ϵ 30; $\lambda_{max}^{CHCl_3}$ 5.80 μ; R.D. (Fig. 1) in dioxane (*c* 0.107 on freshly prepared material): $[\phi]_{650}$ ±0°, $[\phi]_{589}$ +26°, $[\phi]_{465}$ +130°, $[\phi]_{425}$ +56°, $[\phi]_{300}$ +521°, $[\phi]_{270}$ −88°, $[\phi]_{260}$ ±0°.

6β-Bromo-5α-cholestan-3-one (XI).[27]—A sample of this compound kindly provided by Professor Shoppee had m.p. 180° after crystallization from acetone. Shoppee and Lack[27] report m.p. 155° for this compound. In a personal communication, Professor Shoppee suggested that these different m.p.'s arise from different polymorphic forms. In agreement, it was found that infrared spectra of the two forms were identical. 6β-Bromo-5α-cholestan-3-one had $\lambda_{max}^{CHCl_3}$ 282 mμ, ϵ 25; R.D. (Fig. 1) in dioxane (*c* 0.125): $[\phi]_{650}$ ±0°, $[\phi]_{589}$ −27°, $[\phi]_{323}$ −237°, $[\phi]_{310}$ −100°, $[\phi]_{260}$ 1113°, $[\phi]_{250}$ −987°; R.D. in methanol (*c* 0.100): $[\phi]_{650}$ −149°, $[\phi]_{589}$ −140°, $[\phi]_{300}$ −37°, $[\phi]_{255}$ −465°.

5α,6β-Dibromocholestan-3-one (VI).[19]—After crystallizing from cold ether this compound had m.p. 82–84° dec.; λ_{max}^{diox} 280 mμ, ϵ 150; $\lambda_{max}^{CHCl_3}$ 5.90 μ; R.D. (Fig. 2) in dioxane (*c* 0.096): $[\phi]_{650}$ −424°, $[\phi]_{589}$ −424°, $[\phi]_{307}$ −4134°, $[\phi]_{270}$ −794°, $[\phi]_{250}$ −1642°; R.D. in isoöctane (*c* 0.079): $[\phi]_{650}$ −256°, $[\phi]_{589}$ −248°, $[\phi]_{310}$ −3569°, $[\phi]_{265}$ −65°, $[\phi]_{250}$ −968°.

5α-Bromo-6β-chlorocholestan-3-one (VIII).[21]—After crystallizing from ether–methanol, this substance had m.p. 70° dec.; λ_{max}^{diox} 285 mμ, ϵ 50; $\lambda_{max}^{CHCl_3}$ 5.85 mμ; R.D. (Fig. 2) in dioxane (*c* 0.103): $[\phi]_{600}$ −255°, $[\phi]_{589}$ −255°, $[\phi]_{312}$ −2120°, $[\phi]_{277}$ −630°, $[\phi]_{260}$ −1360°.

Cholestan-3-one (I): m.p. 129°; λ_{max}^{diox} 287 mμ, ϵ 25; R.D. (Fig. 1) in dioxane (*c* 0.108): $[\phi]_{600}$ +170°, $[\phi]_{589}$ +170°, $[\phi]_{317}$ +2749°, $[\phi]_{275}$ −1972°, $[\phi]_{260}$ −1318°.

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

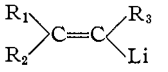
Effect of Solvent on the Steric Stability of Lithium Reagents[1]

BY DAVID Y. CURTIN AND WILLIAM J. KOEHL, JR.[2]

RECEIVED NOVEMBER 15, 1961

It has been found that solutions of *cis*-α-stilbenyllithium (*cis*-I) and of *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenylvinyllithium (*cis*- and *trans*-V) in hydrocarbon solvents have very much greater stereochemical stability than in diethyl ether. Tetrahydrofuran is still much more effective than ether in promoting the isomerization of *cis*- to *trans*-I. It has been found further that optically active *sec*-butyllithium in the absence of ether can be prepared and carbonated with at least 83% retention of configuration. Again the isomerization (racemization in this case) is greatly accelerated even by small amounts of added diethyl ether. It has been found that *t*-butyllithium can be conveniently prepared from lithium metal containing only 0.2% sodium if the surface is coated with copper powder before reaction.

It has been demonstrated previously[4] that the vinyllithium group can be formed and caused to react with a high degree of retention of steric configuration. The steric stability of a lithium compound with the structure A or B furthermore is known to be highly dependent on the nature of the R groups.[4–9] The present paper is concerned with another aspect of the loss of configuration of such compounds, the effect of solvent.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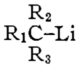


$$R_1\overset{R_2}{\underset{R_3}{C}}\text{–Li}$$

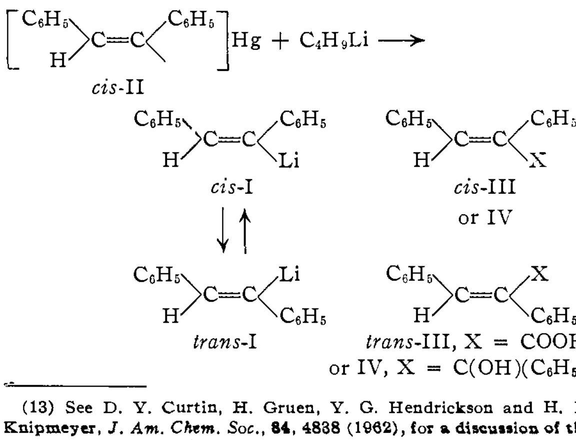
B

(R = alkyl or H)

Both the formation and reactions of lithium reagents have for many years been known to proceed much more slowly in hydrocarbon solvents than in solvents such as diethyl ether.[10]

The system chosen initially for study was the equilibration of *cis*- and *trans*-stilbenyllithium (*cis*- and *trans*-I).[11,12] These two isomers had been prepared by a lithium–bromine exchange from the corresponding bromides in benzene–ether at temperatures of −35° and below and react with no observable loss of configuration.[11] On the other hand, at higher temperatures or with sufficiently prolonged reaction times there was isomerization of the *cis* isomer to the *trans*, the equilibrium lying far toward the *trans* isomer.[12] The one-sided equilibrium, presumably due to the large unfavorable steric interaction of the two phenyl groups in the *cis* isomer[13] made the study of this equilibration particularly attractive.

The *cis*-α-stilbenyllithium (*cis*-I) was prepared from bis-*cis*-α-stilbenylmercury[12] (*cis*-II) by a lithium–mercury exchange in the appropriate solvent. This method, rather than the more conventional ones involving lithium metal or a lithium–halogen exchange with butyllithium, was chosen because of the slowness of such reactions in hydrocarbon solvents. The lithium reagent thus formed was then converted to the carboxylic acid(s) *cis*-



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[1] Taken from the Ph.D. Thesis of W. J. Koehl, Jr., submitted to the University of Illinois, 1960. The work was presented at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960; Abstracts, p. 52P. A part of the work has been published in preliminary form.[3]

[2] National Science Foundation Fellow, 1958–1960.

[3] D. Y. Curtin and W. J. Koehl, Jr., *Chemistry & Industry*, 262 (1960).

[4] See D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958), and references therein cited.

[5] R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 4842 (1950).

[6] R. L. Letsinger, *Angew. Chem.*, **70**, 151 (1958).

[7] D. E. Applequist and A. H. Peterson, *ibid.*, **83**, 862 (1961).

[8] H. M. Walborsky, unpublished results, quoted in the Communication to the Editor by H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **83**, 2595 (1961).

[9] D. Y. Curtin and J. W. Hausser, *ibid.*, **83**, 3474 (1961).

[10] See K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930), for example.

[11] D. Y. Curtin and E. E. Harris, *J. Am. Chem. Soc.*, **73**, 4519 (1951).

[12] A. N. Nesmeyanov, A. E. Borisov and N. A. Vol'kenau, *Izvest. Akad. Nauk (S.S.S.R.) Otdel. Khim. Nauk*, **992** (1954).

[13] See D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **84**, 4838 (1962), for a discussion of the phenyl–phenyl interaction in other systems.

(or *trans*)-III by carbonation or to the corresponding benzhydrol(s) *cis*- (or *trans*)-VI by treatment with benzophenone. The composition of the product mixtures was determined by ultraviolet spectrophotometry. The results are summarized in Table I.

TABLE I

ISOMERIZATION OF *cis*- TO *trans*-α-STILBENYLLITHIUM (I) AFTER 30 MINUTES

Solvent	Temp., °C.	Yield of product, %	% retention of configuration
3:1 ether–benzene	-54 ± 3	65	100^a
Tetrahydrofuran	-45 ± 4	73	1^b
1:1 ether–benzene	3–4	77	0^a
1:1 benzene–pentane	2–3	69	96^b
	2–3	23	100^b
	2–3	68	98^c
1:1 benzene–pentane with 0.54% ether	2–3	63	81^b
1:1 benzene–pentane with 1.08% ether	2–3	. .	76^b
	2–3	55	89^b
	2–3	78	78^c
	2–3	59	71^d
	2–3	65	77^e
Benzene	27 ± 1	49	29^b

[a] Product of carbonation showed no evidence of the isomeric acid. [b] Product of carbonation analyzed by ultraviolet spectrophotometry. [c] Products of benzophenone reaction with the ratio determined from the ultraviolet spectrum. [d] Product of carbonation of lithium reagent made from lithium containing 2.3% sodium. [e] Product from lithium reagent prepared from lithium containing 0.005% sodium.

It may be seen that in ether–benzene (a solvent employed because of the insolubility of the mercury compound in ether alone) at −54° there was retention of configuration in agreement with previous work.[11,12] In tetrahydrofuran, a solvent well known to be unusually effective in promoting the formation of Grignard reagents[14] at a temperature (−45°) which was shown previously[11,12] to lead to retention of configuration, there was only 1% retention, 99% of the carbonation product being the *trans*-acid *trans*-III. Similarly, raising the temperature of the reactions in benzene–ether (1:1) to 2–3° led to complete loss of configuration and formation of the *trans* products. When the ether was replaced by pentane in reactions at 2–3°, essentially complete retention of configuration (96–100%) was observed. In other words, at this temperature replacement of the pentane by ether changes the steric course of the reaction from one of complete retention of configuration to complete *cis*–*trans* "inversion." In fact, in benzene solution there was 29% retention of configuration even at 27° when no ether was present. The presence of even small amounts of ether have a significant effect as shown by the data in Table I. Even as little as 0.54–1.08% ether in 1:1 benzene–pentane lowers the retention of configuration from 98% to 78%. Since the lithium metal employed was known to contain 0.2% of sodium the effect of sodium on the configurational stability of the lithium reagent *cis*-I was investigated. In addition to the lithium with 0.2% sodium, lithium containing 0.005% and 2.3% sodium was used for reactions with 1.08% ether in benzene–pentane. The percentage retention of configuration was found to be unaffected by these changes in sodium content.

Before any interpretation of these data can be made it is necessary to decide at what point the solvent effect occurs. Thus, in the "slow" solvents, if the exchange rate is markedly slower it might be argued that the *cis*-lithium compound *cis*-I is being formed later than in the "fast" solvents and therefore is being subjected to the isomerizing conditions for a shorter period of time. That this is not a major factor to be considered is shown by the fact that a reaction carried out in benzene–pentane at 2–3° like those in Table I except that the time was shortened from 30 to 8 minutes gave a 63% yield as compared with the 69% yield obtained with the 30-minute run. Thus at least 63% of the lithium compound was present for 75% of the reaction time and the increased configurational stability in the less polar solvents must be due primarily to a decrease in the rate of isomerization. The further possiblity that the increased isomerization in the more polar solvent is due to the incursion of non-stereospecific exchange reactions in these solvents is unlikely because of the retention of configuration at lower temperatures in ether–benzene. A more direct piece of evidence is provided by the report[12] that at a given temperature the fraction of isomerization increases with increasing time. In the present study it was found that an increase of the time in a reaction in 1:1 benzene–pentane containing 1.08% ether from 30 minutes to 60 minutes resulted in a 61% yield of acids *cis*- and *trans*-III, the composition of which showed that the fraction of retention of configuration had dropped from 76 to 48%.

Similar effects of even small amounts of diethyl ether were found in a study of the equilibration of *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenylvinyllithium (*cis*- and *trans*-V). Previous work[15] had shown that these lithium compounds are configurationally stable for short times at temperatures of −20° and below but that extensive equilibration occurred at +20°. In the present work the lithium compounds *cis*- and *trans*-V were prepared from the reaction of the corresponding *cis*- and *trans*-mercury compounds[12] *cis*- and *trans*-VI by an exchange with butyllithium. The lithium reagents were then treated either with carbon dioxide or with methanol to give a mixture of *cis*- and *trans*-carboxylic acids (*cis*- and *trans*-VII) or of *cis*- and *trans*-olefins (*cis*- and *trans*-VIII) which was analyzed by infrared analysis. The results, presented in Table II, are in good qualitative agreement with those obtained with the lithium reagent I. At −50°, even with much ether present there was substantially complete retention of configuration. At 22°, however, in a solvent with much ether there was extensive (and perhaps complete) equilibration. In benzene or cyclohexane at 20° without ether there was again nearly complete retention of configuration and the addition of even 0.68% of ether lowered the % retention very

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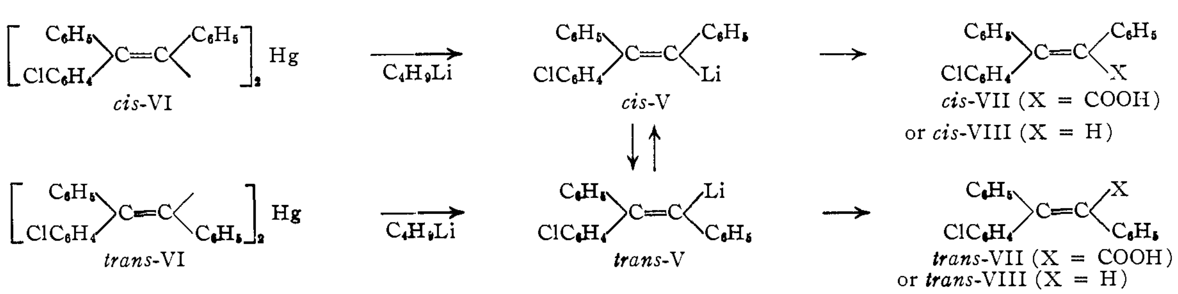
(14) See H. Normant, "Advances in Organic Chemistry: Methods and Results," Vol. 2, Edited by R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, Inc., New York, N. Y., 1960, p. 5 ff.

(15) D. Y. Curtin, H. W. Johnson, Jr., and E. C. Steiner, *J. Am. Chem. Soc.*, **77**, 4566 (1955).



appreciably. It may be noted that in benzene (without ether) the isomerization was slowed to such an extent that even after 7 days (10,080 minutes) it had apparently not reached equilibrium.

TABLE II

Configuration of starting material VI	Solvent	Time, min.	Temp., °C.	% *cis* product
cis	3:1 ether–benzene	30	−50 ± 5	97[a,b]
cis	1:1 ether–benzene	30	22 ± 1	47[a,b]
cis	Benzene	30	20 ± 1	94[a,b]
cis	Cyclohexane	60	22 ± 1	92[a,c]
cis	Benzene + 0.68% ether	30	25 ± 2	85[a,b]
cis	Benzene + 0.68% ether	60	25 ± 2	65[a,b]
trans	Benzene	10,080	28 ± 2	32[a,c]
trans	Benzene	10,080	28 ± 2	36[a,b]
cis	Benzene	60	80°	51[a,c]

[a] The estimated reliability is ±5%. [b] Lithium reagent carbonated. [c] Lithium reagent treated with methanol.

The configurational assignments of the lithium reagents I and VI requires some comment. The exchange reactions have been formulated here as proceding with retention of configuration. This assumption is supported by the internal consistency of a large body of evidence[16] and no one has ever seriously proposed a mechanism with inversion of configuration at the olefinic double bond for a replacement of this type. The infrared spectra of the propenyllithiums have been used to assign configurations to these substances[16] and provide direct evidence, at least for this system, that replacements of the kind being considered here proceed with retention of configuration.

Optically Active *sec*-Butyllithium.—In a number of investigations in which lithium or magnesium is attached directly to an asymmetric carbon atom in an acyclic molecule, optical activity was completely lost.[17] It was found by Letsinger,[5] however, that by working for short times and at −70°, optically active 2-iodoöctane underwent a lithium–iodine exchange with the formation of a lithium reagent which when carbonated gave 2-methyloctanoic acid with about 20% retention of configuration. An attempt to carry out the exchange in petroleum ether alone had been unsuccessful so that the solvent employed was petroleum ether and diethyl ether in a ratio of about 17 to 1.

Our results on the effect of even minute amounts of ether on the configurational stability of vinyllithium compounds suggested the desirability of carrying out the preparation of an asymmetric lithium reagent in a non-polar solvent with ether totally absent. Because of the marked fall-off of the rate of lithium–iodine exchange under these conditions, an alternative method of obtaining the lithium compound was selected. Optically active *sec*-butylmercuric bromide ((−)-IX) had been reported previously[18,19,20] and it was converted to (−)-*sec*-butyl-(±)-*sec*-butylmercury-(−)(±)-X by treatment with *sec*-butyllithium. It has been shown by Jensen that a similar conversion with *sec*-butylmagnesium bromide and subsequent conversion of the bis compound (−)-(±)-X back to *sec*-butylmercuric bromide proceeds with the loss of just one-half of the optical activity, showing that these reactions proceed with complete retention of configuration. In the present work the (+)- or (−)-*sec*-butyl-(±)-*sec*-butylmercury employed was not completely resolved but contained also "racemic" *sec*-butylmercury.[21]

TABLE III

REACTION OF *dl*-2-OCTYLLITHIUM WITH DI-*sec*-BUTYLMERCURY FROM (+)- OR (−)-*sec*-BUTYLMERCURIC BROMIDE IN PENTANE FOLLOWED BY CARBONATION

Temp., °C.	Time, min.	Total yield of acids	Mole % 2-methylbutyric acid	R_2Hg $[\alpha]_D$	2-Methylbutyric acid $[\alpha]_D$	Retention, %
1	60	72	58.4	0°	.....	..
−60 ± 5	510	82	13	0	.....	..
− 8 ± 2	30	94	4.7[a]	−12.6	−2.84°	55
− 7 ± 2	30	89	10.4	− 3.4	−0.65	46
− 3 ± 2	60	91	31	− 8.9	−0.49	14
−40 + 5	240	39	24	+ 3.9	+1.33	83
− 8 ± 2	20			+ 3.2	+0.39	30
	45				+ .26	20
	90				+ .17	13
− 8 ± 2[b]	30	90	52	+ 0.89	.00	0

[a] The recovered di-*sec*-butylmercury (82%) had retained 98% of its activity. [b] Solvent for the exchange was pentane (94%) containing diethyl ether (6%).

The optically active di-*sec*-butylmercury was allowed to react with 2-octyllithium prepared from

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(16) See N. L. Allinger and R. B. Hermann, *J. Org. Chem.*, **26**, 1040 (1961), for a recent discussion of the problem and for references to previous work.

(17) See ref. 6 for a review of early work.

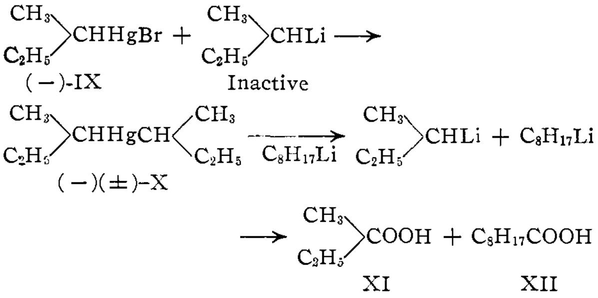
(18) H. B. Charman, E. D. Hughes and C. K. Ingold, *Chemistry & Industry*, 1517 (1958); *J. Chem. Soc.*, 2523 (1959).

(19) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner and J. A. Landgrebe, *J. Am. Chem. Soc.*, **81**, 1262 (1959); **82**, 2466 (1960).

(20) F. R. Jensen, *ibid.*, **82**, 2469 (1960).

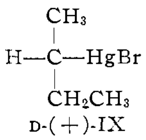
(21) It may be noted that (−)-*sec*-butyl-(+)-*sec*-butylmercury and (−)-*sec*-butyl-(−)-*sec*-butylmercury are diastereoisomers and therefore could complicate the stereochemical argument by being formed and reacting at different rates. However, the linear C–Hg–C geometry [L. Pauling, "The Nature of the Chemical Bond," Third Edition, Cornell University Press, 1960, p. 125] provides sufficient separation of the two alkyl groups so that to a good approximation they act independently (see Table III, note *a*).

dl-2-octyl chloride in pentane. Carbonation after 30 minutes gave a mixture of 2-methylbutyric (XI) and 2-methylcaprylic acid (XII) which were separated by distillation. Vapor chromatography of the 2-methylbutyric acid so obtained showed that it contained small amounts of 2-octanol and 2-methylcaprylic acid. It was further purified by extraction of an aqueous solution of its sodium salt with ether. The resulting 2-methylbutyric acid when subjected to vapor phase chromatography showed no evidence of the presence of any impurities. Specific rotations of the acid so obtained are reported in Table III.



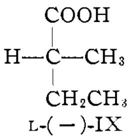
The data in Table III show that in the absence of diethyl ether the lithium–mercury exchange is rather slow at temperatures below 0° but that considerable retention of optical activity is observed. In the reaction, carried out for 240 minutes at −40°, in which the highest degree of retention was found, the conditions were a compromise between the slowness of the exchange on the one hand and the undesirability of prolonging the exposure of the activity *sec*-butyllithium to the reaction conditions unnecessarily on the other. In this case the amount of retention obtained was 83%. A set of runs at −8°, identical except for reaction time, showed that racemization was occurring in the solution at an appreciable rate. As was found with the vinyllithium reagents, the reaction described in the last line of Table III showed that the incorporation of 6% of diethyl ether into the medium led to complete loss of activity in 30 minutes. This is in agreement with Letsinger's[5] observation that a reaction allowed to warm to 0° over a period of 20 minutes gave completely racemized product.

The absolute configurations of *sec*-butylmercuric bromide[19] and 2-methylbutyric acid[22] have been shown to be



$$\begin{array}{c} CH_3 \\ | \\ H\text{—}C\text{—}HgBr \\ | \\ CH_2CH_3 \end{array}$$

D-(+)-IX



$$\begin{array}{c} COOH \\ | \\ H\text{—}C\text{—}CH_3 \\ | \\ CH_2CH_3 \end{array}$$

L-(−)-IX

The over-all steric course in the present exchange followed by carbonation is accordingly one of retention of configuration. It seems likely that the % retention of activity found in the experiments above is a minimum value since the sensitivity of the reaction to small amounts of ether suggests that part or all of the racemization might have been brought about by the products formed by reaction of the lithium reagents with traces of oxygen or by products present during the carbonation step. It seems likely that a better method of producing the lithium reagent, that is, one which is faster in non-polar solvents such as pentane, should lead to practical stereospecific syntheses with organolithium compounds.

It was hoped that by employing *t*-butyllithium as the exchange reagent in the reaction with active *sec*-butylmercury it might be possible to establish an equilibrium which was more favorable for the formation of the secondary lithium reagent. It was found, however, that the exchange was too slow with *t*-butyllithium to be practical, presumably due to a steric effect. For example, in pentane after 94 minutes the exchange with 2-butyllithium had occurred to a negligible extent, although in 1:1 pentane–ether at 3° the exchange had proceded to the extent of 73% after 24 minutes.

In the course of the work with *t*-butyllithium it was found that repeated attempts to prepare this reagent in pentane were unsuccessful. It has recently been reported[23] that this reaction proceeds readily only when the lithium metal employed for reaction with *t*-butyl chloride has a higher-than-normal sodium content. Before we became aware of these results an alternative method of preparing *t*-butyllithium in pentane was developed which might under certain circumstances be preferred and is therefore presented here. It was found that if lithium sheets were coated with copper powder before being cut into strips to be used for the reaction with the *t*-butyl chloride, a 38% yield could be obtained as shown by titration. It is not clear whether the effect of the copper is mechanical (exposing fresh lithium surface when it separates in solution) or chemical, but the method would have a practical advantage if the presence of sodium were undesirable for some reason

Discussion.—It is premature to discuss in detail the mechanism of racemization of *sec*-butyllithium and the isomerization of the vinyllithium reagents. Brown, Dickerhoof and Bafus[24] have provided strong evidence that ethyllithium is present in non-polar solvents almost entirely as an associated species, probably the hexamer, which together with the tetramer is one of the two species present in the vapor. Although the large effect of solvents like ether and tetrahydrofuran on the rate of isomerization (or racemization) suggests a mechanism in which ionization of the carbon–lithium bond is promoted by association of the lithium atoms with the oxygen atoms of the solvent, it is highly probable that the anion involved in such a process is not the simple vinyl or *sec*-butyl anion but is a complex ion containing a number of alkyl lithium units.

It is of interest that the polymerization of isoprene by butyllithium leads to very largely *cis*-1,4-product in hydrocarbon solvents but to *trans*-1,2-

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(22) J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

(23) M. Stiles and R. P. Mayer, *J. Am. Chem. Soc.*, **81**, 1510 (1959); J. B. Wright and E. S. Gutsell, *ibid.*, **81**, 5193 (1959); J. A. Beel, W. S. Koch, G. E. Tomasi, D. E. Hermansen and P. Fleetwood, *J. Org. Chem.*, **24**, 2036 (1959); C. W. Kamienski and D. L. Esmay, *ibid.*, **25**, 1807 (1960).

(24) T. L. Brown, D. W. Dickerhoof and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

and 1,4-polymer in diethyl ether.[25] Furthermore, even small amounts of diethyl ether, dioxane, triethylamine or tetrahydrofuran have been shown to have large effects on the rate of polymerization of styrene and dienes in toluene, the effect of tetrahydrofuran being much larger than that of the other oxygen-containing solvents employed.[26]

It can be added that the large solvent effects here observed make it necessary to be careful when making comparisons of steric stability to keep the solvent constant. Thus, Walborsky and Young[8] have observed that a large amount of racemization was obtained when a cyclopropylmagnesium bromide (prepared in tetrahydrofuran) was carbonated, whereas complete retention[7,8] was found in a study of cyclopropyllithium compounds (in diethyl ether). Conclusions about the relative stereochemical stabilities of lithium and magnesium compounds are unwarranted until comparisons are made in the same solvent.

Experimental[26a]

***n*-Butyllithium** was prepared in ether under an argon atmosphere from *n*-butyl bromide and lithium metal by the method of Jones and Gilman.[27] In dry unsaturate-free pentane or in hexane, *n*-butyllithium was prepared from *n*-butyl chloride and lithium (containing 0.2% sodium, available from the Maywood Chemical Co., Maywood, N. J.) under reflux according to the directions of Gilman, Moore and Baine.[28] Lithium reagents were stored under argon and titrated by the double titration method[27] immediately prior to use.

Bis-(*cis*-α-stilbenyl)-mercury (*cis*-II), m.p. 147–149° (lit.[12] 145–147°), was obtained in a yield of 82% (after purification by recrystallization from 1:1 benzene–ethanol) from *cis*-α-bromostilbene, m.p. 20–21° (lit.[11] 19.5–20.5°), by exchange with butyllithium and treatment with mercuric chloride in ether at −55°.[12]

Isomerization of *cis*- to *trans*-Stilbenyllithium (I).—In a typical experiment *n*-butyllithium (0.0072 mole, 6.3 ml. of 1.15 *N* solution) in pentane was added rapidly from a hypodermic syringe to 2.00 g. (0.0036 mole) of *cis*-II in 35 ml. of benzene and 100 ml. of ether and stirred for 30 min. at −54 ± 3°. The solution was then added to 1 kg. of finely crushed Dry Ice slurried in ether over a period of 6 min. by forcing the solution under argon pressure through an inverted U-tube which was drawn out to a 1 mm. i.d. jet at the delivery end.

On warming to room temperature the solution was washed with 0.4 *N* hydrochloric acid and water, and the acid extracted into 0.4 *N* sodium hydroxide. The aqueous solution was filtered, acidified to congo red with 10 *N* sulfuric acid, cooled in ice-water and filtered to get 1.03 g. (65%) of acid, *cis*-III, m.p. 174–176° (lit.[11] m.p. 174–175°). When 0.186 g. was dissolved in 6.5 ml. of benzene and 0.2 ml. of freshly distilled aniline was added, none of the salt of the *trans*-acid *trans*-III precipitated on standing for 12 hr. at 5°. Recrystallization of 0.84 g. from 1:1 benzene–hexane gave 0.66 g. of *cis*-III, m.p. 175–176°. Reaction mixtures in which equilibration had occurred (Table I) were carbonated as above and the carboxylic acid mixture analyzed by ultraviolet spectroscopy by the method described in a following section. Alternatively, treatment of the lithium reagent with an equivalent amount of benzophenone added rapidly in pentane–benzene solution from a hypodermic syringe gave *cis*- and *trans*-carbinol IV. The mixture was analyzed by the spectral method to be described below.

***cis*- and *trans*-1,1,2,3-Tetraphenyl-2-propenol** (*cis* and *trans*-IV).—A mercury–lithium exchange of *cis*-II, in 1:1 benzene–pentane for 30 min. at 2°, followed by treatment with benzophenone as described immediately above gave an oil which was purified by chromatography on neutral alumina. Elution with ether and then with methanol gave 0.29 g. (68%) of *cis*- and *trans*-IV, m.p. 102–104°, shown by ultraviolet analysis as below to contain 98% of the *cis* and 2% of the *trans* isomer. Recrystallization from hexane gave a 44% yield of the *cis* isomer, m.p. 104–105° (lit.[29] 106–107°).

A similar reaction in 1:1 benzene–ether for 30 min. at 2° gave 79% of *trans*-IV, m.p. 110–112°, which after recrystallization from hexane amounted to 35%, m.p. 113–114°.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.5; H, 6.1. Found: C, 89.3; H, 6.3.

Ultraviolet Spectrophotometric Analyses. (*a*) **2,3-Diphenylacrylic Acids** (*cis*- and *trans*-III).—Spectra were measured of ethanol solutions in 1.0-cm. cells with a Cary model 14M recording spectrophotometer. The absorbances of known mixtures of the acids[11] *cis*- and *trans*-III (*cis*, m.p. 175–176°; *trans*, m.p. 139–140°,) was measured at 280 and 287 mμ. Plots of the molar extinction coefficients at each wave length against the % *trans*-acid in the mixture gave working curves used to analyze the reaction mixture. The results presented in Table I are averages of the values obtained at 280 and 287 mμ. Analyses of known mixtures by this method suggests that the accuracy is ±2%.

(b) **1,1,2,3-Tetraphenylpropenols** (*cis*- and *trans*-IV).—The propenols (*cis*- and *trans*-IV) described above were used as standards. Data at 250, 255, 258, 262.5, 270, 275, 280 and 285 mμ were employed using the method of Dewar and Urch,[30] the % *trans* being obtained from the slope of the linear plot. Detailed data obtained are available elsewhere.[26]

Bis-(1,2,2-triphenylvinyl)-mercury.—Triphenylvinyllithium was prepared from 5.0 g. (0.015 mole) of 1,2,2-triphenylvinyl bromide in 100 ml. of ether by addition of 0.018 mole of *n*-butyllithium in ether at −40°. After stirring at −40° for 10 min., 2.5 g. (0.0093 mole) of mercuric chloride in 75 ml. of ether was added rapidly. The mixture was stirred for 45 min. at −40 to −30°, warmed to room temperature and 5% hydrochloric acid was added. After separation of the layers 2.78 g. of a white powder, m.p. 224–227°, was filtered from the ether layer. An additional 0.28 g. (total yield, 58%), m.p. 223–227°, was obtained when the ether solution was washed with water, dried over calcium chloride and concentrated to a small volume. These two crops were combined and recrystallized from 1:1 benzene–ethanol to give 2.51 g. (48%), m.p. 232–233°.

Anal. Calcd. for $C_{40}H_{30}Hg$: C, 67.6; H, 4.3. Found: C, 67.8; H, 4.3.

1,2,2-Triphenylvinylmercuric Chloride.—Refluxing 0.2 g. of bis-(1,2,2-triphenylvinyl)-mercury and 0.5 g. of mercuric chloride in 25 ml. of ethanol for 4 hr. gave on cooling 0.22 g. (78%) of product, m.p. 199–201°. Recrystallization from ethanol gave pale yellow needles, m.p. 200.5–201.5°.

Anal. Calcd. for $C_{20}H_{15}HgCl$: C, 48.9; H, 3.1. Found: C, 48.5; H, 3.3.

Bis-(*trans*-2-*p*-chlorophenyl-1,2-diphenylvinyl)-mercury (*trans*-VI).—To 5.0 g. (0.0135 mole) of *trans*-2-*p*-chlorophenyl-1,2-diphenylvinyl bromide,[15] m.p. 112–113°, in 100 ml. of ether, 0.016 mole of *n*-butyllithium was added at −40°. After 5 min., 2.2 g. (0.0081 mole) of mercuric chloride in 100 ml. of ether was added and the mixture was stirred for 30 min. at −40° before warming to room temperature and adding 50 ml. of 5% hydrochloric acid. Filtration of the ether layer gave 1.56 g. (30%) of material, m.p. 213–225°, which on recrystallization from benzene gave 1.02 g. (20%), m.p. 235–236°. Concentration of the

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[26a] All melting points are corrected. Microanalyses were performed by Mr. J. Nemeth, Mrs. A. Bay, Miss J. Liu and Miss C. Higham. Infrared spectra were obtained with a Perkin–Elmer model 21 spectrophotometer by Mr. P. McMahon, Mr. W. Dalton, Mr. D. Johnson and Mrs. J. Verkade. The ultraviolet spectra were obtained with a Cary model 14M recording spectrophotometer by Miss C. Juan. Infrared and ultraviolet spectra are available in the Ph.D. Thesis of W. J. K., Jr.,[1] available from University Microfilms, Ann Arbor, Mich.

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TABLE IV

PREPARATION OF OPTICALLY ACTIVE DI-*sec*-BUTYLMERCURY ((−)(±)-X)

s-BuHgBr		*s*-BuLi		Time and temp.			Di-*s*-BuHg	
Mole	[α]D	mole	Pentane total ml.	For addn.	Until quench.	Yield, %	[α]D[a]	[α]D calcd.[b]
0.0375	−17.4°	0.0375	148	10 min. 0 to 5°	15 min. 5°	81	−12.6°[c]	−18.8°
.037	− 4.91	.040	140	10 − 5 to 0°	35 0 to 10°	86	− 2.81	−14.8
.032	−10.7	.033	155	25 5 to 10°	30 5 to 18°	11	−10.1[d]	−24.4
.040	+ 3.21	.038	155	20 −10 to −5	35 − 5 to 15°	77	+ 2.08	+16.8
.118	+ 3.92[e]	.110	400	20 −40 to −45	60 −40 to −45	40	+ 3.89	+25.7

[a] αD measured on neat liquid in 0.5-dm. tube; [α]D calculated using d. = 1.76. [b] Calculated for optically pure (−)-*sec*-butyl-(±)-*sec*-butylmercury (or (+)-(±)) using $[\alpha]^{22}\text{D}$ −25.9° for optically pure *sec*-butylmercuric bromide.[46] [c] *Anal.* Calcd. for $C_8H_{18}Hg$: C, 30.5; H, 5.8. Found: C, 30.8; H, 5.7. [d] *Anal.* Found: C, 30.6; H, 5.8. [e] A mixture of fractions for which [α]D +4.01° was calculated; hence, the observed value may not be reliable.

ether solution gave a second crop, 0.25 g., m.p. 231–234°, and *trans*-1-*p*-chlorophenyl-1,2-diphenylethylene.

Anal. Calcd. for $C_{40}H_{28}Cl_2Hg$: C, 61.6; H, 3.6. Found: C, 61.7; H, 3.6.

Bis-(*cis*-2-*p*-chlorophenyl-1,2-diphenylvinyl)-mercury (*cis*-VI).—To 10.0 g. (0.027 mole) of *cis*-2-*p*-chlorophenyl-1,2-diphenylvinyl bromide,[15] m.p. 157.5–158.5°, in 75 ml. of ether, 0.030 mole of *n*-butyllithium in ether was added at −50 to −40°. The suspension was stirred for 20 min. at −40° and 4.1 g. (0.015 mole) of mercuric chloride in 100 ml. of ether was added over 10 min. After stirring for 30 min. at −40° 20 ml. of methanol was added and the solution was warmed to room temperature. Filtration gave 7.84 g. (74%) of crude product, m.p. 205–220°. Recrystallization from benzene gave 6.24 g. (59%), m.p. 228–229°. A further recrystallization from benzene to which ethanol was added to incipient precipitation at reflux gave on cooling very fine yellow needles, m.p. 229–230°.

Anal. Calcd. for $C_{40}H_{28}Cl_2Hg$: C, 61.6; H, 3.6. Found: C, 61.3; H, 3.5.

Configurational Stability of *cis*- and *trans*-2-*p*-Chlorophenyl-1,2-diphenylvinyllithium (V).—A typical experiment was conducted as follows. In 40 ml. of benzene under argon at 20 ± 1° 0.0013 mole of *n*-butyllithium in pentane (1.2 ml. of 1.12 *N* solution) was added rapidly from a hypodermic syringe to 0.50 g. (0.00064 mole) of bis-(*cis*-2-*p*-chlorophenyl-1,2-diphenylvinyl-)mercury. After stirring for 30 min. the mixture was transferred in 2 min. under argon pressure in the usual way to a flask containing 500 g. of Dry Ice slurried in ether. The solution was washed with 0.2 *N* hydrochloric acid and then with water. Extraction with 25 ml. of 0.2 *N* sodium hydroxide and acidification (congo red paper) with 10 *N* sulfuric acid gave, after collection by filtration, washing with water and drying for 12 hr. at 2 mm. over potassium hydroxide pellets, 0.284 g. (66%), m.p. 199–204°. Quantitative infrared analysis as described below showed that it contained 94% of the acid *cis*-VII and 6% of *trans*-VII. This and the other results are presented in Table II.

In those reactions which were not completed by carbonation, methanol (7 ml.) was added to the lithium reagent after the appropriate time and after neutralization with 1 *N* hydrochloric acid the mixture was heated under reflux for 2 hr. with mercuric chloride to convert unreacted divinylmercury VI to the more easily removed vinylmercuric chloride. After the organic layer was washed with water, dried over magnesium sulfate and the solvent distilled, trituration of the remaining solid with pentane and evaporation of the pentane gave *cis*- and *trans*-olefin (*cis*- and *trans*-VIII) as an oil which was subjected to infrared analysis as described below. It will be seen by inspection of the data in Table II that substantially the same stereochemical results were obtained when the reaction was treated with methanol as when it was carbonated.

Infrared Spectrophotometric Analyses. (a) *cis*- and *trans*-1-*p*-**Cholorophenyl-1,2-diphenylethylene** (*cis*- and *trans*-VIII).—The infrared spectra were measured in cyclohexane in 0.1-mm. cells with a Perkin–Elmer model 21 double beam recording spectrophotometer on a scale of 5 cm.⁻¹/cm. The absorbance (*A*) of the *cis*-ethylene,[15] m.p. 63–64°, was measured at 722 cm.⁻¹ and of the *trans*,[15] m.p. 90–91°, at 738 cm.⁻¹. Base lines were drawn by measuring the spectrum with pure solvent in both cells. The product compositions were obtained from calibration curves made using known mixtures of the ethylenes and plotted in each of two different ways. In method I, the absorbance of the *cis* isomer (A_c) was plotted against the concentration of the *cis* isomer (C_c) and A_t against C_t to obtain independent values of the concentrations of *cis*- and *trans*-VIII. In method II, the ratio A_c/A_t, was plotted against % *cis*, in order to minimize the errors resulting from accidental evaporation of solvent from the relatively concentrated solutions. The results reported in Table II are averages of the values (which agreed within 4% or better) of the values obtained by these two methods.

(b) *cis*- and *trans*-**2,3-Diphenyl-3-*p*-chlorophenylacrylic Acids** (*cis*- and *trans*-IX).—The absorbance of the *cis*-acid,[15] m.p. 205–206°, was measured at 720 cm.⁻¹ and of the *trans*,[15] m.p. 213.5–215°, at 729 cm.⁻¹ in 5% dioxane solutions. Method II above was used to obtain the values summarized in Table II.

***t*-Butyllithium.**—Lithium metal (containing 0.2% sodium) was cut into clean 1 × 1 × 0.5 cm. pieces under mineral oil, and 6.0 g. (0.87 g.-atom) was weighed out after blotting off the excess oil. These pieces were hammered into thin foil, and without removing the remaining mineral oil they were coated with fine copper bronze powder which was applied by sprinkling the copper (dried for 12 hr. at 1 mm.) onto the foil and rubbing it into the surface with a mortar and pestle. Enough copper was used to coat the lithium evenly and completely. The foil was then cut into 1 × 1 cm. pieces and dropped directly into 160 ml. of pentane in the reaction flask which was being swept by a stream of argon.

The *t*-butyl chloride, b.p. 50–51°, was stirred with anhydrous potassium carbonate until it was neutral to moist litmus, filtered and freshly distilled.

The mixture of lithium and pentane was heated under gentle reflux and stirred with a high speed stirrer while about 10% of a solution of 28 g. (0.3 mole) of *t*-butyl chloride in 65 ml. of pentane was added. After the reaction had started, the remainder was added continuously over 5 hr. Gentle reflux was maintained throughout the addition, and the mixture was heated under reflux for an additional 2 hr. The mixture was filtered and titrated. In three successive runs 0.51 *N* solutions (38% yield) were obtained. When aliquots of these solutions were carbonated, 80% of the expected quantity of pivalic acid was obtained. When graphite was substituted for copper bronze a 0.18 *N* solution (14% yield) was obtained which on carbonation gave 82% of the expected quantity of pivalic acid. A number of attempts to prepare *t*-butyllithium in pentane without the copper or graphite treatment gave no lithium reagent.

Optically Active *sec*-Butylmercuric Bromide.—*sec*-Butylmercuric bromide[18,19] was resolved by the method of Charman, Hughes and Ingold.[18]

(−)-*sec*-Butyl-(±)-*sec*-butylmercury.—The *sec*-butylmercuric bromide resolved above was suspended in pentane and *sec*-butyllithium in pentane[30] was added with efficient stirring. The reaction mixture was quenched by the addition of 5–10 ml. of methanol and after dilution with ether, washing and drying of the ether layer and evaporation of the solvent the residue was distilled through a 5-in. Vigreux column and the fraction b.p. 50–51° (1.8 mm.) collected. Preparations of the compound are summarized in Table IV.

Optically Active *sec*-Butyllithium.—2-Octyllithium (0.058 mole, 73 ml. of 0.802 *N* solution) in pentane was added over 8 min. from a hypodermic syringe to 9.16 g. (0.029 mole) of di-*sec*-butylmercury ((−)(±)-X), $[\alpha]^{21}\mathrm{D}$ −12.6°, in 200 ml. of pentane while stirring at −7 to −5°. The solution was then stirred at −10 to −7° for 22 min. and added to Dry Ice over 12 min. After warming to room temperature the mixture was diluted with an equal volume of ether and extracted with 5% aqueous sodium hydroxide and then with water. Acidification of the aqueous extracts with sulfuric acid (congo red) and extraction with ether gave after drying and evaporation of the ether 8.46 g. of oil with $\alpha^{21}\mathrm{D}$ − 0.06 ± 0.04° (0.5-dm. tube, neat). Gas phase chromatography at 175° on a didecyl phthalate column in a Perkin–Elmer Vapor Fractometer, model 154B, showed the presence of 2-methylbutyric acid (4.7 mole %) and 2-methylcaprylic acid (95.3 mole %). Distillation at 1.6 mm. gave 0.22 g. of 2-methylbutyric acid, b.p. 45–50°, $\alpha^{21}\mathrm{D}$ −1.30 ± 0.03°; 0.60 g. of an intermediate fraction, b.p. 50–90°, $\alpha^{21}\mathrm{D}$ −0.19 ± 0.03°; and 6.61 g. of 2-methylcaprylic acid, b.p. 90–95° $\alpha^{21}\mathrm{D}$ −0101 ± 0.03°. The vapor chromatograph of the 2-methylbutyric acid fraction showed that it was contaminated by about 5% of a mixture of 2-octanol and 2-methylcaprylic acid. It was purified further by extraction of an aqueous solution of its sodium salt with ether. The resulting acid showed the presence of no impurities on gas phase chromatography and had $\alpha^{22}\mathrm{D}$ −1.32 ±0.03° (0.5-dm., neat) and $[\alpha]^{22}\mathrm{D}$ −2.84° (d^{22} 0.931). Distillation of the neutral portion of the reaction mixture after drying over magnesium sulfate gave 7.47 g. (82%) of di-*sec*-butylmercury, $\alpha^{22}\mathrm{D}$ −10.82 ± 0.03° (0.5-dm., neat), $[\alpha]^{22}\mathrm{D}$ −12.3°. This and other results obtained similarly are summarized in Table III.

***sec*-Butyl-α-naphthylmercury.**—α-Naphthylmagnesium bromide, made from 29.6 g. (0.143 mole) of α-naphthyl bromide and 6.58 g. (0.271 g.-atom) of magnesium turnings in 170 ml. of ether and 30 ml. of benzene, was added over 15 min. to a solution of 40.0 g. (0.119 mole) of *sec*-butylmercuric bromide in 100 ml. of ether. After 1 hr. under reflux the mixture was poured into 400 ml. of ice-water, the ether layer washed with water, dried over magnesium sulfate and the ether distilled. The remaining orange colored oil was chromatographed on 250 g. of alumina. Elution with hexane gave 31.4 g. of a yellow oil and benzene–ether mixtures eluted 9.6 g. (24% recovery), m.p. 41–43°; mixed with *sec*-butylmercuric bromide, m.p. 41–43°. From the oil 9.5 g. of naphthalene, m.p. 74–79°, was sublimed during 15 hours at 1 mm. as the material was slowly heated to 140°. The remaining oil (21.9 g., 48%) crystallized on cooling; m.p. 39–42°. Recrystallization from 95% ethanol gave 17.8 g. (39%) of white platelets, m.p. 42–43°. A portion recrystallized from methanol had m.p. 42–43°. A similar product could also be obtained from the reaction of α-naphthyllithium and *sec*-butylmagnesium bromide.

Anal. Calcd. for $C_{14}H_{16}Hg$: C, 43.7; H, 4.2. Found: C, 43.7; H, 4.3.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Hydroxyl Group Catalysis. III.[1] The Nature of Neighboring Hydroxyl Group Assistance in the Alkaline Hydrolysis of the Ester Bond

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The extent and nature of internal hydrogen bonding, the rates of alkaline hydrolysis and associated activation parameters as well as the solvent deuterium isotope effects on the rates of alkaline hydrolysis were determined for a number of cyclopentane and norbornane acetates and diol monoacetates. The neighboring hydroxyl group in all sterically favorable instances assists alkaline hydrolysis. The assistance is not associated with a deuterium solvent kinetic isotope effect divergent from that for the specific base-catalyzed hydrolysis of an aliphatic ester. Furthermore, there is no clear-cut alteration of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ that can be associated with neighboring hydroxyl group facilitation. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the alkaline hydrolysis of the esters studied exhibit compensation and the isokinetic temperature is −17°. Arguments are presented, on the basis of steric, ground state hydrogen bonding and kinetic considerations, that the most likely mechanism for neighboring hydroxyl group facilitation involves internal solvation of the transition state for attack of OH^- at the ester carbonyl group.

Introduction

The purpose of the present investigation has been to determine the nature of the neighboring aliphatic hydroxyl group facilitation of OH^- catalyzed ester hydrolysis. Possibly the first report of hydroxyl group facilitation of nucleophilic displacement at the ester bond was that of Henbest and Lovell[3] who studied the solvolysis of 3-acetoxy-5-hydroxy steroids of the cholestane and coprostane series in aqueous methanolic potassium carbonate solution (20°). They found that the axial esters were, unexpectedly,[4] hydrolyzed faster than the equatorial esters if *cis* to the 5-hydroxyl group. Similar facilitation of the base-catalyzed methanolysis of the C_7- and C_{16}-O-acetates of germine by hydroxyl groups at C_{14} and C_{20} and the C_{16}-O-acetate of cevine by a hydroxyl group at C_{20} was reported by Kupchan, Johnson and co-workers.[5–7] These studies, representing apparent cases of neighboring hydroxyl group facilitation in cyclohexane-1,3-diol monoacetates, were of a qualitative nature and do not allow the calculation of rate constants. In a preliminary communication, Kupchan, Slade and Young[8] describe studies on the hydrolysis of cholestane-3β,4β,-diol monoacetates. The neighboring hydroxyl group was reported to increase the rate of ester hydrolysis in these vicinal cyclohexanediol monoacetates by 8 to 9 times over that noted in corresponding cyclohexane monoacetates (30°). Zachau and Karau[9] investigated the rates of alkaline hydrolysis of monoglycyl derivatives of *cis*-

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