extracts were combined, dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated to about 50 ml. and chilled; the semisolid residue was treated with 75 ml. of petroleum ether (b.p. 95–110°), rechilled and filtered to give 18.7 g. of crude product. After three recrystallizations from petroleum ether (b.p. 95–110°) there was obtained 16.1 g. (61.5%) of 1-isobornyl-5-*n*-butyl tetrazole, m.p. 63.5–65°. The data for the tetrazoles are in Table II.

West Lafayette, Ind.

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Effect of Associated Salts and Amines on Polymerization of Butadiene by Amylsodium[1]

AVERY A. MORTON and FRANK K. WARD

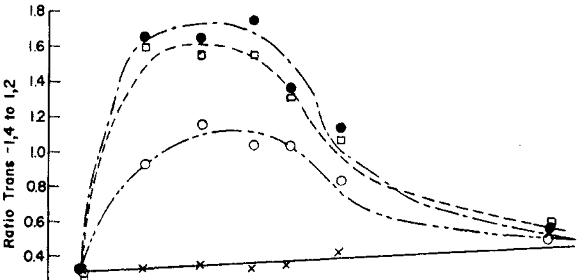
Received November 10, 1958

Triethyl amine and sodium hydroxide caused amylsodium to polymerize butadiene in a 1,4- rather than the usual 1,2- manner. The combination resembles in some aspects the alfin group of reagents but is less satisfactory with respect to the yield, size of polymer and freedom from gel of the polybutadiene. The conditions under which this combination operates are described.

Prior work has demonstrated that the association of sodium isopropoxide and sodium chloride with allylsodium caused the predominant polymerization of butadiene to change from a 1,2- to a 1,4-process. Similar effects were achieved with other straight chain alkenyl- or benzyl-sodium reagents. These combinations are known generally as alfin catalysts.[2] The organosodium components have unsaturation in the chain or the ring. No such change has been found, hitherto, when the organic moiety is saturated.[2a,3] The present paper reports that the association of triethyl amine and sodium hydroxide—sodium chloride happened to be present also—with amylsodium caused a similar alteration in the polymerization of butadiene. Alone, amylsodium polymerized butadiene largely in a 1,2- manner, the ratio of *trans*-1,4- to -1,2- structures being 0.3 or 0.4 (only 23–28% *trans*-1,4-), but with appropriate amounts of triethyl amine and sodium hydroxide the ratio became as high as 1.75 ,that is, 64% *trans*-1,4-structure, only a little less than the 75% achieved with a good alfin reagent which in turn is as much as in free radical polymerization.

Around 200 experiments (not all reported in this paper) were made in demonstrating this effect. Amylsodium was made from amyl chloride and sodium. Water was added in varying amounts to different preparations so that different ratios of sodium hydroxide to amylsodium were obtained. Then a specific quantity (usually 10 ml.) of each reagent was added to 30 ml. of butadiene in 200 ml. of solvent, said solvent being cyclohexane, triethyl amine, or mixtures of these two liquids. By this means a wide coverage of conditions was assured although the experiments by no means encompassed all possible variations. Adequate controls and tests with other components were made.

The principal results are shown in six graphs. In the first the highest proportion of 1,4-polymerization was realized when the ratio of sodium hydroxide to amylsodium was around 0.8 and the amine was approximately one half by volume of the total solvent. The bottom curve on the graph shows a control series where no amine was present; the proportion of 1,4-structure increased only a



10-ml. catalyst suspension
30-ml. butadiene
One-hour polymerization

	Solvent	
	Cyclohexane, ml.	$(C_2H_5)_3N$, ml.
×	200	0
○	150	50
●	100	100
□	50	150

Fig. 1. Infrared ratio as a function of amine concentration and oxide ratio

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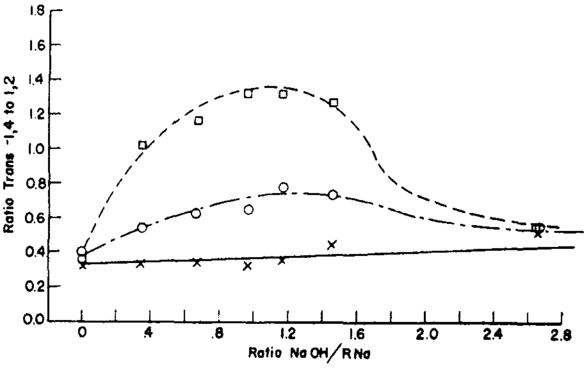
(1) This work was performed as part of a research project sponsored by the National Science Foundation.

(2) (a) A. A. Morton, E. E. Magat, and R. L. Letsinger, *J. Am. Chem. Soc.*, 69 950 (1947); (b) A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950); (c) A. A. Morton, F. H. Bolton, F. W. Collins, and E. F. Cluff, *Ind. Eng. Chem.*, **44**, 2876 (1952); (d) A. A. Morton, I. Nelidow, and E. Schoenberg, *Proc. Third Rubber Tech. Conf.*, 108 (1954); (e) A. A. Morton, *Advances In Catalysis*, IX 745 (1957), Academic Press, Inc. New York.

(3) British Patent **782970**, Sept. 18, 1957, issued to Polymer Corp. Ltd., of Canada, describes the use of amylsodium with sodium isopropoxide and sodium chloride as a reagent which can cause a high proportion of 1,4- polymerization. However, their amylsodium was prepared in xylene, which would react at once to give xylylsodium.

trifle (0.3 to 0.5) as the proportion of hydroxide increased.

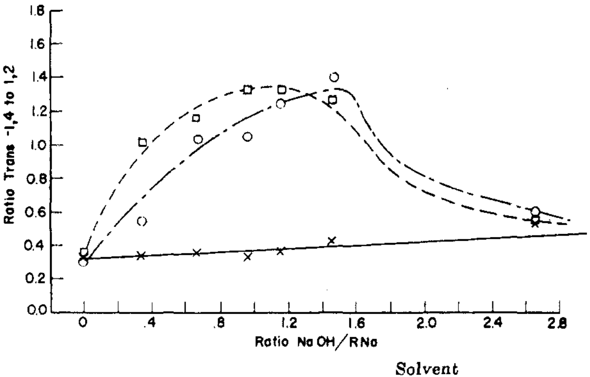
The second graph shows the effect of time on polymerization. The shortest time tested was 1 hr. although the 1,4- process was probably over within a few minutes. Thereafter the slower and longer lasting 1,2- process lowered the over-all value for the final product. Even after 24 hr., however, an area of optimum 1,4- activity could be seen. The curve at the bottom of the graph shows again the low ratio which was found in the absence of any triethyl amine.



		Solvent		
		Cyclohexane, ml.	$(C_2H_5)_3N$, ml.	Time, Hr.
10-ml. catalyst suspension 30-ml. butadiene	X	200	0	1
	☐	0	200	1
	○	0	200	24

Fig. 2. Infrared ratio as a function of polymerization time and oxide ratio

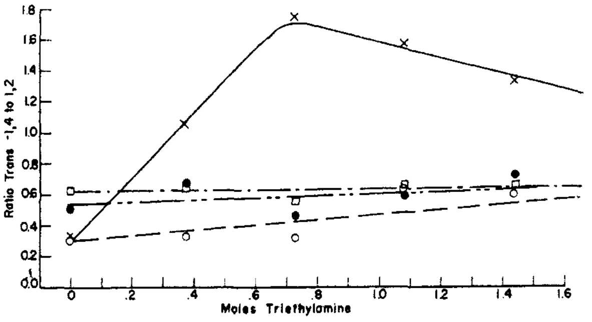
The third graph shows that the same high ratio of *trans*-1,4- to -1,2-structure was realized by two different quantities of reagent but the proportion of sodium hydroxide to amylsodium had to be increased a little when more reagent was used. This result might be explained on the ground that some moisture was present on the walls of the glass bottle used as the polymerization vessel in spite of moderate heating and drying in dry nitrogen. This moisture would react with amylsodium to produce some sodium hydroxide *in situ*. When larger quantities of sodium reagent were used this loss by hydrolysis was proportionately less and more sodium hydroxide had to be added to get the proper proportion for high activity.



		Solvent		
		Cyclohexane, ml.	$(C_2H_5)_3N$, ml.	Catalyst, ml.
One-hour polymerization 30-ml. butadiene	X	200	0	10
	☐	0	200	10
	○	0	200	25

Fig. 3. Infrared ratio as a function of the amount of catalyst and the oxide ratio

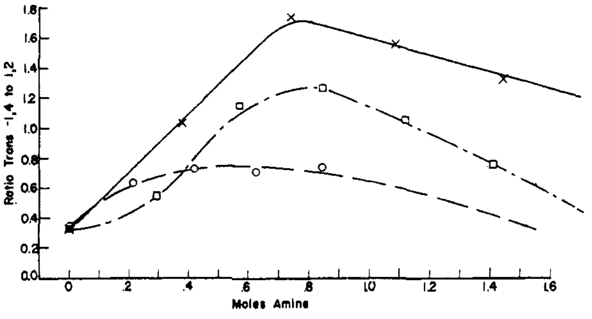
The three remaining graphs show the effect of changes in the components which make up the mixture of reagents. Neither sodium methoxide, sodium isopropoxide nor sodium *t*-butoxide could be used in place of sodium hydroxide (graph 4); in no case did the ratio rise above 0.7. Triethyl amine was the best of the three amines tried (see graph 5). Less than half of the polymerization in the presence of tributyl amine was 1,4-. Allylsodium, which was such an important component of the alfin catalyst, was relatively ineffective in this amine system, the ratio of *trans*-1,4- to -1,2-structures being not above 0.9 (see graph 6).



10-ml. catalyst suspension
30-ml. butadiene
One-hour polymerization
Oxide ratio = 1

X $NaOH/C_5H_{11}Na$
○ $CH_3ONa/C_5H_{11}Na$
☐ $(CH_3)_2CHONa/C_5H_{11}Na$
● $(CH_3)_3CONa/C_5H_{11}Na$

Fig. 4. Comparison of oxide components in the amine catalyst



10-ml. catalyst suspension
30-ml. butadiene
One-hour polymerization
Oxide ratio = 1

X $(C_2H_5)_3N$
○ $(n\text{-}C_4H_9)_3N$
☐ $(CH_3)_3N$

Fig. 5. Comparison of amines in the amine catalyst

Diethyl amine proved incapable of causing 1,4-polymerization either in the absence or presence of triethyl amine. If this amine, as a sodium salt (R_2-NNa), caused any effect at all, it was toward more 1,2- structure and a lower viscosity polymer. This secondary amine might be assumed to have been formed by cleavage of triethyl amine with amylsodium. Another paper,[4] however, reports

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(4) A. A. Morton and F. K. Ward, unpublished work

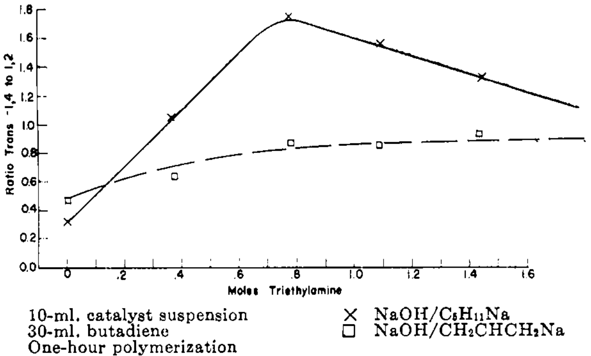

Fig. 6. Comparison of organosodium reagents in the amine catalyst

the failure to find any such cleavage and the present tests show that any diethylsodamide, if it had formed, would have been ineffective in causing 1,4-polymerization.

Table I shows a comparison of the hydroxide-amine-organosodium combination with the alfin system. Three different components have proved essential for each. If sodium chloride should happen to be required for a new system as it proved to be for the alfin combination,[2c] and if some olefin or butadiene remained coordinated with the reagent in the alfin catalyst, each might be regarded as a four component combination, broadly similar to the other. Specifically, however, some of the components show wide differences. A transposing of either the organosodium or the sodium oxide salt from one system to the other destroys the capacity for 1,4-polymerization. Sodium chloride is common to both. Triethyl amine is essential for the new system and can be present also with the alfin system without special harm.[5]

TABLE I

COMPARISON OF THE COMPOSITION OF THE AMINE WITH AN ALFIN SYSTEM

Components	Amine	Alfin
RNa salt	$C_5H_{11}Na$	$CH_2{=}CHCH_2Na$
Oxide salt	NaOH	$(CH_3)_2CHONa$
Halide salt	[NaCl][a]	NaCl
Coordinating agent	$(C_2H_5)_3N$	[C_4H_6 or C_nH_{2n}][b]

[a] Sodium chloride was introduced during the preparation of amylsodium but has not been proved to be essential. [b] No liquid coordinating agent has been proven to be a part of the alfin reagent but that role might be fulfilled by the olefin or diene itself.

Were it not for the differences in composition this new system, in its present state of development, might be called a very poor alfin catalyst. The viscosity (DSV) was 2.5 to 4 which is within the range shown by some of the alfin catalysts[2e] though far below the values of 10 and higher found with the best members of that group. The conversion (not above 1 or 2%) was very low but that value probably could be changed by more reagent or improvements in the conditions for polymerization. A major difficulty was the unusually high percentage of gel, often being 85–95%. Consequently the polymer rapidly enclosed the catalyst in an insoluble shell which retarded or stopped polymerization within a few minutes while the conversion was still low. Undoubtedly this tendency to form gel came from the very high metalating activity of amylsodium, because metalation has been shown to cross-link rubber.[6] The same trouble was experienced with the alfin catalyst where the gel was 100% when the reagent was first discovered but was gradually reduced to zero as the amount of reagent and the proportions of its components were adjusted. The problem seems unusually difficult in the present case because amylsodium is noted for its metalating[7] activity. However, the gel was reduced greatly —to around 6%— by the use of triethyl amine as the medium instead of a mixture of triethyl amine and cyclohexane but the use of more reagent thereafter in order to increase the yield caused a high gel again. Some improvement would be expected with butyl-, propyl-, or ethyl-sodium which are less active metalating agents[8] than the very powerful amylsodium but no time was available to investigate those and other possibilities. Another hundred or so experiments might have been required. The study was not intended as a survey of optimum conditions. The prime interest was theoretical.

This work was done with the idea of demonstrating that amylsodium could function as a radical pair and thereby could induce 1,4-polymerization of butadiene. Some details in the formation of radical pairs from sodium reagents[9] and of alfin polymerizations as a radical process[2d,e] have been published. The interpretation which this laboratory considers most suitable for the present case would parallel closely the prior explanations.

EXPERIMENTS

Preparation of amylsodium. Amylsodium was prepared in the usual way[10,11] from 0.5 mole of amyl chloride and 1 g.-

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(5) Unpublished work with F. W. Collins.

(6) A. A. Morton and H. E. Ramsden, *J. Am. Chem. Soc.*, **70**, 3132 (1948); A. A. Morton, R. P. Welcher, F. Collins, S. E. Penner, and R. D. Coombs, *J. Am. Chem. Soc.*, **71**, 481 (1949).

(7) (a) A. A. Morton and C. E. Claff, Jr., *J. Am. Chem. Soc.*, **76**, 4933 (1954); (b) A. A. Morton and J. L. Eisenmann, *J. Org. Chem.*, **23**, 1469 (1958).

(8) A. A. Morton, G. M. Richardson, and A. T. Hallowell, *J. Am. Chem. Soc.*, **63**, 327 (1941).

(9) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **21**, 93 (1956).

(10) A. A. Morton and A. E. Brachman, *J. Am. Chem. Soc.*, **76**, 2980 (1954).

(11) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, Jr., and R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 3785 (1950).

atom of sodium sand in 500 ml. of n-heptane. Water, alcohol, or diethyl amine was added dropwise while the mixture was maintained at 0°. Then the mixture was stirred an additional hour at 0° before being transferred to a dry quart bottle which had been evacuated and filled with nitrogen. The reaction flask was rinsed twice with heptane and each time the rinsings were transferred to the bottle as before. Finally the volume of the suspension was adjusted to 800 ml. by addition of more heptane and the bottle was closed with a cork and sealed with glyptal cement. All operations of preparing and handling the suspension were carried out under an atmosphere of dry nitrogen. After 24 hr. the bottle was shaken and a 50-ml. aliquot was removed and carbonated in order to determine the carboxylic acids and thus the amount of sodium reagent. When the reagent was allylsodium the same technique was followed except that after the addition of water, propylene was passed into the flask in order to convert the remainder of the amylsodium to allylsodium.

In a series of 24 different preparations by the above means the average yield of combined organosodium reagent and sodium oxide (or amide) salt was 87.4% and the extremes were 80.7 and 93.8%, but some variation existed between classes of reagent. For instance, without any oxide salt the average yield in seven preparations was 83.8 and the extremes were 80.7–87.0. When sodium hydroxide was present the average yield from eight preparations was 89.3% and the extremes were 84.0–93.8. In the presence of diethylsodamide the average of six preparations was 89.5% and the extremes were 83.8–93.0%. Single preparations only were made with sodium methoxide, sodium isopropoxide, and sodium *t*-butoxide and the respective yields were 90.2, 86.4, and 85%. It is unlikely that these differences can be attributed to a small amount of reaction between water, alcohol or amine, and small bits of sodium metal left over because of the incompleteness of the reaction between amyl chloride and sodium, because diethyl amine does not react with sodium metal. An alternative idea, particularly applicable to sodium hydroxide, is that the salt helped to stabilize the amylsodium against decomposition, even as it had made it less reactive in other work.[7b] Possibly some of the variations are typical for heterogeneous systems.

In any event the ratio of oxide salt to organosodium reagent was calculated from the total sodium salt (oxide salt plus organosodium reagent), the reasonable assumption being made that the reaction between amylsodium and the active hydrogen of water, alcohol or amine was complete.

Polymerizations. The usual practice was to add 10 ml. of the amylsodium reagent to 30 ml. of Phillips research grade of butadiene to each of five 12-oz. beverage bottles each containing 200 ml. of liquid. This liquid was cyclohexane, triethyl amine, or mixtures of the two. The amount of triethyl amine varied progressively from 0, 50, 100, 150 to 200 ml. while the cyclohexane correspondingly decreased. The bottles were capped after addition of the reagent, shaken by hand a few times to mix the contents, and then allowed to stand at room temperature. At the end of a given time (usually 1 hr.) the contents were poured into 500 ml. of methanol. The precipitated polymer was collected, washed, and dried over night at 40°/1 mm.

For analysis an aliquot of this polymer was suspended in toluene and shaken gently for 48 hr. before filtering through silk gauze in order to separate the gel. An aliquot of this filtrate was evaporated and the residue weighed in order to determine the proportion of soluble polymer. The difference between the total polymer and this soluble product was credited as gel. The dilute solution viscosity (DSV) was determined on this soluble portion.

Another part of the polymer was suspended in carbon disulfide, shaken gently for 48 hr., filtered, and concentrated. Its infrared absorption was determined in a Baird Double Beam recording spectrophotometer, model B, with particular attention to the values at 965 cm.$^{-1}$ and 910 cm.$^{-1}$ favorable to measurements of the *trans*-1,4- and -1,2-structures, respectively.[2d] A ratio of *trans*-1,4- to 1,2-structure exceeding 1 indicated that over half of the polymerization was 1,4-. The *cis*-1,4- was not measured chiefly because only a very small amount was present, organosodium reagents being very active in converting *cis* to *trans* structure.[12]

Drying of the triethyl amine. The initial tests with amylsodium were made with triethyl amine which had stood over potassium hydroxide pellets for several months. A ratio of *trans*-1,4- to -1,2- structure of 1.5 was obtained but the progressively lower yield as more and more triethyl amine was used suggested three questions: (1) Was a reaction product of amylsodium with triethyl amine responsible; (2) Did moisture in the triethyl amine cause the high ratio; or (3) Did some impurity such as diethyl amine react with amylsodium? Accordingly, triethyl amine was pretreated with amylsodium. Thereafter in two separate series in which the amine progressively replaced cyclohexane as the medium, the ratio of trans-1,4- to -1,2- structures ranged from 0.30 to 0.42. These tests eliminated the first possibility and showed that the cause of the unusual polymerization lay in either the second or third proposition.

Potassium hydroxide alone was effective as a drying agent when the mixture was stirred in the high-speed stirring apparatus for 4 days. In that way the hydroxide was broken into small particles and the surface coating was removed. After decantation the amine was used in varying proportions with cyclohexane as already described. The ratio of *trans*-1,4- to -1,2- structures varied 0.3–0.35. This test eliminated the possibility that dissolved potassium hydroxide could have been responsible for the high ratio and also eliminated the second possibility above, namely that diethyl amine had been present, because potassium hydroxide would not react with the secondary amine. Water alone, which would react with amylsodium and form sodium hydroxide *in situ*, was responsible for the special activity; and this idea was reinforced by positive evidence from vapor phase chromatography (silicon oil on firebrick at 80°) that a small amount of water remained in the amine dried over sodium hydride but was absent in the liquid dried by long stirring over potassium hydroxide.

Drying by filtration through a 4-ft. column filled with calcium sulfate (Drierite) and potassium hydroxide was tested also. That the ratio varied 0.32–0.52 suggested that this method of drying was almost as good as the other two. A longer column probably would have given entirely satisfactory results.

In subsequent experiments the triethyl amine was dried over amylsodium.

1,2- Polymerizations. Some of the experiments in cyclohexane which resulted in 1,2- polymerization are recorded in Table II. As the proportion of sodium hydroxide increased (column 3) the yield per milliequivalent of amylsodium generally decreased (column 6) while the viscosity (DSV in column 7) correspondingly increased. The infrared ratio also increased a little. Diethylsodamide behaved a little differently. The yield, viscosity, and infrared ratio all tended to decrease as the proportion of diethylsodamide increased. Also the yield per milliequivalent in the presence of diethylsodamide seemed a little higher than with the corresponding amount of sodium hydroxide.

Table III shows 1,2- polymerization in triethyl amine. The yields and viscosities were considerably lowered in this medium. The tendency to form gel was also greater. The results discourage the idea that solution of the reagent was much of a factor. The yield was decreased rather than increased. In this medium diethylsodamide increased slightly the yield per milliequivalent.

1,4- Polymerizations. The most significant results have been presented already in the graphs. Table IV records, however, the yields and other information in triethyl amine as the medium. The yields per milliequivalent were much

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[12] A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, 20, 839 (1955).

TABLE II

1,2- POLYMERIZATION OF BUTADIENE IN CYCLOHEXANE BY AMYLSODIUM IN THE PRESENCE OF SODIUM HYDROXIDE OR DIETHYLSODAMIDE

RNa,[a] Me.	Assoc. Salt[b] Type	Assoc. Salt[b] Me.	Yield,[c] G.	Yield,[c] %	Yield,[c] G./Me.	DSV	Gel, %	I.R.[d] Ratios
5.1	N		18.0[e]	93	3.6	0.60	0	0.32
5.3	N		18.2[f]	93	3.4	0.62	0	0.30
5.1	N		15.4[g]	79	3.0	0.45	0	0.33
5.1	N		10.0[h]	51	2.0			0.30
5.1	N		0.1[i]	1	.1			0.52
4.0	H	111	9.2	47	2.3	0.50	0.3	0.34
3.2	H	167	6.5	33	2.0	0.57	1.6	0.37
2.9	H	222	7.7	39	2.6	0.70	0.8	0.33
2.7	H	250	5.5	28	2.0	0.59	6.0	0.39
2.4	H	278	4.4	22	1.8	0.95	0	0.44
1.6	H	333	0.6	3	0.4	1.20	3.3	0.56
4.5	A	67	12.5	64	2.8	0.51	0	0.37
3.9	A	150	11.6	60	3.0	0.64	0	0.34
3.8	A	205	11.3	58	3.0	0.30	0	0.29
3.1	A	273	8.3	43	2.7	0.28	0.1	0.30
2.7	A	342	6.8	35	2.5	0.19	0.1	0.30
1.9	A	411	4.5	23	2.4	0.18	0.1	0.29

[a] R signifies amyl. [b] N, H, and A are abbreviations for none, hydroxide and amide and signify, respectively, no other salt, sodium hydroxide and diethylsodamide. The milliequivalents listed for these added salts is the amount added to the preparation of amylsodium from 500 me, of amyl chloride and 1 g.-atom of sodium metal. [c] Yield after 1 hr. unless otherwise specified. [d] Ratio of *trans*-1,4- to -1,2-structures as determined by infrared measurements. [e,f,g,h,i] represent respectively 4, 24, 2, $^1/_3$, and $^1/_6$ hr. reaction time. The last named experiment was done in order to demonstrate that a yield of 1% or less was not responsible for IR ratios greater than 1.

TABLE III

1,2-POLYMERIZATION OF BUTADIENE IN TRIETHYL AMINE BY AMYLSODIUM WITH AND WITHOUT DIETHYLSODAMIDE

RNa,[a] Me.	Amide,[b] Me.	Yield[c] G.	Yield[c] %	Yield[c] G./me.	DSV	Gel, %	IR Ratio
5.1	0	0.1[d]	0.7	0.03	2.1	39	0.52
5.1	0	2.2[e]	11.2	0.42	0.2	18	0.35
5.3	0	5.7[f]	29.1	1.08	0.7	23	0.38
5.3	0	2.7	14	0.52	0.2		0.31
3.0	0	2.6	13	0.87	0.1		0.40
4.4	67	4.8	25	1.1	0.2		0.39
3.6	150	4.0	20	1.1	0.2		0.41
3.7	205	3.8	20	1.2	0.2	1	0.39
2.2	273	3.0	15	1.4	0.2	6	0.41
1.5	342	2.5	13	1.7	0.2	11	0.38
1.4	411	1.0	5	0.7	0.21	14	0.36

[a] R signifies amyl. [b] This column records the milliequivalents of diethyl amine added to the preparation of amylsodium. [c] Yield after 1 hr. polymerization unless otherwise specified. [d] The reaction time was four hours and the triethyl amine was dried by passage through a column filled with potassium hydroxide and Drierite. [e] The reaction time was 2 hr. and the triethyl amine was dried by high-speed stirring with potassium hydroxide. [f] The reaction time was 24 hr.

TABLE IV

EFFECT OF AMOUNT OF REAGENT IN POLYMERIZATION OF BUTADIENE IN TRIETHYL AMINE

Molal ratio, NaOH/RNa		0.95		1.15		1.46	
Reagent	Ml.	10	25	10	25	10	25
	Me.	2.9	7.3	2.7	6.8	2.4	6.0
Yield	G.	0.05	0.07	0.04	0.09	0.03	0.13
	%	0.3	0.5	0.2	0.5	0.2	0.7
	G./me.	0.02	0.02	0.01	0.03	0.01	0.05
DSV		3.2	2.4	2.9	2.6	2.7	2.9
Gel	%	6	44	8	73	3	89
I.R. ratio		1.31	1.05	1.31	1.25	1.29	1.40

lower than in the 1,2- polymerizations recorded in Table III but this feature is probably an illusion. Actually, kernels of 1,4- polymer were formed within 5 min. They were insoluble and enclosed the reagent, thereby shutting off 1,4- and also 1,2- polymerization. By contrast, the product from 1,2-polymerization (Table III) was soluble and generally free from gel; hence that reagent was free to continue its action. The low conversion of butadiene by 1,4- polymerization could have been increased by the use of more reagent as shown by comparison of the yields with 25 ml. and 10 ml. of reagent, but little would be gained thereby. A better reagent and its more efficient use would have to be developed, and the final result would probably be no better than is achieved by the present alfin catalyst.

Acknowledgment. The authors are indebted to Elizabeth Driscoll Ward for the measurements of viscosity and to Prof. N. A. Nelson for the infrared values.

CAMBRIDGE 39, MASS.

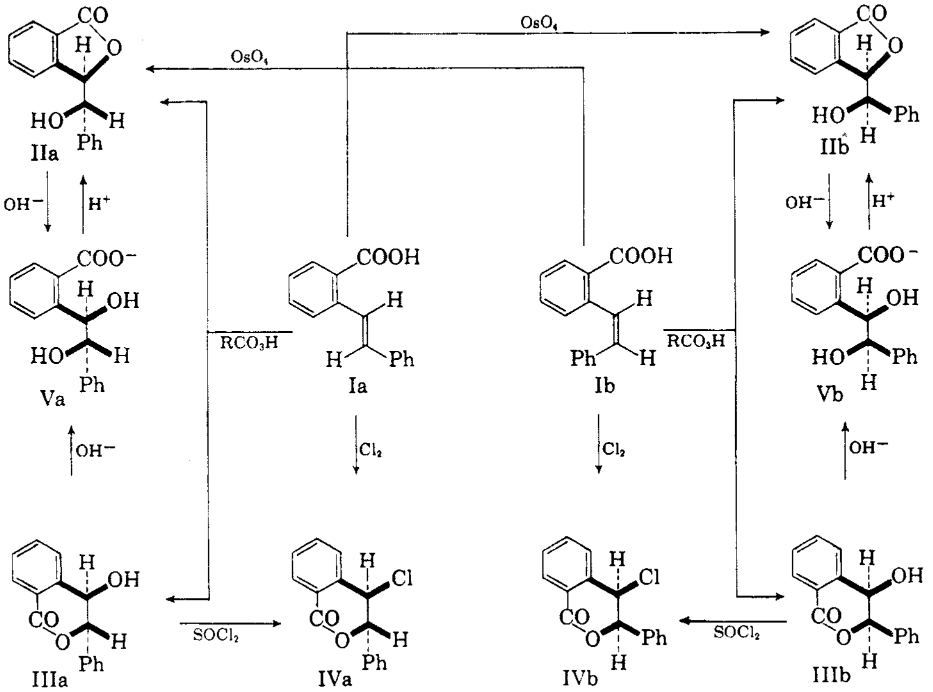
[CONTRIBUTION FROM THE INSTITUTE OF PHARMACEUTICAL CHEMISTRY OF THE UNIVERSITY OF PISA]

The Reaction of *cis-* and *trans-*Stilbene-2-carboxylic Acids with Peroxyacids[1]

GIANCARLO BERTI

Received January 5, 1959

The reaction of derivatives of *o*-vinylbenzoic acid with organic peroxyacids does not lead to the corresponding epoxides, hydroxylactones being the main products. The stereochemistry of this reaction was investigated, using the *cis-* and *trans-* forms of stilbene-2-carboxylic acid. The products were either the diastereomeric racemates of 3-phenyl-4-hydroxy-3,4-dihydroisocoumarin, or those of 3-(α-hydroxybenzyl)phthalide, higher temperatures or the presence of stronger acids favoring the formation of the former. A complete stereospecificity was observed, the products having the configurations to be expected from a *trans-* addition to the ethylenic double bond of a hydroxyl and of the carboxyl group. The possible mechanisms are discussed.



In continuation of earlier work on the formation of lactones from unsaturated acids, the reaction of *trans-* and *cis-*stilbene-2-carboxylic acid (Ia and Ib) with organic peroxyacids was investigated. When the acids Ia and Ib were treated with peroxyphthalic acid, no evidence was found for the formation of the corresponding epoxides, and the only identified products were two isomeric lactones, $C_{15}H_{12}O_3$, which were not identical with the diastereomeric 3-(α-hydroxybenzyl)phthalides (IIa and IIb), previously prepared by a different method,[2] but were transformed into them by a treatment with alkali, followed by one with acid. Such behavior led to the identification of the lactones as the two racemates of 3-phenyl-4-hydroxy-3,4-dihydroisocoumarin (IIIa and IIIb), whose rings were opened during the treatment with alkali to give the salts Va and Vb, which under acidic conditions were transformed into the more stable γ-lactones (IIa and IIb). A further proof was given by the fact that thionyl chloride transformed the two lactones into the compounds IVa and IVb,

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[1] Presented in part at the 16th International Congress of Pure and Applied Chemistry, Paris, 1957.

[2] G. Berti, *Tetrahedron*, **4**, 393 (1958).