

with dilute sulfuric acid, followed by ether extraction, washing with cold 5% sodium bicarbonate solution, concentrating *in vacuo* and recrystallizing with 95% ethanol gave 72% of 1,4-dinitrobutane, m.p. 33–34°, lit. value¹ m.p. 33–34° (based on starting cyclopentanone). Treating Ia with base resulted in very little cleavage and converted it to dipotassium α, α' -dinitrocyclopentanone. On the other hand, potassium 2,6-dinitrocyclohexanone (Ib, $n = 3$) and potassium 2,7-dinitrocycloheptanone (Ic, $n = 4$) underwent cleavage in basic as well as acidic media. Dissolving Ib in hot water, basifying with 85% potassium hydroxide at room temperature, acidifying with glacial acetic acid, extracting with ether and distilling gave 78% 1,5-dinitropentane. Its infrared spectrum was superimposable with that of authentic 1,5-dinitropentane.¹ Similar treatment of Ic gave 75% 1,6-dinitrohexane, m.p. 37–39°, lit. value,¹ m.p. 38–39°.

The basic cleavage of negatively substituted ketones has been known for some time. Hauser, *et al.*,⁵ have noted the effect of ring size on the site of basic cleavage of negatively substituted ketones. The cleavage of the five-membered compound Ia in acidic medium only is the first example of the effect of ring size on the pH at which cleavage occurs.

Extension of this ring opening reaction to the synthesis of substituted α, ω -dinitroalkanes, which are at present unknown or which are accessible only with difficulty, is in progress.

Support of this work by the Office of Naval Research is gratefully acknowledged.

(5) P. J. Hamrick Jr., C. F. Hauser and C. R. Hauser, *J. Org. Chem.*, **24**, 583 (1959).

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THE DIRECT DETERMINATION OF THE ABSOLUTE CO-POLYMERIZATION RATE CONSTANT IN ANIONIC POLYMERIZATION¹

Sir:

The conventional method for determining the absolute co-polymerization rate constants $k_{1,2}$ and $k_{2,1}$ is tedious and laborious.² It involves two steps, (1) analysis of the co-polymer composition from which one calculates the reactivities ratios, *e.g.*, $k_{1,1}/k_{1,2}$ ($k_{1,1}$ refers to the reaction $\sim\sim\sim\text{M}_1 + \text{M}_1 \rightarrow \sim\sim\sim\text{M}_1.\text{M}_1$, whereas $k_{1,2}$ to the reaction $\sim\sim\sim\text{M}_1 + \text{M}_2 \rightarrow \sim\sim\sim\text{M}_1.\text{M}_2$); and (2) determination of the absolute value of the rate constant $k_{1,1}$ of the respective homopolymerization. The latter entity is not easily available and its de-

(1) This work was supported by the National Science Foundation through Grant G-14393 and by Quartermaster Corp. Contract DA19-129-QM:1297.

(2) T. Alfrey, J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952.

termination requires studies of the kinetics of polymerization in a non-stationary stage. In addition, there is a doubt whether the approach based on the composition of the copolymer is reliable in studies of ionic co-polymerization.³

We now have developed a technique which permits the direct determination of the co-polymerization rate constant $k_{1,2}$ in an anionic polymerization. The method is illustrated by an example of styrene addition to α -methylstyrene polymer.

A solution of "living" α -methylstyrene tetramer of a known concentration of "living" ends is mixed rapidly in a three-way T-shaped stopcock (2 mm. bore) with a dilute solution of styrene monomer in tetrahydrofuran. The mixture flows through a capillary into a beaker containing wet tetrahydrofuran which terminates the reaction instantly. If CH_3I is used instead of water, titration of NaI determines the concentration of "living" ends at the end of the capillary. Thus it has been shown that no "killing" takes place in the reaction. The time of mixing is less than 5% of time of flow. The time of reaction, *i.e.*, the total time of flow, is varied from less than 0.1 of a sec. to less than a second by changing the pressure of pure nitrogen above the ingredients solutions. The final concentration of the unreacted monomer is determined by measuring the optical density at 290 $m\mu$. To correct for a very small absorption due to the polymer, a solution of the polymer of the same concentration has been inserted in the second beam of the spectrophotometer.

In all these experiments the concentration of monomeric styrene in the capillary was smaller than that of the "living" ends; thus, on the average less than one molecule of styrene was added to the "living" α -methylstyrene. The log of the ratio initial styrene concentration over its final concentration, plotted against time gives a straight line, at least for the initial stages of the reaction. The slopes of these lines divided by the concentration of "living" ends give the respective copolymerization rate constant $k_{1,2}$ (1- α -MS, 2-Styrene). The data obtained by this method are

["living" ends] $\times 10^3 M$	1.3	1.3	1.3	3.0	3.0	3.5
[styrene] $\times 10^3 M$	1.1	1.0	1.1	2.2	2.6	3.0
$k_{1,2}$ l. moles ⁻¹ sec. ⁻¹	1100	1070	990	780	780	780
["living" ends] $\times 10^3 M$	4.0	4.0	5.4	7.0	7.3	9.5
[styrene] $\times 10^3 M$	2.0	3.0	3.0	3.0	2.6	5.5
$k_{1,2}$ l. moles ⁻¹ sec. ⁻¹	665	660	610	645	565	655

The increase in the rate constant for very low concentration of "living" ends was observed also in the homo-polymerization of "living" poly-styrene.⁴ The reason for this phenomenon is not yet clear.

It is interesting to compare these $k_{1,2}$ values to those obtained for styrene homo-polymerization⁴ (*i.e.*, $k_{2,2}$). At the same temperature and concentration of "living" ends $k_{1,2}$ is slightly larger than $k_{2,2}$ (*e.g.*, 770 l. moles⁻¹ sec.⁻¹ as compared

(3) R. K. Graham, D. L. Dunkelberger and W. E. Good, *J. Am. Chem. Soc.*, **82**, 400 (1960).

(4) C. Geacintov, J. Smid and M. Szwarc, *ibid.*, **83**, 1253 (1961).

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 Bywater⁶). In the same units we find $k_{1,2} = 770$, $k_{2,2} = 560$ ⁸ 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).

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CYCLOPROPANES. XI. SOLVENT EFFECT IN PARTIAL ASYMMETRIC SYNTHESIS¹

Sir:

Cram,² Prelog³ 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, Collins⁵ 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

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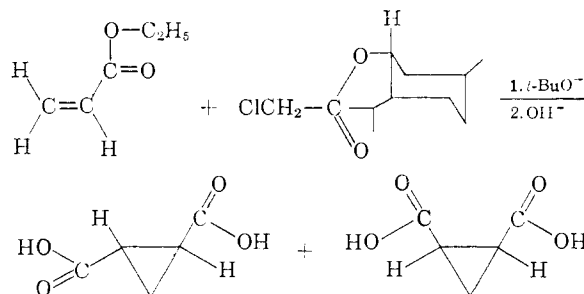
(2) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952).

(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).



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 saponified⁸ 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°, [α]^{25D} -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_D^{25} 1.4368 [α]^{25D} -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

(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, [α]^{25D} -0.61° (*c*, 6.4, H₂O). 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 [α]^{25D} - 9.1° (*c* 4.2 CHCl₃). 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, [α]^{25D} 84.5°.