mine to its solution of carbon tetrachloride. This reaction recalls the behavior of azulenes. Similar color reactions of many essential oils may be due to the presence of such compounds of unknown structure.

Experimental

Separation of Natural Menthofuran.—The fraction of peppermint oil possessing a slight dextro-rotation was subjected to several fractionations and the fractions having a rotation of +15 to +20° were collected. The menthone present in these fractions was removed by means of semicarbazide hydrochloride. On fractionation the unreacted oil gave a product having a rotation of +61°, d^{20}_{25} 0.930, n^{25}_D 1.4657, b. p. (17 mm.) 92–94°. Carles[2] obtained a purer sample of natural menthofuran with the following constants: rot. +81°, b. p. (20 mm.) 95°, d^{15} 0.965, n^{20}_D 1.4807.

Maleic Anhydride Addition Product of Natural Menthofuran.—The above impure menthofuran (5 g.) was added to 15 ml. of benzene containing 5 g. of maleic anhydride. There was a noticeable rise in temperature and the mixture was allowed to stand for two hours. The crystals obtained after several recrystallizations from benzene had a m. p. of 133–133.5°. The mixed m. p. with the synthetic product showed no depression (m. p. 133°).

Preparation of Pulegenol Sulfonic Ester.—Oil of pennyroyal (100 g.) was fractionated and the fraction having a b. p. of 100–101° (17 mm.), rot. +21.50, d^{25}_{25} 0.939, n^{20}_D 1.4850, was taken as pure pulegone. Forty grams of pulegone was treated with 80 g. of an ice cold mixture of 2 moles of acetic anhydride and 1 mole of sulfuric acid. The temperature rose to 25° and the mixture was allowed to stand for two hours. The crystals obtained were filtered, washed and recrystallized from methyl alcohol, m. p. 86°. Treibs reports m. p. 85° for pulegenol sulfonic acid cyclic ester.

Formation of Menthofuran.—The above product (20 g.) was mixed with 20 g. of zinc oxide and heated at atmospheric pressure. When the oil-bath reached 280–290° strong fumes of sulfur dioxide came off followed by an oil of bluish color. The oil (13 g.) was first washed with water, then with a 5% solution of sodium carbonate, redistilled and the fraction (8 g.) of b. p. 205–206°, rot. +92° n^{20}_D 1.4855, d^{25}_{25} 0.966, was taken as menthofuran. It was a colorless oil which turned purplish on exposure to air. Treibs gives the following constants for synthetic menthofuran: b. p. 80° (18 mm.), d^{15} 0.972, n_D 1.4890, rot. +92°.

Maleic Anhydride Addition Product.—The same procedure was followed as with natural menthofuran. The maleic anhydride addition product had a m. p. of 133–133.5°. Treibs reports 138° for the m. p. of the addition product of menthofuran. Both the natural and synthetic menthofuran exhibited a greenish coloration and fluorescence in benzene solution although the crystals themselves were colorless.

Summary

A dextro-rotatory substance occurring in oil of peppermint (*Mentha piperita vulgaris S.*) was shown to be menthofuran (tetrahydro-4,5,6,7-dimethyl-3,6-coumarane). Its identity was established by the fact that its maleic anhydride addition product did not give a depression in m. p. when mixed with the maleic anhydride addition product of synthetic menthofuran.

CROTON-ON-HUDSON, N. Y.

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[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Monomers and Polymers. II. α-Methylstyrenes and the Steric Hindrance of *ortho*-Substituents[1]

BY G. BRYANT BACHMAN AND R. W. FINHOLT[2]

Although styrene (S) itself polymerizes readily in the presence of peroxides, α-methylstyrene (AMS) resists polymerization with peroxides and forms high polymers only in conjunction with other vinyl compounds.[2a] This is in part advantageous since the AMS may be stored even in the presence of air without loss (except by partial oxidation to acetophenone), and may be recovered from reaction mixtures with ease. The copolymers of AMS do not appear to differ markedly in physical properties from the analogous copolymers of S.

In undertaking a study of synthetic rubbers prepared by copolymerizing substituted α-methylstyrenes with butadiene we soon became aware of the importance of the relative positions of the substituent groups. Thus, 3,4-dichloro-AMS gave good rubbers with butadiene while 2,4-dichloro-AMS did not copolymerize. Construction of molecular models showed that the isopropenyl group is not free to rotate through 360° in the 2,4-isomer because of the hindering effect of the *ortho* chlorine atom. Such hindrance is not apparent in the S series, and there are numerous references in the literature to the polymerization of ortho substituted S's.[3] Models of the polymers of 2-chloro-AMS show that the phenyl groups are forced to lie at right angles to the direction of prop-

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(1) From the Ph.D. thesis of R. W. Finholt, Purdue University, June, 1947.

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(2a) Note, however, that acid and ionic catalysts cause polymerization of α-methylstyrenes. Staudinger and Breusch, *Ber.*, **62**, 442 (1929); Bergmann, Tanbadel and Weiss, *Ber.*, **64**, 1493 (1931); Hershberger, Reid and Heiligmann, *Ind. Eng. Chem.*, **37**, 1073 (1945).

(3) o-F-S, Brooks, THIS JOURNAL, **66**, 1295 (1944), and private communication. 2-CH_3O-S, Walling and Wolfstirn, *ibid.*, **69**, 852 (1947), and private communication; Pschorr and Einbeck, *Ber.*, **38**, 2076 (1905); Klages and Eppelsheim, *ibid.*, **36**, 3590 (1903). 2,3-, 2,4-, 2,5- and 2,6-diCl-S's, British Patent 564,828 (Oct. 16, 1944); Marvel, Overberger, Allen, Johnston, Saunders and Young, THIS JOURNAL, **68**, 861 (1946); Michalek and Clark, *Chem. Eng. News*, **22**, 1559 (1944). 2-CH_3-S, v. Auwers, *Ann.*, **413**, 295 (1917). 2,4-diCH_3 and 2,5-diCH_3-S's, Marvel, Saunders and Overberger, THIS JOURNAL, **68**, 1085 (1946). 2-OH-S, Fries and Fickewirth, *Ber.*, **41**, 369 (1908). 2,4-di(OH)-S, Flood and Nieuwland, THIS JOURNAL, **50**, 2568 (1918); etc.

agation of the chain, like pennies strung on a wire through a small hole in their centers.

While the above-described steric hindrance is not great enough to preclude ordinary reactions of AMS's, it does effectively prevent polymerization reactions, probably because of the small free energy changes (about 8 cal./mole) involved in going from a monomer to a polymer. An *ortho* fluorine atom, which is about midway in size between a hydrogen and a chlorine atom, is apparently just small enough to permit copolymerizations. This is evident in the models and corresponds with our experience. On the other hand, an *o*-methoxy group prevents copolymerization of AMS. The CH_3O- group is larger than the F atom but may, through restricted rotation, assume a position that is not in interference with the isopropenyl group. It is apparent, however, that rotation of the methoxy group is not restricted sufficiently to permit copolymers to form.

2,3-Dimethoxy- and 3,4,5-trimethoxy-AMS's not only did not copolymerize but also inhibited the polymerization of butadiene. This is not the result of steric hindrance, but is probably associated with the well-known inhibiting action of *o*- and *p*-dihydroxy aromatic compounds in polymerizations catalyzed by peroxides. It is even possible that traces of these methoxy compounds were hydrolyzed to the corresponding hydroxy compounds during their purification or polymerization.

The substituted AMS's, like AMS itself, did not polymerize on standing alone or in the presence of peroxides.

In Table I are summarized the results obtained with eleven AMS's. The rubbers from the unhindered AMS's were about equal to GR-S in their properties except for those from 4-chloro- and 3,4-dichloro-A7S which were superior. Table II compares the properties of these rubbers with a GR-S control.

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Experimental

Known Styrenes.—The following were prepared in the indicated yields by published procedures: 2-methoxy-AMS[4], 64% yield from methyl 2-methoxybenzoate; 2-fluoro-AMS[4] (d^{25}_{25} 1.004), 65% yield from methyl 2-fluorobenzoate; 4-methoxy-AMS,[5] 73% yield from 4-methoxyacetophenone; 4-ethoxy-AMS,[5] 65% yield from 4-ethoxyacetophenone; 3,4,5-trimethoxy-AMS.[6] (m. p. 34°), 66% yield from methyl 3,4,5-trimethoxybenzoate.

2,4-Dichloro-AMS.—A solution of 110 g. (0.5 mole) of ethyl 2,4-dichlorobenzoate in 300 ml. of ether was added slowly with cooling to 9.1 moles of methylmagnesium iodide in 750 ml. of ether. After refluxing for half an hour, the mixture was hydrolyzed with aqueous ammonium chloride and the ether extract was dried and evaporated. Without further treatment the residue was slowly distilled at 70 mm. pressure from 0.5 g. of phosphorus pentoxide and 6 g. of sodium acid sulfate. Rectification of the dried distillate gave 64 g. (68% yield) of the desired AMS, b.p. (15 mm.) 103–104°, d^{25}_{25} 1.182, n^{25}_D 1.5460.

Anal. Calcd. for $C_9H_8Cl_2$: Cl, 37.91. Found: Cl, 37.85, 37.72.

3,4-Dichloro-AMS.—Saturation of a solution of 382 g. of 3,4-dichlorobenzoic acid in 2 l. of ethanol with dry hydrogen chloride followed by neutralization and distillation gave 410 g. (95% yield) of the ester. Reaction of this with an excess of methylmagnesium iodide and conversion to the AMS as described in the preceding preparation gave 248 g. (70% yield) of product, b. p. (3 mm.) 94°, d^{25}_{25} 1.224, n^{25}_D 1.5732.

Anal. Calcd. for $C_9H_8Cl_2$: Cl, 37.91. Found: Cl, 37.69, 37.61.

2-Chloro-AMS.—From 313 g. of *o*-chlorobenzoic acid was obtained 317 g. (87% yield) of the ethyl ester. This was reacted with methylmagnesium iodide, the resulting crude alcohol was dehydrated and the styrene was obtained in 60% yield, b. p. (14 mm.) 75°, d^{25}_{25} 1.057, n^{25}_D 1.5329.

Anal. Calcd. for C_9H_9Cl: Cl, 23.23. Found: Cl, 22.92, 22.82.

TABLE I

COPOLYMERIZATION OF SUBSTITUTED α-METHYLSTYRENES WITH BUTADIENE[a] AT 40°

Substituents	Copolymerization	Yield	Hr.	Quality of rubber
2-Cl[c]	No	70	20	Dry[b]
2-F	Yes	75	25	Good
2-MeO	No	60	40	Dry[b]
4-Cl[c]	Yes	76	20	Good
4-MeO	Yes	80	38	Good
4-EtO	Yes	75	30	Good
2,4-Cl_2[c]	No	78	24	Dry[b]
3,4-Cl_2[c]	Yes	78	20	Good
3,5-Br_2[c]	Yes	100	44	Good
2,3-$(MeO)_2$[c]	No	...	..	Inhibits
3,4,5-$(MeO)_3$	No	...	..	Inhibits

[a] Butadiene 75%, α-methylstyrene 25%. [b] These rubbers were dry and brittle polybutadienes. [c] New compound.

TABLE II

PHYSICAL PROPERTIES[a] OF RUBBERS FROM BUTADIENE WITH 4-CHLORO- AND 3,4-DICHLORO-α-METHYLSTYRENES

Comonomer	3,4-Cl_2[b]	4-Cl[b]	GR-S control[c]
% Conversion	82	84	75
Modulus at 300%[d]	930 (705)	1260 (930)	800 (200)
Elongation[d]	705 (520)	613 (415)	600 (320)
Tensile[d]	4440 (1570)	4600 (1755)	3000 (800)
Durometer hardness	64	65	62
Bashore	37	37	36
Goodrich flexometer			
Change in T, °F.	68	63	65
Static compression, %	15.5	14.3	16.1
Change in height	4.4	3.9	2.6
Permanent set	2.0	1.4	3.3

[a] Physical tests were determined by the General Tire and Rubber Company. [b] Butadiene 70%, α-methylstyrene 30%. [c] Butadiene 75%, styrene 25%. [d] The figures in parentheses were obtained with the sample immersed in hot water (*ca.* 95°).

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(4) Bergman and Weizman, *Trans. Far. Soc.*, **32**, 1327 (1931).

(5) Behal and Tiffeneau, *Bull. soc. chim.*, [4] **3**, 321 (1908).

(6) Bogert and Isham, THIS JOURNAL, **36**, 516 (1914).

4-Chloro-AMS.—A solution of 154.5 g. of *p*-chloroacetophenone in 700 ml. of ether was added slowly with cooling and stirring to 1.2 moles of methylmagnesium iodide in 1200 ml. of ether. The crude tertiary alcohol obtained as a product was dehydrated at 15 mm. pressure by heating with 2 g. of sodium acid sulfate. Rectification gave 110 g. (71% yield) of the desired AMS, b. p. (10 mm.) 86°, d^{25}_{25} 1.073, n^{25}_{D} 1.5540.

Anal. Calcd. for C_9H_9Cl: Cl, 23.23. Found: Cl, 23.09. 22.90.

2,3-Dimethoxy-AMS.—A solution of 77 g. (0.4 mole) of methyl 2,3-dimethoxybenzoate in 300 ml. of ether was reacted with 0.8 mole of methylmagnesium iodide in 700 ml. of ether to obtain the tertiary alcohol which was dehydrated by slow distillation at normal pressure from 5 g. of phosphorus pentoxide. The resulting AMS was obtained in 28.5 g. (42% yield); b. p. (3 mm.) 78°, d^{25}_{25} 1.026, n^{30}_{D} 1.5237.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.89, 73,80; H, 7.89, 7.76.

3,5-Dibromo-AMS.—A solution of 200 g. of anthranilic acid in 2 l. of methanol was saturated with hydrogen chloride and refluxed for twenty hours. The ester solution was treated with 160 ml. of bromine in 400 ml. of concentrated aqueous potassium bromide maintaining the temperature at 25–30°. After three hours the dibromo ester (376 g., 83% yield) was precipitated in 25 liters of water. A solution of 154.5 g. of the ester in a mixture of 50 ml. of water, 50 ml. of acetic acid and 300 ml. of 95% ethanol was heated to boiling and treated with 85 g. of isopropyl nitrite added slowly over a period of three hours. The deaminated acid (88 g., 62% yield) was precipitated by pouring into 2 liters of water. It was esterified by saturating the solution in 1 l. of methanol with hydrogen chloride and refluxing for eight hours. The ester (86.5 g., 94% yield) separated on cooling as long white needles, m. p. 62-63°.

A solution of 99 g. (0.34 mole) of methyl 3,5-dibromobenzoate in 300 ml. of benzene was reacted with 0.7 mole of methylmagnesium bromide in 650 ml. of ether. Distillation of the resulting tertiary alcohol from 4 g. of phosphorus pentoxide at 20 mm. pressure and rectification of the product gave 65 g. (70.3%) yield of the desired AMS; b. p. (3 mm.) 98°, d^{25}_{25} 1.750, n^{30}_{D} 1.6097.

Anal. Calcd. for $C_9H_8Br_2$: C, 39.16; H, 2.92. Found: C, 39.33, 39.40; H, 2.78, 2.85.

Polymerization Experiments.—Each monomer was copolymerized with butadiene on a small scale (2.5 g. of AMS) to approximate the rate, then on a larger scale (50 g. or more of AMS) to compound, cure and test the rubber. The polymerization recipe was: butadiene 75 parts, AMS 25 parts, soap 5 parts, OEI (a mercaptan mixture from the Naugatuck Chemical Company) 0.6 part, a peroxide salt 0.3 part, water 175 parts by weight. The polymerizations were done in small sealed Pyrex tubes or quart size soda water bottles immersed and rotated in a thermostat bath. The conditions and results are summarized in Tables I and II.

Summary

The copolymerizations of eleven different nuclearly substituted α-methylstyrenes with butadiene have been studied. The effects of the natures and positions of the substituents on the rates of copolymerization have been discussed and the hindrance of *ortho* substituents has been indicated. Six new α-methylstyrenes have been prepared and characterized.

LAFAYETTE, INDIANA RECEIVED JULY 23, 1947

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Some Properties of Phenanthrene Semiquinone

BY L. MICHAELIS AND S. GRANICK

It has been shown in previous papers[1,2,3,4] that phenanthrenequinone or its sulfonate on partial reduction establishes a compound intermediate between the quinone and the hydroquinone. This intermediate compound, when in the dissolved state, is in equilibrium with the two "parent substances" and furthermore exists in two modifications which also are in equilibrium with each other, namely, the free paramagnetic semiquinone radical and its diamagnetic, quinhydrone-like dimerization product. All of the equilibrium constants for an aqueous solution at 30° and at different acidities have been determined. The equilibrium between the free radical, the quinone and the hydroquinone is displaced in favor of the radical by increase of *p*H up to about 11, and remains constant at its maximum value on further increase of *p*H. The percentage of dimerization of the free radical is increased with increasing total concentration, as expected for a bimolecular reaction. Two more properties of that intermediate compound will be described in this paper.

(1) The dimerization of the free radical is counteracted by water-miscible organic solvents such as ethanol or pyridine. Even at a very high concentration of potassium phenanthrenequinone-3-sulfonate, 0.05 *M*, no noticeable dimerization of the free radical takes place if the solvent is 50% pyridine instead of pure water. Evidence for this statement is produced by the measurement of the change of magnetic susceptibility of the quinone in alkaline solution during the slow reduction by glucose using the method described previously.[5] In the three experiments plotted in Fig. 1 the alkalinity is always great enough to make the semiquinone formation constant maximal and independent of minor variations of *p*H. In a purely aqueous solution, at the very high concentration of the substance used in this experiment, the change of susceptibility in time is such as to indicate *in maximo* not more than about 16% (3) of the substance in the state of a free radical. Such

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[1] L. Michaelis and M. P. Schubert, *J. Biol. Chem.*, **119**, 133 (1927).

[2] L. Michaelis and E. S. Fetcher, THIS JOURNAL, **59**, 2460 (1937).

[3] L. Michaelis, G. B. Boeker and R. K. Reber, *ibid.*, **60**, 202 (1938).

[4] L. Michaelis, R. K. Reber and J. A. Kuck, *ibid.*, **60**, 214 (1938).

[5] L. Michaelis, *ibid.*, **63**, 2446 (1941). (1) Calculated as shown in (5).