[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION[1]]

The Preparation of Some Mono- and Dialkyl Pinates from Pinic Acid[2]

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Received April 7, 1959

Half saponification of diethyl pinate has been reported by Guha and Rao to involve the acetate moiety. This reaction has been used for the preparation of a number of half esters, *viz.* 2,2-dimethyl-3-(alkoxycarbonyl) cyclobutaneacetic acids when the alkyl was ethyl, *n*-butyl, 2-ethylhexyl, and hydronopyl. Direct esterification of pinic acid with an equimolar amount of ethyl, *n*-butyl, 2-ethylhexyl, and hydronopyl alcohols gave in addition to 10 mol. % each of diester and pinic acid, the corresponding alkyl 2,2-dimethyl-3-carboxycyclobutaneacetates. Conversion of each of the half esters, to mixed esters and half saponification gave essentially the pure free acetic acid form of monoester. Similarly, direct esterification was proved to yield only the 3-carboxycyclobutane form.

A program in this laboratory involving the preparation of a number of vinyl esters for use as comonomers for internal plasticization studies of polyvinyl chloride[3] included the preparation of a number of vinyl alkyl pinates[4] derived from monoalkyl pinates. There are no literature references alluding to higher monoalkyl pinates and mixed esters. It has been found that either half ester of pinic acid can be prepared readily, one by half saponification of diesters and the other by direct monoesterification of the free acid. The pinic acid used in this work was obtained by the usual hypohalite oxidation of pinonic acid prepared by permanganate oxidation of commercial α-pinene. Although Guha and Rao,[5] to whom reference is made later, considered pinic acid thus prepared to be the *trans*- form, the recent assignment by Trave and Cignarella[6] of the *cis* structure to *dl*-pinic acid, m.p. 100–102°, appears to be correct. The corresponding optically active isomers, m.p. 78°, obtained in the same manner[7] must also have the *cis* configuration. The Trave *et al.* assignment is used in this paper.

Guha and Rao[5] prepared a liquid 2,2-dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid (amide m.p. 97°) by half saponification of diethyl pinate (presumably *cis*) but failed to record its optical rotation. They established the existence of the free acetic acid group in this particular ester and reported additional confirming evidence in another reference.[8]

In the work reported herein half saponification of diethyl pinate by the Guha and Rao procedure[5] resulted in two monoesters. One was a solid, m.p. 80–81°, which gave an amide, m.p. 74.8–75.6°. Acid hydrolysis of the ester and its amide gave *cis-dl*-pinic acid, m.p. 100–102°. The other was a liquid consisting of a mixture of monoesters. The amide from the liquid melted at 97° which on hydrolysis gave *cis-d*-pinic acid m.p. 78° described by Grandperrin. The solid half ester was obviously *cis-dl*-2,2-dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid. Furthermore, the principal component of the liquid half ester and the product of Guha and Rao must have been the *cis-d*-isomer of the ethoxycarbonyl derivative of pinic acid. It was concluded that the pinic acid used for the work reported herein was a mixture of *cis-d* and *cis-dl* isomers.

Both the *cis-d-* and the *cis-dl*-2,2-dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acids had sharp, moderate to strong absorbances at 7.5 microns in the infrared. This same band is present in *cis-dl*-2,2-dimethyl-1,3-bis(alkoxycarbonyl)cyclobutanes and in *cis-d* and *cis-dl*-dialkyl pinates but absent in *cis-dl*-dialkyl 2,2-dimethyl-1,3-cyclobutanediacetates, and hence appears to be characteristic of the alkoxycarbonylcyclobutane group.

Direct esterification of pinic acid with one mole of ethanol using *p*-toluenesulfonic acid as a catalyst gave a half ester which did not absorb in the infrared at 7.5 microns and could not be induced to crystallize. The amides from a number of amines were all liquids. It was concluded this reaction resulted in the formation of ethyl *cis-d-* and *cis-dl*-2,2-dimethyl-3-(carboxy)cyclobutaneacetate with little or none of the alkoxycarbonyl form present in the mixture.

The presence of the characteristic absorbance at 7.5 microns in the infrared in a number of half esters prepared by half saponification of higher di- and mixed esters and absence of the absorbance in a number of monoesters prepared by direct monoesterification with higher alcohols demonstrates that the selectivity in these reactions observed for the ethyl esters also holds for higher esters. Furthermore, when mixed esters were subjected to

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Presented at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 13–18, 1959.

[3] In cooperation with Dr. C. S. Marvel, University of Illinois, under contract with the U. S. Department of Agriculture.

[4] J. B. Lewis and G. W. Hedrick, *J. Org. Chem.*, in press.

[5] P. C. Guha and P. L. N. Rao, *Ber.*, **71**, 1591 (1938).

[6] R. Trave and G. Cignarella, *Rend. ist. lombardi sci.*, **91**, 329 (1957); *Chem. Abstr.*, **52**, 11782 (1958).

[7] M. Grandperrin, *Ann. chim.*, **6**, 5 (1936).

[8] P. C. Guha and P. L. N. Rao, *J. Ind. Chem. Soc.*, **20**, 97 (1943).

half saponification the monoester obtained was always the alkoxycarbonyl derivative. Thus, ethyl *cis*-2,2-dimethyl-3-(*n*-butoxycarbonyl)cyclobutaneacetate on half saponification gave *cis*-2,2-dimethyl-3-(*n*-butoxycarbonyl)cyclobutaneacetic acid. This was true when the mixed ester was prepared from ethyl *cis*-2,2-dimethyl-3-(chlorocarbonyl)cyclobutaneacetate by reacting with *n*-butanol or obtained by reduction of vinyl *cis*-2,2-dimethyl-3-(*n*-butoxycarbonyl)cyclobutaneacetate.[4]

The lability of the alkyl group in the acetate form of the half ester led to ester interchange and formation of symmetrical as well as mixed diesters during direct esterification using an acid catalyst. Little or no ester interchange occurred with the alkoxycarbonyl half ester under the same conditions. Pure mixed esters were readily prepared from the alkyl acetate forms by way of the acid chloride.

EXPERIMENTAL

2,2-Dimethyl-3-(carboxy)cyclobutaneacetic acid (pinic acid). Crude pinic acid was prepared by hypochlorite oxidation of pinonic acid, $[\alpha]^{26}_{D}$ +29.1° (10% acetone) obtained from α-pinene $[\alpha]^{20}_{D}$ +23.1° (1 dm.) in the usual manner.[9] Esterification of the crude product according to Wielicki, *et al.*[10] and distillation yielded good quality *cis*-diethyl pinate, $[\alpha]^{25}_{D}$ 0.0 (8%, acetone), +2.2 (1 dm.).

For the preparation of pinic acid, acid hydrolysis was superior to alkaline saponification which was slow and often incomplete. Diethyl pinate, 484.6 g. (2 mol.) was dissolved in 420 g. glacial acetic acid (7 mol.). Aqueous 6*N* sulfuric acid, 500 ml., was added and ethyl acetate azeotrope (8.5% water) was distilled, b.p. 71°, through a 24-in. Vigreux column. Residual acetic acid was removed by steam distillation or by washing with water. Ninety per cent yields of crude pinic acid, neut. equiv. 94 to 96, were obtained by ether or benzene extraction, drying the extract with sodium sulfate and stripping the solvent *in vacuo*. Pure acid, neut. equiv. 93 to 93.5 was obtained by distillation of the crude acid, b.p. 163–165° (0.2 mm.).

Monoalkyl pinates by half saponification. 2,2-Dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid. Diethyl pinate, 800 g. (3.3 mol.), was dissolved in 1 l. of 95% ethanol. To this a solution consisting of 132 g. (3.3 mol.) sodium hydroxide dissolved in 132 ml. water was slowly added while stirring. The reaction mass warmed to about 70° and the *p*H changed from about 14 initially to between 7 and 8 at the end of the reaction. The ethanol was removed under reduced pressure and the residue was diluted with 1 to 2 l. water. Extraction with ether gave 80 g. (10 mol. %) of diester.

The monoester and pinic acid were recovered by acidification and ether extraction of the aqueous layer in the usual manner. Vacuum distillation of the dried extract after removal of solvent gave 656 g. (80 mol. %) of colorless monoester and 62 g. (10 mol. %) pinic acid, b.p. 163–165° (0.2 mm.).

On standing, the monoester partially solidified and the solid and liquid portions were separated by crystallization first from hexane and then from methyl ethyl ketone–hexane mixture (1:1). Treatment of the solid product, neut. equiv. 214.3, saponification equivalent 107.1 $[\alpha]^{26}_{D}$ 0.0 (10% acetone), m.p. 80–81°, with thionyl chloride and liquid ammonia in ether yielded an amide, m.p. 75–76°.

Anal. Calcd. for $C_{11}H_{19}O_3N$: N, 6.57. Found: N, 6.62.

Acid hydrolysis of the monoester and its amide using acetic acid–sulfuric acid gave *cis-dl*-pinic acid, m.p. 100–102°. The solid *cis-dl*-2,2-dimethyl-3-(ethoxycarbonyl)-cyclobutaneacetic acid was further characterized by reaction of its acid chloride with ethylene diamine to give an amide, m.p. 166–168°.

Anal. Calcd. for $C_{24}H_{40}O_6N_2$: N, 6.23. Found: N, 6.29.

Treatment of the liquid portion with thionyl chloride yielded an acid chloride, b.p. 87° (1 mm.) in 98% yield, from which an amide, m.p. 97°, $[\alpha]^{26}_{D}$ −8.1 (10% acetone) was obtained.

Anal. Calcd. for $C_{11}H_{19}O_3N$: N, 6.57. Found: N, 6.71.

This same amide was obtained when the crude monoester was converted to the amide and hence, appears to be identical with that reported by Guha and Rao.[5] Acid hydrolysis of this amide gave *cis-d*-pinic acid, m.p. 78°. The infrared (spectra of the two recovered pinic acids were identical with each other and with that of authentic *cis-dl*-pinic acid.

Higher monoalkyl pinates by half saponification. A number of higher monoalkyl pinates, 2,2-dimethyl-3-(alkoxycarbonyl)cyclobutaneacetic acids, Table I, were prepared similarly by half saponification of an appropriate symmetrical or mixed diester, *e.g.*, *n*-butyl or ethyl 2,2-dimethyl-3-(*n*-butoxycarbonyl)cyclobutaneacetate. The extent of saponification and yield was independent of the ester used. All these alkoxycarbonylcyclobutaneacetic acids had a sharp, moderate to strong absorbance in the infrared at 7.5 microns[11] which was attributed to the alkoxycarbonyl group.

Direct esterification of pinic acid. Monoethyl, *n*-butyl, 2-ethylhexyl, and hydronopyl[12] 2,2-dimethyl-3-(carboxy)-cyclobutaneacetates were prepared by refluxing 186 g. (1 mol.) of pinic acid and 1 mol. of the alcohol in 480 ml. benzene containing 6 g. *p*-toluene sulfonic acid. When all the water from the reaction had been removed azeotropically and the acid number indicated the reaction was complete, the mass was washed with water to remove the catalyst. The batch was diluted with water and made alkaline by adding approximately 1*N* sodium hydroxide buffered with sodium carbonate, the pinic acid, monoester, and diester separated. The yields were diester 10, monoester 80, and pinic acid 10 mol. %.

The properties and data obtained from characterization of the pinates are tabulated in Table I. None of these esters absorbed in the infrared at 7.5 microns as did the alkoxycarbonyl derivatives.

For comparison of this type ester with the alkoxycarbonylcyclobutaneacetic acids, ethyl 2,2-dimethyl-3-(carboxy)-cyclobutaneacetate was studied further. It was a liquid. The amide prepared by way of the acid chloride was a liquid, b.p. 154° (0.3 mm.), n^{20}_{D} 1.4817, d^{20} 1.0738.

Anal. Calcd. for $C_{11}H_{19}O_3N$: N, 6.57. Found: N, 6.57.

Similarly, amides prepared from *p*-nitroaniline, *p*-aminobenzoic acid, and ethylenediamine were all liquids. The corresponding amides of 2,2-dimethyl-3-(ethoxycarbonyl)-cyclobutaneacetic acid were all solids. These were not characterized.

Symmetrical and mixed dialkyl pinates. A number of dialkyl pinates were made for use in saponification studies. These were prepared by direct esterification, reduction of vinyl alkyl esters,[3] transesterification, and through use of the acid chlorides of some monoalkyl esters, Table II.

Mixed esters by reaction of monoalkyl pinates. Ethyl 2,2-dimethyl-3-(alkoxycarbonyl)cyclobutaneacetates. Ethyl 2,2-dimethyl-3-(carboxy)cyclobutaneacetate, 125 g. (0.58 mol.), was dissolved in 120 ml. benzene with one equivalent of 2-

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(9) V. M. Loeblich, F. C. Magne, and R. R. Mod, *Ind. Eng. Chem.*, **47**, 855 (1955).

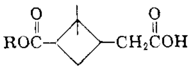
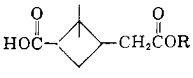
(10) E. A. Wielicki, C. J. Boone, R. D. Evans, M. R. Lytton, H. B. Summers, Jr., and G. W. Hedrick, *J. Polymer Sci.*, in press.

(11) Two per cent carbon tetrachloride solution, Perkin Elmer Infrared Spectrometer, Model 21, sodium chloride optics.

(12) J. P. Bain, *J. Am. Chem. Soc.*, **68**, 638 (1946).

TABLE I

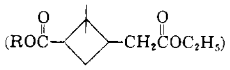
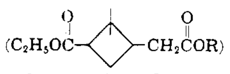
MONOALKYL PINATES

			Composition, %			Neutral Equivalent		Saponification Equivalent		Refractive Index,	Density,
	B.P.	Mm./ Hg	a[a]	b[a]	c[a]	Calcd.	Found	Calcd.[b]	Found	n_D^{20}	d^{20}
Acetic Acid Form											
											
Ethyl	128	0.2		100		214.3	214.3	107.1	107.1	1.4569	1.0736
n-Butyl	142	0.25	2.4	97.6	0	242.3	233.2	120.2	120.1	1.4588	1.0407
2-Ethylhexyl	171	0.15	0	90.0	10.0	298.4	331.0	155.3	154.8	1.4554	.9901
Hydronopyl	202–208	0.45	0.8	99.2	0	336.5	330.3	166.8	166.1	1.4907	1.0572
3-Carboxycyclobutane Form											
											
Ethyl	125	0.1	0	100	0	214.3	214.3	107.1	107.1	1.4583	1.0706
n-Butyl	139.5–144	0.3	0	99.5	0.5	242.3	243.6	121.3	120.2	1.4590	1.0462
2-Ethylhexyl	174	0.17	11.6	88.4	0	298.4	237.4	139.4	139.1	1.4569	1.0090
Hydronopyl	199	0.1	7.2	92.8	0	336.5	283	159.0	158.2	1.4899	1.0652

[a] a. Pinic acid. b. Monoester. c. Diester. [b] Theoretical saponification equivalent calcd. from neutral equivalent found.

TABLE II

DIALKYL PINATES

			Refractive		Saponification Equivalent			Analyses			
								Calcd.		Found	
	B.P.	Mm./ Hg	Index, n_D^{20}	Density, d^{20}	Calcd.	Found	Formula	C	H	C	H
Diethyl	108	1.0	1.4457	1.0123							
Di-*n*-butyl	136	0.4	1.4505	0.9817	149.2	148.4	$C_{17}H_{30}O_4$	68.42	10.13	67.52	9.91
Di-2-ethylhexyl	188	0.12	1.4574	0.9394	205.3	201.0	$C_{25}H_{46}O_4$	73.12	11.29	72.80	11.03
Dihydronopyl	242	0.15	1.4966	1.0241	243.4	244.7	$C_{31}H_{50}O_4$	76.50	10.36	76.27	10.44
											
Ethyl Acetates											
n-Butyl	116	0.3	1.4470	0.9864	135.2	133.2	$C_{15}H_{26}O_4$	66.63	9.69	66.73	9.64
2-Ethylhexyl	151	0.3	1.4519	0.9610	163.2	162.4	$C_{19}H_{34}O_4$	69.90	10.50	69.93	10.48
Hydronopyl	181	0.1	1.4794	1.0201	182.3	184.0	$C_{22}H_{36}O_4$	72.49	9.96	72.71	10.17
											
Ethoxycarbonyl Esters											
n-Butyl	120	0.3	1.4468	0.9868	135.2	134.8	$C_{15}H_{26}O_4$	66.63	9.69	66.43	9.74
2-Ethylhexyl	148	0.3	1.4516	0.9612	163.2	162.2	$C_{19}H_{34}O_4$	69.90	10.50	70.01	10.30
Hydronopyl	182	0.1	1.4796	1.0192	182.8	185.8	$C_{22}H_{36}O_4$	72.49	9.96	72.67	9.75

ethylhexanol or hydronopyl alcohol and 8 g. *p*-toluene sulfonic acid. The water from the reaction was removed azeotropically and the product isolated by the usual procedure. Distillation of the 2-ethylhexanol ester gave three fractions; 52.3 g., b.p. 79–142° (0.3 mm.); 55.0 g., b.p. 132–142° (0.1 mm.); and 61.9 g., b.p. 142–188° (0.1 mm.). These fractions were redistilled and identified from boiling point and refractive index as diethyl pinate, ethyl 2-ethylhexyl pinate, and di-2-ethylhexyl pinate. With hydronopyl alcohol three fractions were taken: 27.5 g., b.p. 99–172° (0.4 mm.); 88.5 g., b.p. 172–186° (0.1 mm.); and 68.2 g., b.p. 186–250° (0.2 mm.). The distillates were characterized as above and found to be chiefly diethyl pinate, ethyl hydronopyl pinate, and dihydronopyl pinate.

Alkyl 2,2-dimethyl-3-(ethoxycarbonyl)cyclobutaneacetates. 2,2-Dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid, 78.7 g. (0.367 mol.) was esterified with hydronopyl alcohol, 61.8 g. (0.367 mol.) in benzene, 200 ml., with 1 g. *p*-toluene sulfonic acid as a catalyst. By distillation of the ester two fractions were taken: 3.4 g., b.p. 76–164° (0.2 mm.) and a main fraction, 112 g., b.p. 181° (0.1 mm.), with 5 g. still residue. There was no more than a few drops of diethyl pinate, if any, in the forecut.

In another run using a five-fold increase in catalyst there was evidence of only slightly more diethyl pinate as a result of change in catalyst concentration. It was apparent that the alkoxycarbonyl form of monoester was much less susceptible to transesterification than the other form under the conditions of the reaction.

Ethyl 2,2-dimethyl-3-(alkoxycarbonyl)cyclobutaneacetates by use of acid chlorides. *n*-Butyl and hydronopyl alcohols were reacted with ethyl 2,2-dimethyl-3-(chlorocarbonyl)cyclobutaneacetate prepared with thionyl chloride by the Guha *et. al.* procedure.[5] Typically hydronopyl alcohol, 168 g.

(1 mol.) was dissolved in 500 ml. benzene in which 56 g. soda ash was kept suspended by agitation. The acid chloride, 232 g. (1 mol.) was added dropwise while holding the reaction mass at reflux temperature. After washing with water and stripping the solvent, the product was distilled. There was a forecut, 12 g., b.p. 103–178° (0.25 mm.) and the product, 266 g., 71% yield, b.p. 180–182° (0.1 mm.), with 32 g. still residue. An 86% yield was obtained with *n*-butyl alcohol, b.p. 116° (0.3 mm.).

Characterization of half esters by half saponification of mixed esters. Deviations from theoretical values for neutral and saponification equivalents of the various half esters and diesters were used in calculating purity and characterization of the esters. These results, however, gave no indication of the composition with respect to structural differences. This type of difference was established by half saponification of some of the mixed esters.

Half saponification of the butyl and hydronopyl ethyl pinates (ethyl acetate forms) from the above acid chloride reactions gave good yields of the corresponding alkoxycarbonyl half esters. Although some monoethyl pinate may have been present, the foreruns in the distillation (less than 10%) failed to crystallize when seeded with solid *cis-dl*-2,2-dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid.

Similarly, saponification of alkyl ethoxycarbonylcyclobutaneacetates resulted in no detectable amounts of the alkylcarbonyl type monoester. The half ester obtained was good quality *cis*-2,2-dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid.

Acknowledgments. The authors wish to express their appreciation to Messrs. G. S. Fisher and R. L. Kinney, Turpentine Investigations, Naval Stores Research Station, for infrared spectral analyses of the compounds reported in this paper and to Mr. L. E. Brown and Mrs. A. F. Cuculla, Southern Utilization Research and Development Division, New Orleans, Louisiana, for elemental analyses.

OLUSTEE, FLA

[CONTRIBUTION FROM DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, SCHOOL OF PHARMACY, HEBREW UNIVERSITY]

Organic Carbonates. IV.[1a,b,c] Factors Affecting Formation of Homologous Cyclic Carbonates

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Received April 9, 1959

The preparation and properties of a number of branched 1,2-, 1,3-, and 1,4-cyclic carbonates are described. The formation of homologous cyclic carbonates by reaction of diols with diethyl carbonate is described as a two-step mechanism, involving first the formation of a mono-ester and then cyclization with an accompanying elimination of ethanol. The effect of both substitution and chain length in homologous alkylene glycols upon their tendencies to yield monomeric cyclic carbonates is discussed.

In a previous communication[1c] we have described the effect of substitution in 1,3-propanediol carbonates upon their tendencies to undergo reversible polymerization. This paper is concerned with a similar study regarding the effect of both substitution and chain-length in 1,2-, 1,3-, and 1,4-diol upon their tendencies to form cyclic and/or polymeric carbonates.

In this study we employed two methods: (1) ester interchange between an appropriate diol and diethyl carbonate in the presence of catalytic amounts (2.5–5% mole) of dry sodium methoxide[1c]; (2) the reaction of phosgene with diols in the presence of antipyrine, according to the method of Ludwig and Piech.[3] In each method it was found that the nature and yields of the reaction products obtained are largely dependent upon reaction conditions and molecular structure of reactants. For example, in the transesterification of neopentylene glycol by means of diethyl carbonate, three distinct organic carbonates (II, III, and V) could be obtained, upon varying the molar ratio catalyst/reactants. Thus, in the presence of large amounts of dry sodium methoxide catalyst (5–10 mol. %), high yields of the cyclic carbonates (IIId) are obtained. Upon 10-fold decrease of the amount of catalyst (0.5–1.0 mol. %), the polymeric form (Vd) is obtained almost exclusively. Upon further decrease in the amount of catalyst (0.45 mol. %) a monoester (IId) is obtained along with Vd, but none of IIId. A more detailed study of this phenomenon will be given in a subsequent paper.

In the series of 1,3-propanediols, we observed that branching at carbon atoms 1, 2, and 3, favors the formation of the requisite cyclic esters, and at the same time it exerts a hindrance upon their tendencies to undergo a polymerization reaction. Thus, upon ester interchange between 1,3-butanediol (Ib) and 2,4-pentanediol (Ic) and diethyl carbonate, the corresponding 1,3-cyclic carbonates (IIb and IIc) were produced in 70–72% yields, whereas IIIa was obtained in 50% yield. Similarly, disubstitution at carbon atom 2, while it suppresses or even abolishes the tendency to polymerization, has, however, an enhancing effect toward the formation

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[1] (a) Part I, *Compt. rend.*, **245**, 2321 (1957); (b) Part II, *Bull. Research Council Israel*, **7A**, 42; (c) Part III, S. Sarel and L. A. Pohoryles, *J. Am. Chem. Soc.*, **80**, 4596 (1958).

[2] Formerly Shalom Israelashvili; to whom inquiries should be sent.

[3] B. J. Ludwig and E. C. Piech, *J. Am. Chem. Soc.*, **73**, 5779 (1951).