with 560 l. moles^{-1} sec.$^{-1}$). This may indicate that in spite of some steric strain the electron-donating effect of the methyl group makes the poly-α-MS-anion more reactive toward styrene than the polystyrene anion.

It was frequently claimed that for ionic polymerization the reactivity ratio's product $r_1.r_2$ is close to unity.[5] This need not always be the case. For example, in anionic co-polymerization of α-methylstyrene and styrene at 25° the $k_{1,1}$ is about 2.5 l. moles^{-1} sec.$^{-1}$ (extrapolated value from data of Worsfold and Bywater[6]). In the same units we find $k_{1,2} = 770$, $k_{2,2} = 560$[3] and the preliminary data for $k_{2,1}$ give $k_{2,1} \sim 20$. Thus, $r_1.r_2$ is probably less than 0.1.

Studies of other co-polymerization systems are in progress. The method may be applied also for determining the rate constant of homopropagation as a function of *DP* (for low-molecular weight polymers). Such a work is also in progress in our laboratory, and it will be reported in due course.

(5) G. M. Burnett, "Kinetics and Mechanism of Polymerization," Interscience Publishers, Inc., New York, N. Y.

(6) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **36**, 1141 (1958).

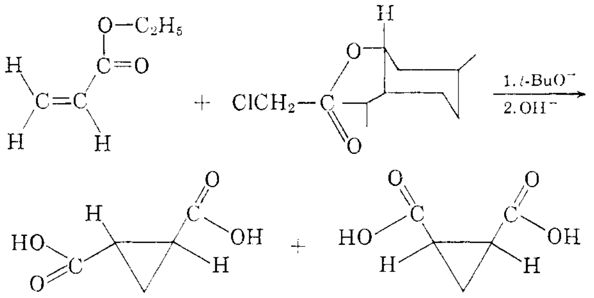
DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY COLLEGE OF FORESTRY
AT SYRACUSE UNIVERSITY
SYRACUSE 10, N. Y.
C. L. LEE
J. SMID
M. SZWARC

RECEIVED APRIL 28, 1961

CYCLOPROPANES. XI. SOLVENT EFFECT IN PARTIAL ASYMMETRIC SYNTHESIS[1]

Sir:

Cram,[2] Prelog[3] and their co-workers have studied the course of asymmetric syntheses in a variety of systems and have found that the configuration of the newly created asymmetric center was dependent on the conformation of the original asymmetric center. The concepts derived from this work have been applied, with some success, to the correlation of configuration.[4] However, certain anomalous results recently have been reported. For example, Collins[5] has shown that in the addition of Grignard reagents to phenylacetoin the use of phenylmagnesium chloride or phenylmagnesium bromide resulted in a preponderance of the *threo* isomer whereas with phenylmagnesium iodide the *erythro* isomer predominated. Therefore a subtle change of reagents has resulted in a reversal of the stereoselectivity. That temperature also can have a marked effect on changing the course of an asymmetric synthesis recently has been demonstrated by Pracejus.[6] We wish, at this time, to report that a change in solvent can also result in a reversal of stereoselectivity in a partial asymmetric synthesis. The synthesis involves a base catalyzed Michael type addition of (−)-menthyl chloroacetate to ethyl acrylate.[7]



That partial asymmetric synthesis was achieved in the above condensation is not surprising since this has been observed in mechanistically similar reactions.[8] However, as will be shown below, changing the solvent medium from toluene to that of N,N-dimethylformamide (DMF) or to nitrobenzene resulted in a complete reversal of sign in the resulting optically active *trans*-cyclopropane-1,2-dicarboxylic acid.[9]

In a typical experiment dry potassium *t*-butoxide (6.7 g., 0.06 mole) was added slowly, in order to maintain the temperature at 30°, to a solution of (−)-menthyl chloroacetate (11.6 g., 0.05 mole) and ethyl acrylate (5.0 g., 0.05 mole) in 15 ml. of toluene. After stirring for three hours the reaction mixture was washed with water and the solvent was removed *in vacuo*. The residue was completely saponified[8] by potassium hydroxide in boiling ethyleneglycol and yielded, upon acidification and extraction, 3.9 g. (60%) of *trans*-cyclopropane-1,2-dicarboxylic acid, m.p. 173–174°, $[\alpha]^{25}\text{D}$ −1.5° (*c*, 7.1, water). The infrared spectrum was identical with that of an authentic sample.[10] Treatment of the acid with diazomethane produced the dimethyl ester, b.p. 94–96° at 15 mm., $n^{25}\text{D}$ 1.4368 $[\alpha]^{25}\text{D}$ −2.3° (*c*, 8.0, ethanol). The identical procedure was followed for the experiments in DMF and nitrobenzene. Table I summarizes the results and shows the excellent reproducibility of the experiments. The marked increase in optical yield in DMF should be noted.

The mechanistic implications of this solvent effect in asymmetric syntheses are currently under

---

[1] This work was supported in part by a grant from the National Science Foundation.

[2] D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952).

[3] V. Prelog, *et al.*, *Helv. Chim. Acta.*, **36**, 308 (1953).

[4] For a review of this work, see J. A. Mills and W. Klyne, Ch. 5 in "Progress in Stereochemistry," Vol. I, Academic Press, Inc., New York, N. Y., pp. 198–201.

[5] J. H. Stocker, P. Sidisunthorn, B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 3913 (1960).

[6] H. Pracejus, *Ann.*, **634**, 9 (1960).

[7] This type of condensation to yield derivatives of cyclopropane was first described by E. R. Buchman and D. Deutsch [*Experientia*, **6**, 462 (1950)]. Currently, this method is being exploited as a general method, see R. Fraisse and R. Jacquier, *Bull. Soc. Chim. (France)*, 986 (1957); L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958); D. T. Warner, *J. Org. Chem.*, **24**, 1536 (1959).

[8] F. J. Impastato, L. Barash and H. M. Walborsky, *J. Am. Chem. Soc.*, **81**, 1514 (1959). We also have observed that the Darzens condensation of (−)-menthyl chloroacetate with acetophenone, followed by saponification, leads to the formation of sodium β-methyl, β-phenylglycidate, $[\alpha]^{24}\text{D}$ −0.61° (*c*, 6.4, H_2O). Lithium aluminum hydride reduction of the condensation product resulted in the formation of a mixture of glycols consisting of 95% 3-phenylbutane-1,3-diol and 5% 3-phenylbutane-1,2-diol. Removal of the 1,2-glycol by periodate oxidation yielded the pure 1,3 glycol $[\alpha]^{24}\text{D}$ − 9.1° (*c* 4.2 $CHCl_3$). NOTE ADDED IN PROOF.—Prof. K. Sisido has informed us that he has also observed asymmetric synthesis in the Darzens reaction.

[9] L. L. McCoy, *J. Am. Chem. Soc.*, **82**, 6416 (1960), has observed an exciting but much less subtle effect of solvent in this type of condensation. McCoy showed that changing the solvent medium from benzene to N,N-dimethylformamide changed the *cis*:*trans* isomer ratio. In our work we could only isolate minor to trace amounts of the *cis* acid.

[10] K. B. Wibert, R. K. Barnes and J. Albin, *J. Am. Chem. Soc.*, **79**, 4944 (1957), report m.p. 176–177° for the racemic acid. E. Buchner and R. von der Heide, *Ber.*, **38**, 3112 (1905), report m.p. 175° for the active acid, $[\alpha]^{27}\text{D}$ 84.5°.

TABLE I

ASYMMETRIC SYNTHESES OF *trans*-CYCLOPROPANE-1,2-DICARBOXYLIC ACID

Run	Solvent	Acid, % yield	$[\alpha]^{24}D$, H_2O	Optical yield	Dimethyl ester ester $[\alpha]^{24}D$ EtOH
1	Toluene	60.0	−1.5°	1.8	−2.3°
2	Toluene	41.5	−1.9°	2.2	−2.8°
3	Toluene	40.1	−2.7°	3.1	−4.0°
4	DMF	46.0	+8.6°	10.2	+12.8°
5	DMF	46.0	+8.7°	10.3	+13.0°
6	DMF	51.0	+9.3°	10.9	+13.8°
7	Nitrobenzene	34.1	+0.25	0.3	+0.38°

investigation and will be the subject of a future publication.

INSTITUTE FOR CHEMICAL RESEARCH Y. INOUYE
KYOTO UNIVERSITY S. INAMASU
TAKATSUKI, JAPAN, AND M. OHNO
DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY T. SUGITA
TALLAHASSEE, FLORIDA H. M. WALBORSKY

RECEIVED MAY 22, 1961

METHYL-STANNO-SILOXANES AND METHYL-PLUMBO-SILOXANES

Sir:

A recent article[1] prompts us to report some results of our own studies in the field of alkylhetero-siloxanes.

To gain some knowledge on the stability and properties of siloxanes, in which silicon atoms are partly replaced by other IVb elements (Ge, Sn, Pb), we have planned to synthesize heterosiloxanes of low molecular weight and definite composition. First we prepared some alkyl-germanosiloxanes,[2] *e.g.*, hexamethylgermanosilosane $Me_3SiOGMe_3$, by the reaction of $LiOSiMe_3$ with Me_3GeCl. We have found that this type of reaction furnishes also the synthesis of the corresponding tin and lead compounds.

Except for some studies on the tin-alkylsilanolates, compounds without alkyl groups attached to tin,[3,4,5a,5b,6] only few reports on real alkyl-stannosiloxanes have been published.[4,5c,7] Moreover these studies mainly dealt with polymeric materials whereas the first members of those series have not been described.

Okawara, *et al.*,[1] failed to obtain hexamethylstannosiloxane and bistrimethylsiloxy-dimethylstannane by method of transesterification and cohydrolysis. We were able to synthesize these compounds by a simple method: Lithium trimethylsilanolate reacts in anhydrous ethereal solution with trimethylchlorostannane forming insoluble LiCl and hexamethylstannosiloxane in very good yields according to

$$(CH_3)_3SiOLi + (CH_3)_3SnCl \rightarrow LiCl + (CH_3)_3SiOSn(CH_3)_3$$

Dimethyldichlorostannane and methyltrichlorostannane react under the same conditions forming LiCl and bis-trimethylsiloxy-dimethylstannane and tris-trimethylsiloxy-methylstannane, respectively

$$2\,(CH_3)_3SiOLi + (CH_3)_2SnCl_2 \rightarrow [(CH_3)_3SiO]_2Sn(CH_3)_2 + 2\,LiCl$$

$$3\,(CH_3)_3SiOLi + CH_3SnCl_3 \rightarrow [(CH_3)_3SiO]_3SnCH_3 + 3\,LiCl$$

Tatlock and Rochow[4] already had studied the reaction of Me_3SiOK and Me_2SnCl_2 in 1952, but reported only a few analytical data and physical constants of their reaction product. Table I shows the physical constants of the new methylstannosiloxanes.

Hexamethylstannosiloxane shows surprisingly high thermal stability. It may be distilled at atmospheric pressure without decomposition. Bistrimethylsiloxy-dimethylstannane, in contrast to the results of Okawara, *et al.*,[1] forms crystals melting at 48°. The melt is stable up to 150°. It may be vacuum distilled (b.p. (11 mm.) 74°), whereas the distillation under atmospheric pressure at 160° is accompanied by partial decomposition, hexamethyldisiloxane and dimethylpolystannoxane being formed

$$x[(CH_3)_3SiO]_2Sn(CH_3)_2 \rightarrow x(CH_3)_3SiOSi(CH_3)_3 + [(CH_3)_2SnO]_x$$

Under similar conditions tris-trimethylsiloxy-methylstannane undergoes thermal decomposition yielding hexamethyldisiloxane and polymeric methylpolystannoxane, which still contains trimethylsiloxy groups attached to tin.

From ethereal solutions of trimethylbromoplumbane and sodium trimethylsilanolate NaBr precipitates and high yields of hexamethylplumbosiloxane are recovered[8])

$$(CH_3)_3SiONa + (CH_3)_3PbBr \rightarrow NaBr + (CH_3)_3SiOPb(CH_3)_3$$

This first member of the lead–siloxane series forms a colorless liquid of high vapor pressure and unexpected thermal stability. It may be transported in high vacuum even at room temperature and boils without decomposition at 172° under atmospheric pressure of dry nitrogen. At temperatures above 150° the vapor reacts with oxygen with explosion forming elementary lead. Under normal conditions the compound is stable against dry air and the influence of light.

TABLE I

MELTING AND BOILING POINTS OF METHYLSTANNOSILOXANES

Formula	Fp., °C.	B.p.			
		°C.	Mm.	°C.	Mm.
$(CH_3)_3SiOSn(CH_3)_3$	−59	141	720	38	11
$[(CH_3)_3SiO]_2Sn(CH_3)_2$	+48	160 dec.	720	75	11
$[(CH_3)_3SiO]_3SnCH_3$	+34	155 dec.	720	49	11

---

[1] R. Okawara, D. G. White, K. Fujitani and H. Sato, *J. Am. Chem. Soc.*, **83**, 1342 (1961).

[2] H. Schmidbaur and M. Schmidt, *Chem. Ber.*, **94**, 1138 (1961); **94**, 1349 (1961).

[3] W. I. Patnode and F. C. Schmidt, *J. Am. Chem. Soc.*, **67**, 2272 (1945).

[4] W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952).

[5] (a) K. A. Andrianov and A. A. Zhdanov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 779 (1958); *C.A.*, **52**, 19916 (1958); (b) K. A. Andrianov, A. A. Zhdanov and E. A. Kashutina, *Zhur. Priklad. Khim.*, **32**, 463 (1959); *C.A.*, **53**, 11079 (1959); (c) K. A. Andrianov, T. N. Gamina and E. N. Krushtaleva, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 798 (1956); *C.A.*, **51**, 3487 (1957).

[6] E. D. Hornbaker and F. Conrad, *J. Org. Chem.*, **24**, 1858 (1959).

[7] F. A. Henglein, R. Lang and L. Schmack, *Makromol. Chem.*, **22**, 103 (1957).

[8] $LiOSiMe_3$ under the same conditions does not form the plumbosiloxane with Me_3PbBr, because of the solubility of LiBr in diethyl ether, which prevents the metathetic reaction going to completion.