bromonaphthalene (liquid). On reaction with magnesium and then phthalic anhydride, this afforded 11.4 g. of hydrated keto acid, m. p. 110–120° (76%, assuming the substance to be a monohydrate). Reduction as above gave the acid VI, m. p. 142–143.5°, in 60% yield.

1'-Methyl-2,3-benz-10-anthrone (VII).—One gram of the methylnaphthylmethylbenzoic acid VII was treated with hydrogen fluoride at room temperature and after seven minutes was poured onto ice and the light yellow solid was quickly collected and washed. A portion was crystallized from acetone and obtained in two polymorphic forms of the same m. p. 174–176°. Prisms separated when a saturated solution was cooled rapidly in the ice box, while slow crystallization at room temperature gave rise to needles. Recrystallized slowly, the anthrone formed pale yellow needles, melting at 175–176° when heated slowly but liquefying when immersed in a bath at 171°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.35; H, 5.46. Found: C, 88.80; H, 5.63.

With alcoholic alkali the anthrone gives a characteristic[10] purplish color which fades on shaking with air.

1'-Methyl-2,3-benzanthraquinone was obtained by oxidation of 100 mg. of the anthrone with 55 mg. of chromic anhydride in acetic acid. The substance crystallized from this solvent in orange-yellow needles, m. p. 227–229°. It gave no red color with aqueous hydrosulfite–alkali.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.45. Found: C, 83.68; H, 4.66.

1',10-Dimethyl-2,3-benzanthracene (VIII).—After treatment of the crude anthrone VII with excess methylmagnesium chloride the collected product was passed in benzene solution through a tower charged with alumina mixed with Super-cel. On slow crystallization from absolute alcohol the hydrocarbon then formed brilliant, fiery red needles, m. p. 138–139°. When the alcoholic solution is cooled rapidly by cooling in ice the hydrocarbon separates in another modification which forms small, bronze-colored plates. This form melts when inserted in a bath at 133° and then solidifies and remelts at the higher temperature. The solution in concentrated sulfuric acid is olive-green.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.82; H, 6.35.

The **picrate** forms purplish-black needles from absolute alcohol, m. p. 164–165°.

Anal. Calcd. for $C_{20}H_{16}\cdot C_6H_3O_7N_3$: N, 8.66. Found: N, 8.59.

The **trinitrobenzene derivative** resembles the picrate in appearance, m. p. 166.5–167.5° (absolute alcohol).

Anal. Calcd. for $C_{20}H_{16}\cdot C_6H_3O_6N_3$: N, 8.94. Found: N, 9.04.

When the total crude product of cyclization was treated with Grignard reagent there was obtained in addition to the hydrocarbon a small amount of 1'-methyl-1,2-benzanthraquinone.[9]

Summary

Perinaphthane and hydrindene can be acetylated in the presence of hydrogen fluoride at room temperature, and the acylation of naphthalene and phenanthrene can be accomplished in a pressure bomb at somewhat higher temperatures.

9-Methyl- and 9-allyl-1,2-benzanthracene were synthesized successfully by cyclizing *o*-(β-naphthylmethyl)-benzoic acid with hydrogen fluoride and treating the crude anthrone with Grignard reagent, but when this process was applied to *o*-(8-methyl-2-naphthylmethyl)-benzoic acid ring closure occurred chiefly in the alternate direction, giving rise to the linear isomer. 1',10-Dimethyl-2,3-benzanthracene exists in two modifications, one of which has a striking red color.

CONVERSE MEMORIAL LABORATORY
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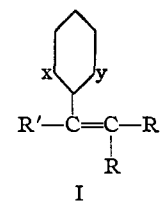
RECEIVED NOVEMBER 2, 1939

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

Restricted Rotation in Aryl Olefins. I. Preparation and Resolution of β-Chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic Acid

BY ROGER ADAMS AND M. W. MILLER[1]

Molecular dissymmetry due to restricted rotation between the ring and the olefinic carbon in appropriately substituted aryl olefins of types I and II was postulated in a previous communication.[2] Synthetic difficulties in preparing such compounds proved to be great and no procedure was found which gave successful results. The



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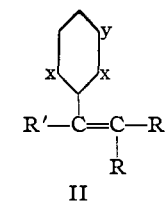


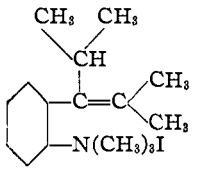
II

introduction of an atom or group other than hydrogen for the R' was complicated when R, x and y represented substituents other than hydrogen.

(1) Portion of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in chemistry: Eastman Kodak Fellow, 1939–1940.

(2) Maxwell and Adams, THIS JOURNAL, **52**, 2960 (1930).

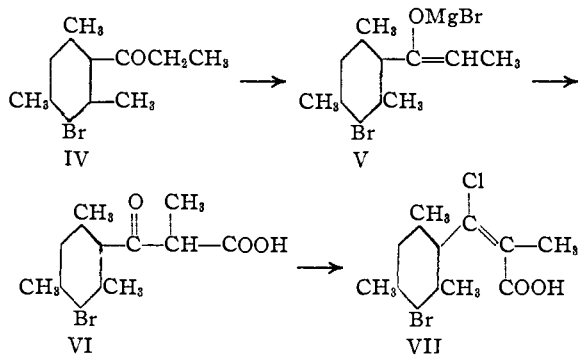
In the last few years several compounds have been prepared in which restricted rotation between an aryl group and an aliphatic nitrogen or carbon atom has been demonstrated.[3] The probability of resolution of properly substituted aryl olefins was thus made to appear more likely. Just recently, Mills and Dazeley[4] have succeeded in synthesizing and resolving *o*-(β,β-dimethyl-α-isopropylvinyl)-phenyltrimethylammonium iodide (III), thus verifying the correctness of the original



III

postulation. They observed also that a hydrogen atom on the olefin carbon not attached to the ring resulted in a compound which they were unable to obtain in enantiomorphic forms.

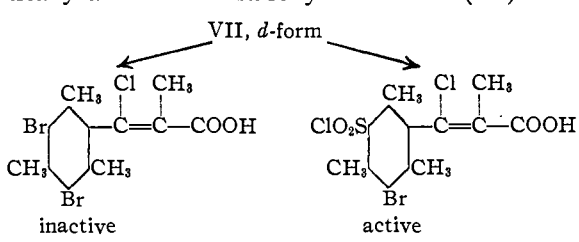
Search has been continued in this Laboratory to find a procedure for synthesizing molecules of types I and II, especially a procedure which would make feasible the preparation of several closely related compounds and thus allow a study of the effect of different groups around the point of restricted rotation. Such a procedure has now been devised. The first compound to be prepared and resolved is β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid. In its synthesis, advantage has been taken of the reports of Kohler[5] that hindered ketones react with ethylmagnesium bromide to give ethane and the magnesium bromide derivative of the enol form, and the observation by Kohler and Baltzly as well as by Fuson, Fugate and Fisher[6] that such enol magnesium bromides and carbon dioxide give β-ketonic acids. Thus, bromopropiomesitylene (IV) gives the magnesium bromide derivative (V), which carbonates to α-methyl-(2,4,6-trimethyl-3-bromobenzoyl)-acetic acid (VI). Molecules of the type shown by VI enolize with great ease and it was possible, therefore, to convert the keto acid (VI) by means of a mixture of phosphorus pentachloride and phosphorus oxy-



IV V VI VII

chloride into the chloro olefin (VII), β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid. Although VII should exist in *cis* and *trans* forms, only one of these isomers was obtained. This isomer was resolved readily through the quinine salt. The *d*-form from the less soluble salt gave $[\alpha]^{20}D$ +52.6° in ethanol and proved to be surprisingly stable. The *l*-form also was isolated. The optical activity of the *d*-form was not changed by refluxing for fifteen hours in ethanol or twelve hours in glacial acetic acid. A very rigid restriction of rotation in this molecule was thus demonstrated.

The necessity for unsymmetrical substitution in the benzene ring in order to produce asymmetry in VII was proved by bromination and by preparing a sulfonyl chloride derivative of the optically active forms. Bromination resulted in symmetrical substitution with formation of an optically inactive dibromo compound (VIII), identical with that prepared by bromination of the racemic form of VII. Chlorosulfonic acid, on the other hand, gave a molecule with unsymmetrical substitution which proved to be the optically active chlorosulfonyl derivative (IX).



inactive VIII active IX

The reactions by which VII was prepared are peculiarly suitable for synthesizing molecules in which the atoms or groups substituted in the benzene ring and on the olefin linkage may be varied. A study of such molecules and others containing two points of restricted rotation is now under way.

(3) Mills and Elliott, *J. Chem. Soc.*, 1291 (1928); Mills, *Trans. Faraday Soc.*, **26**, 431 (1930); Mills and Breckenridge, *J. Chem. Soc.*, 2209 (1932); Mills and Kelham, *ibid.*, 274 (1937).

(4) Mills and Dazeley, *J. Chem. Soc.*, 460 (1939).

(5) Kohler and Tishler, THIS JOURNAL, **54**, 1594 (1932); Kohler, Tishler and Potter, *ibid.*, **57**, 2517 (1935); Kohler and Sonnichsen, *ibid.*, **60**, 2650 (1938).

(6) Kohler and Baltzly, *ibid.*, **54**, 4015 (1932); Fuson, Fugate and Fisher, *ibid.*, **61**, 2362 (1939).

Experimental

Bromopropiomesitylene.—To a mechanically stirred mixture of 300 g. of carbon disulfide, 100 g. of bromomesitylene and 140 g. of aluminum chloride, was added 65 g. of propionic anhydride at such a rate that the solvent refluxed gently. After completion of the addition, stirring was continued for two hours and the reaction product was then poured into iced hydrochloric acid. The carbon disulfide layer was separated, the solvent removed and the residual oil dissolved in ether. This solution was washed with hydrochloric acid, water and finally with aqueous sodium carbonate. The product was a colorless liquid, b. p. 127–129° (3 mm.), $n^{20}D$ 1.5490, d^{24}_{24} 1.2956.

Anal. Calcd. for $C_{12}H_{15}OBr$: C, 56.50; H, 5.88. Found: C. 56.47; H, 6.08.

Dinitrobromomesitylene.—The structure of bromopropiomesitylene was proved by cleavage of the propionyl group with sirupy phosphoric acid[7] and nitration of the product to dinitrobromomesitylene. Following the same nitration procedure, bromomesitylene was converted to an identical product.

A mixture of 50 cc. of sirupy phosphoric acid and 5 g. of bromopropiomesitylene was refluxed for twelve hours and then steam distilled. The distillate was extracted with ether and the ether removed. The oil thus obtained was added slowly to 25 cc. of ice cold fuming nitric acid. After standing for twenty minutes, the mixture was poured on ice. The product was purified by crystallization from ethanol, m. p. 199.5–201.5° (cor.). Fittig and Storer[8] report m. p. of 189–190°.

Anal. Calcd. for $C_9H_9O_4N_2Br$: C, 37.37; H, 3.12. Found: C, 37.60; H, 3.31.

Bromomagnesium Enolate of Bromopropiomesitylene (V); α-Methyl-(2,4,6-trimethyl-3-bromobenzoyl)-acetic Acid (VI).—A solution of 25 g. of bromopropiomesitylene in 25 cc. of dry ether was added to 100 cc. of an ether solution containing slightly over one mole equivalent of ethylmagnesium bromide. The mixture was refluxed for thirty minutes, then transferred to a catalytic hydrogenation apparatus, cooled in an ice-bath, and carbon dioxide passed in at a pressure of 2–3 atm. After forty-five minutes, the temperature was allowed to come to that of the room and addition of carbon dioxide continued for six hours.

The reaction mixture was then chilled in an ice-bath, and poured slowly into iced hydrochloric acid. The ether layer was extracted with aqueous sodium carbonate and the aqueous extract acidified with iced hydrochloric acid. The product was purified by crystallization from benzene; white crystals, m. p. 123–124° (cor.) with decomposition. The crude product was satisfactory for conversion to the chloro compound; yield 15 g. (51%).

Anal. Calcd. for $C_{13}H_{15}O_3Br$: C, 52.17; H, 5.02. Found: C, 52.39; H, 5.55.

β-Chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic Acid (VII).—To a solution of 10 g. of α-methyl-(2,4,6-trimethyl-3-bromobenzoyl)-acetic acid in 50 cc. of ice cold phosphorus oxychloride, was added 25 g. of phosphorus pentachloride.[9] After warming on a steam cone for one hour, the solution was cooled and poured on 300 g. of ice. The product separated as an oil which solidified on standing. It was purified by crystallization from petroleum ether (b. p. 60–110°) as white crystals, m. p. 157–158° (cor.); yield 5.6 g. (53%).

Anal. Calcd. for $C_{13}H_{14}O_2BrCl$: C, 49.12; H, 4.42; neut. equiv., 317.5. Found: C, 48.95; H, 4.58; neut. equiv., 317, 314.

β-Chloro-β-(2,4,6-trimethyl-3-bromo-5-chlorosulfonylphenyl)-α-methylacrylic Acid (IX).—To 5 cc. of chlorosulfonic acid cooled to −10° was added slowly 0.20 g. of β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid. The reaction mixture was allowed to warm to room temperature and then poured on ice. The yellow solid was purified by recrystallization from petroleum ether (b. p. 60–110°): white crystals, m. p. 188–189° (cor.); yield 0.14 g. (53%).

Anal. Calcd. for $C_{13}H_{13}O_4BrCl_2S$: C, 37.59; H, 3.13. Found: C, 37.94; H, 3.26.

β-Chloro-β-(2,4,6-trimethyl-3,5-dibromophenyl)-α-methylacrylic Acid (VIII).—A mixture of 0.2 g. of β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid and 0.5 cc. of liquid bromine (cooled to 0°) was allowed to stand for twenty minutes. The excess bromine was evaporated and the residue treated with aqueous sodium bisulfite. The cream colored solid was purified by crystallization from ethanol; white needles, m. p. 228–229° (cor.).

Anal. Calcd. for $C_{13}H_{13}O_2Br_2Cl$: C, 39.39; H, 3.28. Found: C, 39.26; H, 3.26.

Resolution of β-Chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic Acid.—A solution of 10 g. of β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid in 75 cc. of warm absolute ethanol was added to a solution of 10 g. of quinine in 75 cc. of warm absolute ethanol. After filtration and cooling, 8.45 g. of salt (fraction A) crystallized. Evaporation of the filtrate to 100 cc. and cooling gave an additional 5.34 g. of salt (fraction B). The filtrate from the second fraction was diluted with 50 cc. of water whereupon 3.2 g. of oil separated (fraction C). Decantation of the solvent and slow evaporation yielded an additional crop of crystals (fraction D).

Fraction A was twice recrystallized from ethanol after which a constant rotation had been reached.

Rotation. Less soluble salt (*l*B·*d*A) 0.0995 g. made up to 25 cc. in absolute ethanol at 20° gave α_D −0.37; *l*, 2; $[\alpha]^{20}D$ −46.8°.

Anal. Calcd. for $C_{33}H_{38}O_4N_2BrCl$: C, 61.73; H, 5.92. Found: C, 61.82; H, 6.05.

***d*-β-Chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic Acid.**—To a suspension of 5.2 g. of the purified salt (fraction A) in 100 cc. of water was added 10 cc. of concentrated hydrochloric acid. After stirring for thirty minutes, the product was filtered and washed with 5% hydrochloric acid until quinine-free and then with water. The product (2.4 g.) was purified by recrystallization twice from petroleum ether (b. p. 60–110°). Its rotation was the same after each crystallization; white crystals, m. p. 155–156° (cor.).

Rotation. (*d*-acid) 0.0998 g. made up to 25 cc. with absolute ethanol at 20° gave α_D +0.42; *l*, 2; $[\alpha]^{20}D$

(7) Klages and Lickroth, *Ber.*, **32**, 1549 (1899).
(8) Fittig and Storer, *Ann.*, **147**, 8 (1868).
(9) Perkin, *J. Chem. Soc.*, **49**, 157 (1886).

+52.6°. 0.1008 g. made up to 25 cc. with glacial acetic acid at 20° gave α_D +0.56; *l*, 2; $[\alpha]^{20}_D$ +69.4°.

Anal. Calcd. for $C_{13}H_{14}OBrCl$: C, 49.12; H, 4.42. Found: C, 49.04; H, 4.04.

Decomposition of the oily fraction C in a similar manner gave *l*-acid which after two crystallizations gave a constant rotation; white crystals, m. p. 155–156° (cor.).

Rotation. (*l*-acid) 0.0994 g. made up to 25 cc. with absolute ethanol at 20° gave α_D −0.43; *l*, 2; $[\alpha]^{20}_D$ −54°.

Anal. Calcd. for $C_{13}H_{14}O_2BrCl$: C, 49.12; H, 4.42. Found: C, 49.62; H, 4.52.

Racemization Experiments.—The *d*-acid was refluxed in absolute ethanol for fifteen hours and in glacial acetic acid for twelve hours with no change in rotation in either case.

Bromination of *d*- + *l*-Acids: *dl*-β-Chloro-β-(2,4,6-trimethyl-3,5-dibromophenyl)-α-methylacrylic Acid.—The procedure for bromination was exactly that used in bromination of the racemic compound. The product was optically inactive and proved to be identical with the dibromo compound previously prepared; white needles, m. p. 228–229° (cor.). Bromination of the *l*-acid gave the same compound.

Action of Chlorosulfonic Acid on *d*- and *l*-Acids. Preparation of *d*- and *l*-β-Chloro-β-(2,4,6-trimethyl-3-bromo-5-chlorosulfonylphenyl)-α-methylacrylic Acids.—The procedure in these preparations was identical with that used for the racemic acid. Both *d*- and *l*-forms consisted of white crystals from petroleum ether (b. p. 60–100°), m. p. 183–184° (cor.).

Rotation. (derivative from *d*-acid) 0.1018 g. made up to 25 cc. with benzene at 20° gave α_D −0.07; *l*, 2; $[\alpha]^{20}_D$ −8.6°.

Anal. Calcd. for $C_{13}H_{13}O_4BrCl_2S$: C, 37.59; H, 3.13. Found: C, 37.96; H, 3.29.

Rotation. (derivative from *l*-acid) 0.1002 g. made up to 25 cc. with benzene at 20° gave α_D +0.08; *l*, 2; $[\alpha]^{20}_D$ +10.0°.

Summary

1. β-Chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid has been synthesized. This substance was resolved into its enantiomorphic forms. They proved to be very stable to racemization.

2. The asymmetry of the molecule is undoubtedly due to restricted rotation between the carbon of the benzene ring and the olefinic carbon to which it is attached. Necessity for unsymmetrical substitution in the benzene ring was demonstrated by bromination of the active acids and introduction of a chlorosulfonyl group. Bromination which results in a dibromo compound with symmetrical substitution gave an inactive product. Chlorosulfonic acid, on the other hand, which results in a molecule still containing an unsymmetrically substituted benzene, gave an optically active product.

3. This compound is typical of a general class of aryl olefins which should be capable of resolution.

URBANA, ILLINOIS RECEIVED NOVEMBER 8, 1939

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

The Synthesis of 1,3-Diphenyldihydroisobenzofurans, 1,3-Diphenylisobenzofurans and *o*-Dibenzoylbenzenes from the Diene Addition Products to Dibenzoylethylene

BY ROGER ADAMS AND MARVIN H. GOLD[1]

In a recent paper, the addition of 1,4-dimethylbutadiene to *trans*-dibenzoylethylene was described and a number of the reaction products of this substance was prepared.[2] A more systematic study is now under way on the diene addition products to dibenzoyl and substituted dibenzoyl ethylenes. In this communication will be reported the substances formed by the action of butadiene, 2,3-dimethylbutadiene, and cyclopentadiene on dibenzoylethylene, and the transformations of these substances.

2,3-Dimethylbutadiene and *trans*-dibenzoylethylene react to give a quantitative yield of 1,2-dimethyl-4,5-dibenzoylcyclohexene (I), which adds a mole of bromine to give the expected dibromide (II).

The cyclohexene (I) is converted, by means of a few drops of sirupy phosphoric acid in acetic anhydride, into 1,3-diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran (III).

Compound III, on treatment with two molecules of bromine followed by sodium acetate in acetic acid, gives an excellent yield of 1,2-dimethyl-4,5-dibenzoylbenzene (IV). The exact mechanism of this reaction was not determined but it is probable that one mole of bromine adds to the cyclohexene double bond and one mole to the 1,4-position in the furan conjugated system

(1) An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Adams and Geissman, THIS JOURNAL, **61**, 2083 (1939).