dent in our work would present a practical limitation.

Since completing these experiments, we learned[4] that Tobolsky and Baysal[5] have demonstrated this reaction in the case of styrene. We thank the American Chicle Company for a grant in aid of this investigation, Dr. D. H. Johnson for details of the cyclic disulfide preparation, and S. M. Nagy for the sulfur analysis.

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[4] A. V. Tobolsky, private communication, July 7, 1952.

[5] A. V. Tobolsky and B. Baysal, This Journal, **75**, 1757 (1953).

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The Reaction between Styrene and Ring Disulfides: Copolymerization Effected by the Chain Transfer Reaction

By A. V. Tobolsky and B. Baysal

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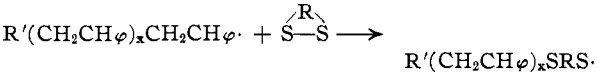
Disulfides such as dibutyl disulfide are active chain transfer agents in the polymerization of vinyl and diene monomers such as styrene and butadiene. The transfer reaction probably proceeds as

$$R'(CH_2CH\varphi)_xCH_2CH\varphi\cdot + RSSR \longrightarrow R'(CH_2CH\varphi)_xSR + RS\cdot$$

$$RS\cdot + CH_2 = CH\varphi \longrightarrow RSCH_2CH\varphi$$

It was therefore conceived that if a ring disulfide was present in a vinyl polymerization, the chain transfer process would result in the incorporation of the ring disulfide molecule in the growing polymer chain; *i.e.*, a copolymerization would be effected by the elementary reaction of chain transfer.



$$R'(CH_2CH\varphi)_xCH_2CH\varphi\cdot + \overset{R}{S{-}S} \longrightarrow R'(CH_2CH\varphi)_xSRS\cdot$$

$$R'(CH_2CH\varphi)_xSRS\cdot + CH_2CH\varphi \longrightarrow R'(CH_2CH\varphi)_xSRSCH_2CH\varphi\cdot \xrightarrow{\text{etc.}}$$

The direct consequence of these considerations is that if a vinyl monomer is polymerized in the presence of a large amount of an open chain disulfide such as dibutyl disulfide, two sulfur atoms should be incorporated in every polymer chain. On the other hand, polymerization of a vinyl monomer in the presence of a ring disulfide such as diethyl ether disulfide,[1,2] should produce polymers with more than two sulfur atoms per polymer chain.

To test this hypothesis we polymerized styrene in the presence of varying amounts of dibutyl disulfide and diethyl ether disulfide. The polymerizations were carried out for 48 hours at 130° followed by 48 hours at 150° in the absence of catalysts. Oxygen was rigorously excluded from the system. The polymers were then twice precipitated in methanol and weighed. Sulfur analyses of the polymers were carried out, and the molecular weights of the polymers determined by measurement of the intrinsic viscosities, using the relation of Mayo, *et al.*[3] This relation was also verified by Pepper[4] for low molecular weight polymers. The use of this relation is only approximate for styrene polymers prepared in the presence of large amounts of disulfide, particularly if the ring disulfide is incorporated in the polymer chain.

The results of these experiments are shown in Table I. Two facts are especially noteworthy. The polymerizations effected in the presence of large amounts of ring disulfide gave a larger weight of polymer than the weight of styrene incorporated in the charge. Also, the number of sulfur atoms per chain in the case of these polymers was much larger than two, whereas in the case of polymers prepared in the presence of dibutyl disulfide the number of S atoms per chain was approximately two.

The results shown in Table I provide a clear indication that a significant difference results in the polymerizations carried out in the presence of chain and ring disulfides, which can only be accounted for by an effective copolymerization in the case of the ring disulfides.

Table I

Chain transfer agent (A)	Charge ratio, c.c.A:c.c. styrene	Total weight charge,[a] g.	Total weight polymer, g.	[η]
Dibutyl disulfide	1:3	3.64	2.64	0.239
Dibutyl disulfide	2:3	4.56	2.11	.145
Diethyl ether disulfide	2:3	5.26	4.37	.048
Diethyl ether disulfide	1:3	3.99	3.25	.094
Diethyl ether disulfide	0.5:3	3.35	2.86	.109
Diethyl ether disulfide	0.3:3	3.10	2.53	.175
Diethyl ether disulfide	0.1:1	2.85	2.56	.492

Chain transfer agent (A)	Charge ratio c.c.A:c.c. styrene	$\overline{M}n$[b]	% S in polymer	% S in polymer/% S in charge	S atom per chain
Dibutyl disulfide	1:3	24600	0.35	0.038	2.69
Dibutyl disulfide	2:3	11800	1.04	.072	3.84
Diethyl ether disulfide	2:3	2570	9.20	.410	7.34
Diethyl ether disulfide	1:3	6560	5.43	.369	11.1
Diethyl ether disulfide	0.5:3	7950	2.72	.310	6.75
Diethyl ether disulfide	0.3:3	15200	0.96	.168	4.56
Diethyl ether disulfide	0.1:1	52500	1.05	.495	17.2

[a] Density of styrene at 20° = 0.905; density of dibutyl disulfide at 20° = 0.919; density of diethyl ether disulfide at 20° = 1.274. [b] Number average molecular weight.

We wish to thank Mr. F. O. Davis and the Analytical Department of the Tiokol Corporation for carrying out the sulfur analyses of the polymer samples.

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[1] E. Fettes and F. O. Davis, This Journal, **70**, 2611 (1948).

[2] A. V. Tobolsky, F. Leonard and G. P. Roeser, *J. Polymer Sci.*, **3**, 604 (1948).

[3] F. R. Mayo, R. A. Gregg and M. S. Matheson, This Journal, **73**, 1691 (1951).

[4] D. C. Pepper, *J. Polymer Sci.*, **7**, 347 (1951).

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Synthesis of Radioactive Noradrenaline

By Richard W. Schayer[1]

Received November 26, 1952

The synthesis of α-C^{14}-*dl*-noradrenaline (norepinephrine, arterenol) was accomplished by known procedures[2] modified for small scale use suitable for the preparation of high activity material.

Chloroacetylcatechol, 210 mg., was converted successively to noradrenalone, 93 mg., noradren-

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[1] Supported in part by a research grant from the U. S. Public Health Service.

[2] W. Langenbeck and F. Fischer, *Pharmazie*, **5**, 56 (1950).

alone hydrochloride, 77 mg., and noradrenaline, 53 mg., a 28% yield. The activity was 8.5 × 10^4 c.p.m. per mg. Identity and purity of the noradrenaline were established by microanalysis, pharmacological activity and isotope dilution assay.

Full experimental details for this synthesis are available on microfilm.[3]

[3] For full experimental details of this synthesis order Document 3847 from American Documentation Institute, c/o Library of Congress, Washington 25, D. C., remitting $1.25 for microfilm (images 1 inch on standard 35-mm. motion picture film) or $1.25 for photostats readable without optical aid.

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Temperature Coefficients of Rotation of Some *o*- and *p*-Nitrophenyl Glycosides and their Polyacetates[1]

BY JACK A. SNYDER AND KARL PAUL LINK

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Pigman[2] has suggested that the anomalous positive rotations of the *ortho*-substituted phenyl β-D-glycoside tetraacetates are due to "interactions between the acetyl and aglycon groups. Such interaction might take the form of weak bonds between these groups or it might operate through steric hindrance to free rotation of the aglycon group about the glycosidic linkage." This was postulated on the basis of the large temperature coefficients of rotation of these glycosides in contrast to those of their *m*- and *p*-isomers. We have determined the rotations of several *o*- and *p*-nitrophenyl glycosides and their polyacetates over the range 15–45°, and find that the *ortho* compounds have large temperature coefficients while the *para* compounds have normal coefficients. This indicates that the acetate groups are not directly concerned with the production of large temperature coefficients and favors their explanation on the basis of steric hindrance.

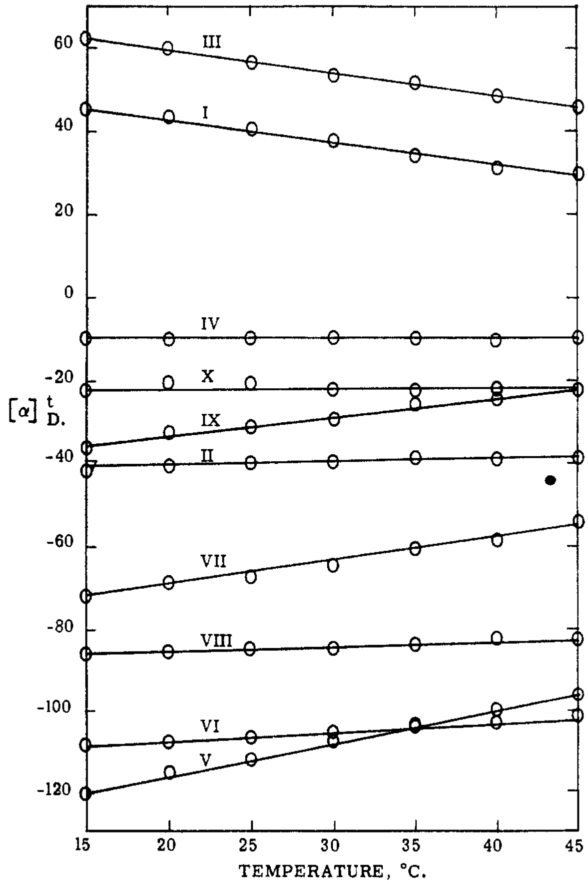

Fig. 1.—Influence of temperature on specific rotation of some *o*- and *p*-nitrophenyl glycosides and their polyacetates.

Experimental

Change of Specific Rotation with Temperature.—The method of preparation of the compounds studied has been reported previously.[3] Rotations were determined with a Schmidt and Haensch polarimeter No. 52-b with monochromator. A 2-dm. jacketed tube was used, with water, maintained at $t \pm 0.2°$ by means of a thermostatically controlled water-bath, as the circulating fluid. No correction was made for liquid density change with temperature.

TABLE I

SOLVENTS AND CONCENTRATIONS IN DETERMINATION OF CHANGE OF SPECIFIC ROTATION WITH TEMPERATURE

Compound	Solvent	Concn., %
o-Nitrophenyl β-D-glucoside tetraacetate (I)	Chloroform	1.966
p-Nitrophenyl β-D-glucoside tetraacetate (II)	Chloroform	1.884
o-Nitrophenyl β-D-galactoside tetraacetate (III)	Chloroform	1.865
p-Nitrophenyl β-D-galactoside tetraacetate (IV)	Chloroform	1.983
o-Nitrophenyl β-D-glucoside (V)	Water	0.828
p-Nitrophenyl β-D-glucoside (VI)	Water	0.987
o-Nitrophenyl β-D-galactoside (VII)	Water	1.065
p-Nitrophenyl β-D-galactoside (VIII)	Water	0.980
o-Nitrophenyl α-L-arabinoside (IX)	Water	.290
p-Nitrophenyl α-L-arabinoside (X)	Water	.265

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[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station. Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

[2] W. W. Pigman, *J. Research Natl. Bur. Standards*, **33**, 129 (1944).

[3] J. A. Snyder and K. P. Link, THIS JOURNAL, **74**, 1883 (1952).

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The Sedimentation Constant of Insulin in Acid Solution: A Re-examination[1]

BY FRANK TIETZE AND HANS NEURATH

RECEIVED NOVEMBER 1, 1952

On the basis of their observations on the sedimentation and diffusion constants of bovine insulin in acid solution, Fredericq and Neurath[2] concluded that the minimum molecular weight of this protein was about 6000. Although this conclusion has received support from the more recent work of Harfenist and Craig[3] on counter-current distribu-

[1] This work has been supported by the Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana, to whom we are also indebted for the supply of crystalline insulin.

[2] E. Fredericq and H. Neurath, THIS JOURNAL, **72**, 2684 (1950).

[3] E. J. Harfenist and L. Craig, *ibid.*, **74**, 3087 (1952).