TABLE I

Compounds			Yield, %	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found		Sulfur, % Calcd.	Sulfur, % Found		Chlorine, % Calcd.	Chlorine, % Found	
4-Nitrophenylsulfen-		Anilide[a]						No rearrangement					
		p-Toluidide[a]						No rearrangement					
		o-Chloroanilide[a]						No rearrangement					
2,4-Nitrochlorophenylsulfen-	Na salt of mercapto-diphenylamine derivative	Anilide[a]	85					10.58	10.53		11.73	11.64	
		o-Toluidide[a]	95					10.11	10.19	10.03	11.22	11.23	
		o-Chloroanilide[a]	90					9.50	9.27	9.42	21.07	21.41	21.30
	Thiomethyl ether of mercapto-diphenylamine derivative	Anilide[a]	85	135–136	9.51	9.33	9.20	10.87	10.56	10.67	12.06	12.34	12.21
		o-Toluidide[a]	80	164–165	9.08	9.13	9.04	10.37	10.10	10.25	11.51	11.70	11.62
		o-Chloroanilide[a]	80	158–158.5	8.51	8.30	8.44	9.73	9.88	9.82	21.58	21.77	21.65
2-Nitrophenylsulfen-*o*-chloranilide[a]	Sodium salt of mercapto-diphenylamine derivative		90					10.58	10.60	10.42	11.73	11.61	11.55
	Thiomethyl ether of diphenylamine derivative		84	144.5–145	9.51	9.61	9.59	10.87	10.90	10.96	12.06	12.05	12.12

[a] For the preparation of these compounds, see THIS JOURNAL, **58**, 1091 (1936).

failed to bring about a rearrangement to their corresponding *o*-mercaptodiphenyl amines. The 2,4-nitrochlorophenyl derivatives, however, undergo a rearrangement to *o*-mercaptodiphenylamines when so treated, and it was possible to isolate the sodium salt as well as the thiomethyl ether without cyclization to thiazine compounds. The study of sulfenanilides will be continued in this Laboratory.

NEW HAVEN, CONN.

RECEIVED JULY 13, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XVI. The Structure of Polystyrene

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND HENRY M. LEICESTER

Polystyrene[1] is a friable solid which exhibits rubber-like properties at temperatures above 65°; it is obtained by heat polymerization of styrene.

Staudinger and his co-workers[2] have stated that polystyrene can be decomposed by heat into a mono-, di- and tristyrene; that the latter two compounds can be decomposed to monostyrene; and that 2,4-diphenyl-1-butene and 1,3-diphenylpropane can be detected among the heat decomposition products. They have therefore reached the conclusion that polystyrene is a long chain of styrene units bound together by ordinary valences, with a phenyl group linked to every second carbon. They have advocated formula I and rejected formula II.

$$\text{—CH}_2\text{CHPhCH}_2\text{CHPhCH}_2\text{CHPh—} \quad \text{(I)}$$

$$\text{—CH}_2\text{CHPhCHPhCH}_2\text{CH}_2\text{CHPhCHPhCH}_2\text{—} \quad \text{(II)}$$

Staudinger's experiments were repeated and found to be correct but the following additional facts were noted: (1) heat decomposition of polystyrene does not yield monostyrene exclusively; (2) rapid decomposition yields large amounts of monostyrene, while slow decomposition yields "di-styrene," "tri-styrene" and other intermediate products; (3) the partially decomposed products are complicated mixtures, and their further decomposition gives a poor yield of monostyrene; (4) diphenylbutene and diphenylpropane are present in very small quantities, and only in products obtained from incomplete decomposition; (5) all efforts to analyze the dimeric fraction by oxidation, reduction, nitration, bromination, etc., gave indifferent results. These additional experimental data cast strong doubts on the significance of the decomposition products in establishing the formula of polystyrene.

An explanation of dependence of the elasticity of natural and synthetic rubbers on their structural formula has been offered by Mack.[3] The application of his ideas to the case of polystyrene leads directly to the conclusion that the elastic properties of this substance are consistent with formula II, and not at all with the heretofore accepted formula I, for the following reasons.

In the case of formula I, the 1,3-placement of the phenyl groups results in optimum packing of the phenyl groups, optimum contacting of the hydrogen atoms, and good satisfaction of the van der Waals forces *when the chain molecule is extended;* consequently there is no tendency to fold

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[1] Whitby, *Rubber Chem. Tech.*, 465 (1931).

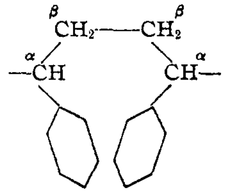
[2] Staudinger, *et. al.*, *Ber.*, **59**, 3019 (1926); **62**, 241–63 (1929); **62**, 2406 (1929); *Ann.*, **517**, 35–53 (1935).

[3] Mack, THIS JOURNAL, **56**, 2757 (1934).

or shorten the chain. But in the case of formula II, the 1,4-placement throws the phenyl groups together into pairs on adjacent carbon atoms, with two chain carbon atoms separating these pairs. Not only do the two phenyl groups within a pair turn into one another to establish better contacting, but van der Waals forces draw together into contact the various separate pairs, thus folding the extended chain and giving automatic retraction, hence elastic, rubber-like behavior. The motion of the bulky phenyl groups is sluggish at room temperature, but becomes more free and more swift with increasing thermal agitation, *i. e.*, at higher temperature.

Since Staudinger's reasons for discriminating against the formula required by Mack's theory were not found convincing, it was decided to apply to styrene the experimental procedure previously used with isoprene and dimethylbutadiene to establish the course of their transformation into synthetic rubber and methyl rubber, respectively.[4] This procedure consists in stopping the polymerization at the dimeric stage by addition of nascent hydrogen generated by the interaction of sodium and ethanol. Sodium chips are added to styrene and alcohol is fed at a rate sufficient to produce a lively evolution of hydrogen; the reaction liberates a considerable amount of heat, but the boiling of the alcohol automatically regulates the temperature. The reaction products consist of about 75% of ethylbenzene and 25% of 1,4-diphenylbutane. Significant is the fact that the reaction products are pure and entirely free from isomers or by-products.

The course of the polymerization is interpreted as follows. If the thermal agitation of the liquid styrene molecules consisted only of Dulong and Petit motions, back and forth, polymerization could take place by the random linking of two carbon atoms in α-position (with regard to the phenyl group), two carbon atoms in β-position, or one α- and one β-atom, and consequently the two phenyl groups of the dimeric compounds would be located in 1,4-, 2,4- or 2,3-position. The molecules are, however, in a liquid, and therefore crowded; they are thus compelled to rotate about the center of their own volume, that is, close to the center of the phenyl group. Then, no matter how the rotation occurs, the β-carbon atoms, at the end of the side-chain, are the only ones which can eventually come close enough to link. The chances of an α-carbon coming close enough to a β-carbon of another molecule to link are very remote, and its chances of coming close enough to another α-carbon are nil, because in addition to being shielded by the bulky phenyl group, it is most effectively buried within the sphere of revolution established by the outlying CH_2 group. As soon as two molecules have linked together the dimeric compound assumes a shape such as:[5]



where the free bonds of the α-carbon atoms are now at the surface and ready to join with the bonds of another dimer. From this stage the process of polymerization takes place by mere repetition.

It is therefore concluded that formula II is the correct representation of polystyrene and that Mack's explanation of its elasticity is consistent with the facts. This conclusion has been obtained in private discussion with Dr. Mack, whom we wish to thank.

Experimental

Preparation of Diphenylbutane with Sodium and EtOH.—Alcohol was added dropwise to 17 g. (20 cc.) of freshly distilled styrene and 5.3 g. of sodium chips at such a rate that hydrogen was steadily evolved. During the first part of the reaction, it was necessary to cool the mixture occasionally. As the reaction proceeded the solution became brown and sodium alcoholate separated, so that when all the sodium had been used up, the reaction mixture was almost solid. Ether was then added and the solution washed three times with water and dried over calcium chloride. The combined ether extracts from three runs (totaling 62 g. of styrene) were fractionated. Two fractions were obtained, one boiling at 135–150°, the other at 304–308°. The latter solidified in the receiver. The first fraction weighed 46 g. (74%) and consisted of ethylbenzene containing almost no styrene, as shown by the facts that no polymerization occurred when sulfuric acid was added to the liquid, or when it was heated for a prolonged period of time. The solid material, which weighed 11.5 g. (18.5%) after crystallization from alcohol, melted sharply at 52–52.5°, and the melting point showed no depression when the crystals were mixed with 1,4-diphenylbutane prepared by the catalytic reduction of 1,4-diphenylbutadiene.[6] The mother liquors from the crystallization were di-

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(4) Midgley and Henne, THIS JOURNAL, **51**, 1294 (1929); **52**, 2077 (1930).

(5) This is more easily seen on a three dimension scale model.

(6) *Org. Syntheses*, **16**, 28 (1936).

luted with water and extracted with ether. From the extract was obtained 2 g. (4.3%) of a semi-solid yellow oil from which more 1,4-diphenylbutane separated.

Summary

Styrene treated with sodium and alcohol gives 75% of ethylbenzene and 25% of 1,4-diphenylbutane. This shows that polystyrene should be represented by formula II, in opposition to the heretofore accepted formula I. Only formula II is consistent with Mack's explanation of the rubber-like elastic properties of polystyrene.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEW HAMPSHIRE]

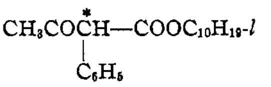
A Comparison of the Rate of Racemization with the Rate of Enolization

BY R. H. KIMBALL

It has long been assumed that optically active ketones, esters and acids can undergo racemization through formation of the inactive enol, which reverts to the racemic mixture. General acceptance of this mechanism has followed recognition of the fact that such substances can only be racemized when they are capable of enolization. This has been confirmed recently by Conant and Carlson,[1] who conclude that the rate of racemization can be considered as the rate of enolization, and point out the significant fact that whatever mechanism is assumed the rate of enolization cannot be faster than that of racemization, since the enol is necessarily inactive.

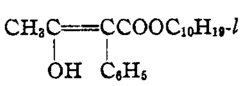
Whether enolization can be *slower* than racemization can only be determined by measuring the loss of optical activity and the development of enol simultaneously by independent methods. The familiar Kurt Meyer method of bromine titration has been applied in the past to measurement of the rate of enolization of acetoacetic ester and related substances.[2] An unsuccessful attempt to combine this method with polarimetric measurements has been described by Wren,[3] who tried to follow the development of enol during the racemization of methyl phenyl succinate by bromine titration, but failed because no detectable amount of enol was present. The difficulty has been that substances appreciably enolized racemize so easily that they cannot be obtained optically active; while substances which can be obtained optically active are not perceptibly enolized.

The substance employed in the present attack on the problem is the menthyl ester of α-phenylacetoacetic acid[4] I.



$$CH_3CO\underset{\underset{C_6H_5}{|}}{\overset{*}{C}}H—COOC_{10}H_{19}\text{-}l$$

I



$$CH_3\underset{\underset{OH}{|}}{C}{=\!=}\underset{\underset{C_6H_5}{|}}{C}COOC_{10}H_{19}\text{-}l$$

II

The form of this substance obtained by crystallization from methyl alcohol is the ketonic modification, as demonstrated by the fact that the fresh solution gives no color with ferric chloride and does not absorb bromine.

Freshly dissolved in benzene or alcohol the substance is dextrorotatory. The rotation at once starts to decrease, passing through zero and finally reaching a constant strongly levo value. This takes weeks without a catalyst, but addition of a small amount of piperidine or barium hydroxide brings it to equilibrium in a few minutes.

Rupe[4] interpreted this to mean that the active menthol has brought about resolution of the α-phenylacetoacetic acid, the form crystallizing from methyl alcohol being the dextro-keto modification I because of its dextro rotation—a long series of similar menthyl esters in which resolution is not possible being strongly levorotatory like menthol itself. He ascribed the mutarotation to formation of the enol II in which the optical activity of the alpha carbon atom is lost. Since only one of the three asymmetric carbon atoms is affected, this is not a true but a partial racemization, and at equilibrium the solution will contain the enol mixed with the diameric dextro-keto and levo-keto modifications.

In the usual true or partial racemization the proportion of enol is always negligible. Here on the contrary the enol steadily increases during the mutarotation until it constitutes the major part of the equilibrium mixture. The most significant comparison between the rate of this development of enol and the rate of racemization of the carbon atom involved will be made during

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(1) Conant and Carlson, THIS JOURNAL, **54**, 4048 (1932).

(2) K. H. Meyer, *Ann.*, **380**, 233 (1911); *Ber.*, **44**, 2725, 2729 (1911); Grossman, *Z. physik. Chem.*, **109**, 305 (1924).

(3) Wren, *J. Chem. Soc.*, **113**, 210 (1918).

(4) Rupe, *Ann.*, **395**, 91 (1913); **398**, 372 (1913).