyl-12-β-benzoxanthenethioglycolic acid (IV) has been subjected to the action of sodium in liquid ammonia in the absence of oxygen. The deep orange-brown sodium triarylmethyl so formed was then treated with a slight excess of dry ammonium bromide. The solution was immediately decolorized, and the colorless methane derivative, 12-phenyl-β-benzoxanthene, precipitated out. This material was found to be free from sulfur and optically active; in one experiment it exhibited $[\alpha]_D^{20}$ $-11.7°$ in acetone solution. From these data it is evident that a triarylmethyl anion can exist in the optically active state for an appreciable length of time, and that its three covalence bonds are not coplanar with the central carbon atom.

The Spatial Configuration of the Valences in Tricovalent Carbonium Ions.—It is a well-known fact that an atom attached to an asymmetric carbon atom can be replaced by another atom without occurrence of complete racemization. In many of these reactions it would appear that the replacement involves an exchange of anions, and that two electrons are withdrawn from the octet of the asymmetric carbon atom. This interpretation involves the momentary existence of a carbonium ion, $\left[\begin{array}{c} R_1 \\ R_2:\underset{\cdot\cdot}{\ddot{C}} \\ R_3 \end{array}\right]^+$ which is sufficiently stable to maintain an asymmetric configuration. Several investigators[11] have made use of this concept to explain their experimental results. However, there are recorded facts which indicate that in the absence of a special mechanism which leads to Walden

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[8] Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

[9] Kraus and Kawamura, THIS JOURNAL, **45**, 2756 (1923); Kraus and Rosen, *ibid.*, **47**, 2739 (1925).

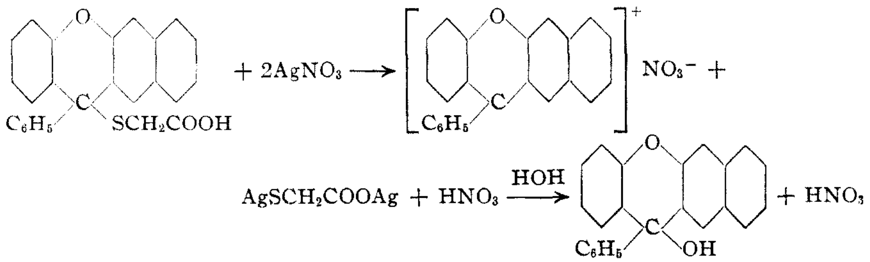
[10] Adams and Wallis, *ibid.*, **54**, 4753 (1932).

[11] Billmann, *Ann.*, **388**, 330 (1912); McKenzie and Clough, *J. Chem. Soc.*, **103**, 687 (1913); Jones and Wallis, THIS JOURNAL, **48**, 169 (1926).

inversion such a carbonium ion is optically unstable. In a study of certain spontaneous migrations of optically active groups from oxygen to sulfur, Kenyon and Phillips[12] have shown that the rearrangement is accompanied by racemization.

In the light of these experiments it therefore seemed important to investigate the problem further. There are many reactions which indicate that triarylmethyl radicals exist as carbonium ions. The physical and chemical properties of solutions of triarylmethyl halides in liquid sulfur dioxide may be cited as an example. Many investigators[13] also believe that such ions are present in the halochromic compounds of triarylmethyl derivatives with inorganic acids and salts. In a recent publication[5b] from this Laboratory this question has been discussed, and experimental facts were submitted which have a direct bearing on the constitution of these compounds. The triarylmethyl derivatives also undergo many reactions which involve substitution on the methane carbon atom. These reactions would imply an exchange of anions and the momentary withdrawal of two electrons from the octet of the central carbon atom. The present investigations include a study of such replacements when the central carbon atom is asymmetric. If the substitution is accompanied by racemization it would appear that not even momentarily can a triarylmethyl positive radical maintain its asymmetry in the absence of a special mechanism which leads to Walden inversion. On the other hand, if optical activity persists after such transformations one must conclude that such positive groups for a certain length of time are able to keep their covalent linkages non-planar with the central carbon atom, and do not "oscillate between the two forms of opposite configuration."

Two optically active triarylmethane derivatives were used for this purpose, *d*- and *l*-12-phenyl-12-β-benzoxanthenethioglycolic acid (IV) and *d*- and *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid (V). Many of our experiments gave results which seemed to support the first conclusion. When compound (IV) was dissolved in acetone containing small amounts of water, and treated in the cold with an aqueous solution of silver nitrate, the —SCH_2COOH group was replaced by —OH. In all cases, however, the carbinol so formed was inactive. The reaction may be formulated as



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(12) Kenyon and Phillips, *J. Chem. Soc.*, 1676 (1930).

(13) Baeyer and Villiger, *Ber.*, **35**, 1189, 3013 (1902); Hantzsch, *ibid.*, **54**, 2573, 2613 (1921); **63B**, 1181 (1930); Dilthey, *J. prakt. Chem.*, [2] **109**, 273 (1925); **118**, 321 (1928); **124**, 81 (1929).

If the reaction was carried out in ethyl alcohol solution, the corresponding ethyl ether was produced. This compound also showed no appreciable rotation. Certain experiments with (V) gave similar results. Replacement of the —SCH_2COOH group by the action of halogens or thionyl chloride gave in every instance an inactive triarylmethyl halide.

However, certain observations[14] have been made which might indicate that a positive radical of the above type under certain conditions can maintain an asymmetric configuration. When compound (V) was treated with silver nitrate under the same conditions as were used in our experiments with compound (IV), optically active products were obtained. It is to be noted that in the case of the carbinols the replacement was accompanied by a change in the sign of the rotatory power. This, however, did not take place when the corresponding optically active ethyl ethers were produced.

If we compare these results with those obtained with compound (IV) it would appear that the stability of the group is somewhat dependent upon the nature of the substituents present. If the molecule is of such a nature that distortion of the valences around the central carbon atom is pronounced, as is most certainly the case in molecules of the above type containing an internuclear oxygen bridge, then such a radical, even though it exists but momentarily, may well lose its asymmetry.

A much clearer case for optical instability was obtained when attempts were made to prepare the corresponding active halides of phenylbiphenyl-α-naphthylcarbinol. They were invariably unsuccessful.

It therefore seems probable that only under special conditions can triaryl substituted groups of the above type maintain even momentarily an asymmetric configuration, and whenever a replacement takes place in such a manner as to involve the intermediate formation of a true carbonium ion racemized products will inevitably result. We would explain this optical instability as being due to the inability of the positive ion to maintain its covalent linkages non-planar with the central carbon atom. When the group X is removed from the central carbon atom in these types of compounds, and takes its pair of electrons with it, the remaining valence electrons and their attached groups are in such an energy state that they readily pass through the plane of the carbon atom, and an optically inactive product is produced.

The Spatial Configuration of the Valences in Free Radicals.—The third possible state in which a group containing a tricovalent carbon atom can exist is that of a neutral free radical. Since it was not found possible to prepare optically active triarylmethyl halides, Gomberg's classical method for the preparation of free radicals could not be used in the present study of the optical stability of these tricovalent carbon com-

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[14] Wallis, THIS JOURNAL, **54**, 1695 (1932).

pounds. It was therefore necessary to carry out experiments along somewhat different lines. Schlenk and Herzenstein[15] have reported that triphenylmethyl in some of its reactions behaves like a metallic element. For instance, it undergoes an equilibrium reaction with phenyldibiphenylchloromethane to form triphenylchloromethane and phenyldibiphenylmethyl. It seemed, therefore, that similar reactions could be carried out on *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid. This was found to be the case. Triphenylchloromethane in dry ether was allowed to react with mercury in the presence of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid. The triphenylmethyl so formed was found to react slowly with the thioglycolic acid derivative. The progress of the reaction could be followed by observing a gradual change of color from yellow to reddish-brown. When this reaction was carried out in a specially constructed polarimeter tube, a gradual decrease of rotation to zero was observed. On admitting air to the apparatus peroxides were formed and precipitated out. These were tested in the polarimeter and found to be inactive. The filtrate was also inactive. Although the reaction did not go to completion, nevertheless optical inactivity resulted. This is undoubtedly due to the fact that the phenylbiphenyl-α-naphthylmethyl formed is unable to maintain its original configuration and therefore racemizes. When this radical returns again to the quadricovalent state as it would do in an equilibrium reaction, the corresponding thioglycolic acid derivative would consist of both *d*- and *l*-forms in equal amounts. Racemization in solution therefore becomes complete. If, as some investigators believe, such free radicals in solution consist of an equilibrium mixture of the benzenoid and quinonoid forms the presence of the latter form would be enough to account for the loss in optical activity in the above experiment. In order to preclude any possibility of tautomerism involving quinonoid forms, experiments were next conducted with aliphatic compounds. Here quinonoidation is obviously impossible.

The Kolbe reaction for the synthesis of hydrocarbons by the electrolysis of the alkali metal salts of fatty acids may be explained by assuming the momentary existence of free radicals. Petersen[16] has shown that when *dl*-methylethylacetic acid is electrolyzed in the form of an aqueous solution of its potassium salt, one of the products of the reaction is a hydrocarbon, 3,4-dimethylhexane. Accordingly Petersen's work was repeated with *l*- and *d*-methylethylacetic acid. In each case the hydrocarbon obtained was optically inactive.

In the Wurtz reaction also the intermediate formation of free radicals has been postulated. Therefore this synthesis was carried out with optically active halides of the type R_1R_2CHX and the hydrocarbon products examined for optical activity. In this case any loss of rotatory power can

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[15] Schlenk and Herzenstein, *Ann.*, **394**, 199 (1912).

[16] J. Petersen, *Z. Elektrochem.*, **12**, 141 (1906).

only be due to optical instability of the intermediate free radicals, for Just[17] has shown that the reaction of metallic sodium on optically active halides of the type $R_1R_2CHCH_2X$, in which the halogen is separated from the asymmetric carbon by a CH_2 group, leads to the formation of an optically active 1,1,4,4-tetrasubstituted butane of the same sign of rotation as the original alkyl halide.

The asymmetric molecules chosen for these experiments were *l*- and *d*-α-bromobibenzyl, $C_6H_5CHBrCH_2C_6H_5$, and *d*-2-bromobutane, $C_2H_5CHBrCH_3$. In every case the corresponding hydrocarbon, 1,2,3,4-tetraphenylbutane, or 3,4-dimethylhexane, was found to be inactive. The reactions were carried out in ether solution, at 35 and 20°, respectively, and the products subsequently treated under conditions which ordinarily do not cause racemization; yet optical activity invariably resulted.[18]

From these experiments we may infer that free radicals in general, whether they be of the classical triphenylmethyl type, or of the aliphatic or mixed aliphatic–aromatic type, even though they exist but momentarily, cannot maintain the asymmetric configuration of the corresponding quadricovalent compounds from which they are derived. Furthermore, the experiments with aliphatic radicals show conclusively that at least in these compounds the loss of optical activity cannot be explained on the basis of a tautomeric change to a quinonoid form. It must be concluded that either the three substituents and the central carbon atom become coplanar, or, if a non-planar configuration is maintained, an oscillation of the groups around the central carbon atom takes place and their relative positions in space continuously change.

Experimental Part

Preparation of Methylethylphenylmethylthioglycolic Acid.—This compound was prepared in poor yields by the action of thioglycolic acid on methylethylphenylchloromethane, which was synthesized according to the method of Klages.[19] The chloride obtained from 50 g. of methylethylphenylcarbinol was treated with 35 g. of thioglycolic acid in 50 cc. of toluene, and the solution was refluxed until no more hydrogen chloride was evolved. On cooling the solution colorless crystals precipitated out. Recrystallization of this material from hot water gave a product which melted at 137–138°; yield, 11.8 g. Attempts were made to resolve this acid by means of its brucine and strychnine salts. These were unsuccessful.

Anal. Carius method (I) and Messinger method (II). Calcd. for $C_{12}H_{16}O_2S$: S, 14.29. Found: (I) S, 14.17; (II) S, 14.13.

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(17) Just, *Ann.*, **220**, 155 (1883).

(18) The Grignard reaction could also be studied from this point of view, inasmuch as intermediate free radical formation may be postulated when metallic magnesium reacts with an alkyl halide. A survey of the literature, however, showed that Pickard and Kenyon [*J. Chem. Soc.*, **99**, 65 (1911)] in attempting to prepare 2-methylbutanol in *d*- and *l*-forms studied the reaction of formaldehyde on the Grignard compound produced by the action of magnesium on *l*-2-iodobutane. No difficulty was encountered in preparing the 2-methylbutanol, but all attempts to prepare it in an optically active condition by this method failed. Although their purpose in investigating such a reaction was different from the one discussed above, yet the results obtained are of interest in this connection.

(19) Klages, *Ber.*, **35**, 3507 (1902).

Preparation of 12-Phenyl-12-β-benzoxanthenethioglycolic Acid.—β-Benzoxanthone was prepared by the method of Ullmann.[20] This ketone was caused to react with phenylmagnesium bromide according to Gomberg and Schoepfle.[6] Five times the theoretical amount of phenylmagnesium bromide was used. The mixture was refluxed on the water-bath, with continued stirring, for at least six hours.

12-Phenyl-12-chloro-β-benzoxanthene hydrochloride was prepared from the xanthenol (m. p. 170–171°) according to the directions of Gomberg and Schoepfle.[6] The yields were practically quantitative.

12-Phenyl-12-β-benzoxanthenethioglycolic acid was prepared by refluxing the chloride–hydrochloride in benzene solution with the theoretical quantity of pure thioglycolic acid. After one hour's heating no more hydrogen chloride was evolved. The solution was decolorized with charcoal and the filtrate set aside to cool; colorless crystals, m. p. 187–188°, were obtained; yield, 86%, based on the amount of carbinol taken.

Anal. Carius method. Calcd. for $C_{25}H_{18}O_3S$: S, 8.04. Found: S, 7.99, 8.16. *Mol. wt.*, cryoscopic method in benzene. Calcd.: 398. Found: 402.

Resolution of 12-Phenyl-12-β-benzoxanthenethioglycolic Acid.—Thirty-five and one-half grams of this acid was resolved by fractional crystallization of its brucine salt from acetone. Ten crystallizations gave 6.2 g. of pure material with a constant rotation in acetone $[\alpha]^{20}_{D}$ −38.2°.

This salt was well pulverized and suspended in 150 cc. of ether in a separatory funnel; 5 cc. of 6 N sulfuric acid diluted to 100 cc. was then added, and the whole shaken vigorously until no more solid was visible. The ether layer was separated and *immediately* washed with water until the washings were free from sulfate. This solution was dried with anhydrous sodium sulfate, and the ether evaporated under reduced pressure; 2.3 g. of fine colorless crystals was obtained, m. p. 183–184°; $[\alpha]^{20}_{D}$ − 48.5° in acetone (*c*, 0.9892 g./100 cc.).

From the mother liquors of the first and second crystallizations was obtained a sample of brucine salt which was treated as described above, except that the ether was allowed to evaporate spontaneously at room temperature. When half of the ether had evaporated, the white crystals which had precipitated were filtered off and found to be optically inactive.[21] The residue obtained by evaporating the remaining ether from the solution was found to give a product which melted at 179°, $[\alpha]^{20}_{D}$ +28.9° in acetone (*c*, 0.8316 g./100 cc.).

Racemization Experiments on *l*-12-Phenyl-12-β-benzoxanthenethioglycolic Acid.—This acid was found to racemize slowly on standing in acetone solution at 20°. In U. S. P. acetone a sample of the acid was found to lose half of its optical activity in two days; in acetone which had been specially purified the specific rotation fell to half its original value in about five and one-half days.

Long standing in the solid state also causes gradual racemization. One sample of the material decreased in specific rotation from −42.3 to −36.9° in two months, and to −13.9° after fourteen months. This change in rotation was accompanied by a development of a slight orange coloration. Racemization was more rapid when the acid was exposed to light. Heating was found to racemize the acid rather rapidly. When an acetone solution of the compound was refluxed for fifteen minutes the specific rotation decreased from −42.3 to −36.8°. Complete racemization was produced when a sample of the material, dissolved in benzene, was boiled for two hours. This acid is also very sensitive to mineral acids. In one experiment 0.2510 g. was dissolved in 25 cc. of acetone and tested in the polarimeter. Two drops of 6 N hydrochloric acid were

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(20) Ullmann, *Ber.*, **38**, 2116 (1905).

(21) A portion of the racemic form of the acid precipitates out, being less soluble in ether than the optically active modification.

then added to this solution, and its rotation determined at several intervals of time. In six hours optical activity had vanished.

The Action of Sodium on *dl*-12-Phenyl-12-β-benzoxanthenethioglycolic Acid in Liquid Ammonia.—The apparatus used, with some simplifications, was that described by Wooster;[22] 1.23 g. of the *dl*-acid was suspended in about 50 cc. of liquid ammonia in a tube immersed in a bath of the same liquid contained in an unsilvered Dewar flask. A current of ammonia gas was continuously circulated through the mixture to ensure thorough stirring and to displace all air from the reaction vessel; 0.25 g. of sodium in the form of small pellets was added from a side-tube. The blue color which at first developed quickly changed to a deep orange-brown. When no more unreacted acid could be seen in the bottom of the tube, 1.25 g. of dry ammonium bromide was added in small portions through another side-tube. A vigorous reaction ensued which resulted in the decolorization of the solution and the formation of a copious white precipitate. The reaction tube was then removed from the cooling bath and the liquid ammonia allowed to evaporate. The residue was taken up in water and washed until the washings were free from halogen and sodium salts. The amorphous white product was dried in air at room temperature. Tests for sulfur were negative. Crystallization of this material, 12-phenyl-β-benzoxanthene, from petroleum ether (60–75°) gave small colorless needles which melted at 153°. Recrystallization from the same solvent failed to raise the melting point.[23]

Anal. Micro method. Calcd. for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.63, 89.42; H, 5.25, 5.73. *Mol. wt.* Calcd.: 308. Found: 300.

Essentially the same method was employed with the *l*-acid as that just described. The reaction was repeated many times, and in every case but one the dry sulfur-free product was found to be optically active in the common organic solvents. In the exceptional case (VII) the solution, after the reaction with sodium, was allowed to stand for a much longer time before the ammonium bromide was added. This indicates that the ion racemizes rather easily. A summary of the results of the various experiments is given.

Run	Acid taken, g.	$[\alpha]^{20}_D$ of sample of acid used	Product taken, g.	$[\alpha]^{20}_D$ of product, 2-dm. tube 25 cc. soln.	$[\alpha]^{20}_D$ product	Solvent
I	2.0	−36.9	0.6015	−0.11	− 2.3	Benzene
II	1.0	−36.9	.1337	− .05	− 4.7	Benzene
III	1.25	−38.2	.2036	− .06	− 3.7	C_2H_5OH
IV	1.25	−38.2	.2032	− .05	− 3.1	C_2H_5OH
V	1.25	−38.2	.2388	− .08	− 4.2	C_2H_5OH
VI	1.23	−48.5	.1812	− .17	−11.7	Acetone
VII	4.0	−41.6	1.6922	.00	0.0	Benzene

Preparation of the sulfur-free levorotatory trisubstituted methane in a crystalline form was not accomplished. All attempts to crystallize the material gave only an amorphous substance. Experiments showed that this compound was easily racemized. Heating of the material in organic solvents produced either a completely inactive material, or one of lower rotation. Samples of the amorphous active compound after it

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[22] Wooster, THIS JOURNAL, **51**, 1859 (1929).

[23] Kauffmann and Egner [*Ber.*, **46**, 3785 (1913)] claim to have prepared this compound by heating 3-hydroxy-β-naphthyldiphenylcarbinol. Their compound melted at 171° and gave a greenish-yellow color with concentrated sulfuric acid, while the compound prepared by us gives the characteristic deep orange coloration observed when all compounds containing the 12-phenyl-β-benzoxanthenyl radical are treated with this reagent. Although their analytical data check with the requirements of the formula, the method of synthesis would indicate that their compound is a derivative of fluorene and not of xanthene.

had been made inactive by the above treatment were found to crystallize as before described. The crystals melted at 153°, and were identical with the product obtained from the *dl*-thioglycolic acid derivative.

Preparation of 12-Phenyl-β-Benzoxanthenyl Ethyl Ether.—One gram of the *l*-acid was dissolved in 90 cc. of absolute alcohol, and to the solution was added 1.2 g. of silver nitrate dissolved in 100 cc. of absolute alcohol. A momentary orange coloration was observed. The light yellow precipitate of silver thioglycolate which formed was filtered off, and the alcoholic filtrate allowed to drip into a liter of distilled water. A white curdy precipitate was immediately produced. This was filtered, washed free of silver ion, and dried in the air; yield of dry sulfur-free product, 0.7212 g. or 88%. This amount of material dissolved in 25 cc. of absolute ether gave no appreciable rotation in a 2-dm. tube. Recrystallization from petroleum ether gave colorless crystals which melted at 118°. This experiment was repeated several times under different conditions but the same inactive product was obtained. Crystallization from an aqueous acetone solution gave crystals which melted at the same temperature as those from petroleum ether.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.18; H, 5.72. Found: C, 84.80; H, 6.02. *Mol. wt.* Carlsohn method. Calcd.: 352. Found: 351.

The corresponding methyl ether was also prepared using a methanol solution; colorless needles (acetone) were obtained which melted at 148°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.21; H, 5.33. Found: C, 85.38; H, 5.64.

Preparation of 12-Phenyl-12-β-benzoxanthenol from the Corresponding Thioglycolic Acid Derivative.—This compound was prepared from the *dl*-acid by a method similar to that above described for the preparation of the ethyl ether, except that acetone and water were used as solvents; yield of crude product, 88%. Crystallization from a mixture of benzene and petroleum ether gave colorless crystals which melted at 170–171°; m. p. by Gomberg and Schoepfle,[6] 171°.

In an entirely similar manner the *l*-acid was converted into the xanthenol. An inactive product was obtained; 0.5706 g. of this compound dissolved in 25 cc. of ether gave no rotation in a 2-dm. tube. Crystallization gave a material which melted at 170–171°.

Preparation of *d*- and *l*-Phenylbiphenyl-α-naphthylcarbinol.—One gram of *d*-phenylbiphenyl-α-naphthylmethylthioglycolic acid[5a] was dissolved in 100 cc. of acetone, and to the solution was added 50 cc. of water. This solution was treated with 1.0 g. of silver nitrate dissolved in 50 cc. of water; yield of product, 0.859 g. Crystallization from aqueous acetone gave colorless crystals which melted at 161–162°, and showed $[\alpha]^{20}_{6563}$ −3.3°; $[\alpha]^{20}_{5893}$ −5.4°; $[\alpha]^{20}_{5463}$ −7.6° (0.1152 g. of substance in 25 cc. of carbon tetrachloride solution, 2-dm. tube; rotation −0.03, −0.05, −0.07°, respectively).

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.13; H, 5.70. Found: C, 90.0; H, 5.9.

In an entirely similar manner 1.0 g. of the *l*-acid was converted into the corresponding carbinol. The product so obtained melted at 160° and showed $[\alpha]^{20}_{5463}$ +7.2° (0.1912 g. in 25 cc. of carbon tetrachloride solution, 2-dm. tube, rotated +0.11°).

Preparation of *d*- and *l*-Phenylbiphenyl-α-naphthylmethyl Ethyl Ether.—One gram of the *d*-acid was dissolved in 50 cc. of absolute alcohol (distilled over calcium) and treated with a solution of 1.0 g. of silver nitrate dissolved in 100 cc. of the same solvent. The solutions were mixed slowly and the product worked up as before described. Crystallization from aqueous alcohol gave a compound which melted at 125–126°, and showed $[\alpha]^{20}_{D}$ +21.7° (0.1495 g. of substance in 25 cc. of ether solution, 2-dm. tube, rotated +0.26°).

These experiments were repeated on the *l*-acid. A crystalline product was obtained which melted at 125.5–126°, and showed $[\alpha]^{20}_{6563}$ −17.4°; $[\alpha]^{20}_{5893}$ −22.7°; $[\alpha]^{20}_{5463}$

-27.0; $[\alpha]^{20}_{4863}$ $-34.0°$ (0.1435 g. in 25 cc. of dry ether solution in a 2-dm. tube, rotated -0.20, -0.26, -0.31, $-0.39°$, respectively).

Anal. Micro method. Calcd. for $C_{31}H_{26}O$: C, 89.85; H, 6.28. Found: C, 89.79, 89.78; H, 6.19, 6.23.

Action of Bromine on *l*- and *d*-Phenylbiphenyl-α-naphthylmethylthioglycolic Acid.—Two grams of the *l*-acid was dissolved in 50 cc. of dry ether and cooled in a bath of solid carbon dioxide and ether. To this solution was added slowly 100 cc. of dry ether containing an equivalent amount of free bromine. A white crystalline precipitate formed almost immediately. A portion of this dried product, dissolved in benzene, showed no rotation; m. p. of crystallized material (benzene) 191°, with decomposition.

Experiments carried out on the *d*-acid gave the same results.

Anal. Carius method. Calcd. for $C_{29}H_{21}Br$: Br, 17.6. Found: Br, 17.8.

Action of Thionyl Chloride on *d*-and *l*-Phenylbiphenyl-α-naphthylcarbinols and their Ethyl Ethers.—One gram of the *d*-carbinol was dissolved in benzene, and to the solution was added the calculated amount of thionyl chloride. To the mixture was added a small amount of petroleum ether (30–60°) and the solution allowed to stand for twelve hours at $-6°$. Beautifully formed crystals of the chloride, m. p. 194–195°, precipitated out; m. p. (Schlenk)[24] 194.5°. A saturated benzene solution showed no appreciable rotation. Experiments on the *l*-carbinol and the *d*- and *l*-ethyl ethers gave similar results.

Action of Triphenylmethyl on *l*-Phenylbiphenyl-α-naphthylmethylthioglycolic Acid in the Presence of Mercury.—One gram of triphenylchloromethane was dissolved in specially pure dry ether, and to the solution was added 1.0 g. of the *l*-acid, and the total solution made up to 25 cc. It showed a rotation at 20° in a 2-dm. tube with the 6563 line of $-0.98°$. This solution was placed in a specially constructed apparatus and shaken with mercury in the absence of oxygen for twenty-four hours. The solution was then allowed to stand in contact with mercury for fourteen days in the dark. After this time had elapsed the rotatory power of the solution was again determined in a specially constructed 2-dm. polarimeter tube. Other readings were taken from time to time: fourteen days $-0.59°$; nineteen days $-0.39°$; twenty-three days $-0.19°$; 27 days $-0.02°$. During this time the color of the solution changed from yellow to reddish-brown. The solution was removed and allowed to come into contact with air. The brown color quickly disappeared, and the solution became nearly colorless. The precipitated peroxides were filtered and found to be optically inactive. The filtrate also showed no appreciable rotation.

Electrolysis of *l*- and *d*-Methylethylacetic Acid.—Fifty grams of the *l*-acid, previously resolved by the method of Schütz and Marckwald[25] (rotation without solvent at 20°, D line, 2-dm. tube, $-12.25°$) was converted into its potassium salt and electrolyzed according to the method used by Petersen[16] for the *dl*-acid. After thirty-one hours seven grams of a yellow oily product was obtained. This oil after treatment and purification according to Petersen's method gave a hydrocarbon which was found to be inactive. The experiment was repeated with the *d*-acid. Similar results were obtained. The boiling point of the hydrocarbon produced was 110–116°. The b. p. of 3,4-dimethylhexane recorded in the literature is 116° (Norris and Green).

Preparation of 1,2,3,4-Tetraphenylbutane.—Phenylbenzylcarbinol was resolved into its pure dextro and mixed levo modifications by the method of Gerard and Kenyon;[26] 4 g. of the dextro compound (m. p. 67°, $[\alpha]^{22}_{D}$ $+52.0$ in alcohol, *c* 1.780 g. per 100 cc.), was dissolved in 50 cc. of benzene. The solution was cooled to 0° and saturated with

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(24) Schlenk, *Ann.*, **394**, 196 (1912).

(25) Schütz and Marckwald, *Ber.*, **29**, 52 (1896).

(26) Gerard and Kenyon, *J. Chem. Soc.*, 2564 (1928).

pure hydrogen bromide gas. Purification of the product by the usual methods gave a levorotatory bromide which was a viscous yellow oil. This was not distilled because of possible decomposition; d_{21}^{21} 1.316; $[\alpha]_D^{22}$ −27.1° in absolute alcohol (*c* 1.642 g. per 100 cc.). In a similar manner a *dl*- and a mixed dextrorotatory α-bromobibenzyl were prepared. The mixed *d*-compound showed a rotation at 22° of +2.69° in a 0.5-dm. tube without solvent, D line.

Anal. *l*-Bromide, Parr Bomb and Volhard Titration. Calcd. for $C_{14}H_{13}Br$: Br, 30.62. Found: Br, 29.41.[27]

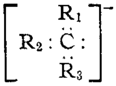
4.0 g. of *l*-α-bromobibenzyl was dissolved in absolute ether, and to the solution was added 3 g. of sodium in the form of small shot. The mixture was refluxed on the water-bath until the ether solution gave no test for bromine. This required about eight hours. The ether was then filtered off, and the residue treated with alcohol, diluted with water, and extracted with ether. The combined ether solutions were dried with calcium chloride and concentrated to 20 cc. Colorless bromine-free crystals precipitated out; 0.1586 g. of this material in 25 cc. of acetone solution gave no rotation in a 2-dm. tube. Recrystallization of the compound from alcohol gave needles which melted sharply at 178°.

The experiment was repeated with the mixed *d*-α-bromobibenzyl. Similar results were obtained. The crystalline material melted at 178° and was inactive. The *dl*-bromide also gave a product which melted at 178°.[28]

Anal. Calcd. for $C_{28}H_{26}$: C, 92.76; H, 7.24. Found: C, 92.59; H, 7.37. *Mol. wt.* (I) Rast Method, (II) Carlsohn Method. Calcd.: 362. Found: (I) 373, (II) 342.

Preparation of 3,4-Dimethylhexane by the Wurtz Reaction.—*d*-2-Bromobutane was prepared from an incompletely resolved *l*-*sec*-butyl alcohol according to the directions of Levene and Marker.[29] It had a specific rotation $[\alpha]_D^{22}$ +10.70° without solvent. Levene and Marker reported $[\alpha]_D^{25}$ +10.81° for the bromide; 8 g. of this material was dissolved in dry ether and treated at room temperature with metallic sodium according to the method of Norris and Green.[30] After the reaction was complete, the bromine-free ether solution was tested in the polarimeter. It gave no rotation. By fractionation a hydrocarbon was obtained which boiled at 115–117°. Examination of this material in the polarimeter showed that it was completely inactive; b. p. (Norris and Green) 116°.

Summary

12-Phenyl-12-β-benzoxanthenethioglycolic acid (IV) has been synthesized and resolved into pure *levo* and mixed *dextro* modifications. The *levo* form has a specific rotation $[\alpha]_D^{20}$ −48.5°. Evidence is submitted which shows that a carbanion of the type  $\left[\begin{array}{c}R_1\\ R_2:\overset{\cdot}{\underset{\cdot\cdot}{C}}:\\ \overset{\cdot\cdot}{R_3}\end{array}\right]^-$ is spatially sufficiently stable to maintain an asymmetric configuration. The three substituents and the central carbon atom, therefore, cannot lie in the same plane.

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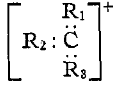
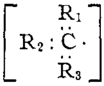
[27] The low value for the bromine in this analysis is undoubtedly due to the presence of small amounts of unchanged carbinol or traces of benzene, since the product was not purified by distillation.

[28] Fromm and Achert [*Ber.*, **36**, 539 (1903)] have prepared a compound, m. p. 255°, by heating benzyl sulfide. To this compound was assigned the structure of 1,2,3,4-tetraphenylbutane. R. Bacon [*Philip. J. Sci.*, **4A**, 166 (1909)] prepared the same compound by heating benzyl chloride with potassium oxalate in a sealed tube. Both these syntheses, however, leave much doubt as to the actual structure of the compound these investigators prepared.

[29] Levene and Marker, *J. Biol. Chem.*, **91**, 405 (1931).

[30] Norris and Green, *Am. Chem. J.*, **26**, 313 (1901). These investigators used the *dl*-bromide.

The stability of the spatial arrangement of the groups in tricovalent carbonium ions,  $\left[\begin{matrix} & R_1 \\ R_2 : & \overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} \\ & R_3 \end{matrix}\right]^+$ has been studied, and evidence has been submitted which indicates that in the absence of a special mechanism which leads to Walden inversion such configurations are optically unstable.

The optical instability of free radicals  $\left[\begin{matrix} & R_1 \\ R_2 : & \overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}\cdot \\ & R_3 \end{matrix}\right]$ has been demonstrated: by the loss of optical activity when *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid was allowed to react with triphenylmethyl; by the production of an inactive hydrocarbon in the electrolysis of *l*- and *d*-potassium methylethylacetate; and by the production of an inactive hydrocarbon by the action of metallic sodium on *d*- and *l*-α-bromobibenzyl and *d*-2-bromobutane.

A discussion of these results is given in the light of certain theories which have been proposed for the constitution of these tricovalent compounds.

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Radical Interchange on the Part of Certain Alkyl Orthoformates[1]

BY HOWARD W. POST AND EDWIN R. ERICKSON

Early work on aliphatic ortho esters, while outlining their preparation and properties, has mentioned as well their instability. Triethyl orthoformate for example is not as stable as are the orthoformates of the higher aliphatic alcohols, but no further suggestions have been advanced on this point to date. Compounds of this type have been prepared from the corresponding alcoholate[2] and from the alcohol and hydrogen cyanide.[3]

It was our original purpose to test the relative reactivity of some alcoholates of simple aliphatic alcohols by mixing one mole of chloroform with three moles each of two different alcoholates and determining the identities of the products but the problem soon resolved itself into a study of the reaction

$$HC(OR)_3 + HC(OR')_3 \rightleftharpoons HC(OR)_2OR' + HC(OR')_2OR \qquad (1)$$

The Reaction of Chloroform with Alcoholate Mixtures.—One equivalent of chloroform was added to a mixture of 1.5 equivalents each of two

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[1] Presented at the Spring Meeting, American Chemical Society, March, 1933, at Washington, D. C.

[2] Deutsch, *Ber.*, **12**, 117 (1897); Claisen, *ibid.*, **31**, 1010 (1898); Sah and Ma, THIS JOURNAL, **54**, 2964 (1932); "Organic Syntheses," Vol. V, 1925, p. 55.

[3] Pinner, *Ber.*, **16**, 356 and 1643 (1883).