

The Catalytic Activity of Potassium Methoxy-Polyethylene Glycolates and Potassium *t*-Butylate

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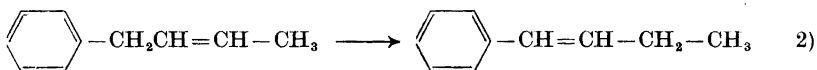
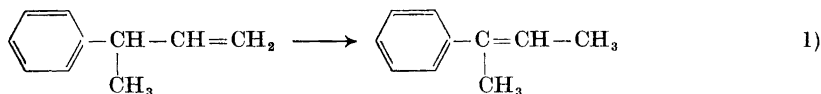
The catalytic activities of potassium methoxy-polyethylene glycolates of various chain lengths and potassium *t*-butylate were compared in diethyl ether and dioxane solution on the base catalysed migration of the double bond in α -methylallylbenzene and 2-butenylbenzene. The catalytic activity of the methoxy-polyglycolates increased markedly as the chain length was increased. Their catalytic activity relative to the catalytic activity of potassium *t*-butylate is greater for the isomerization of α -methylallylbenzene than for 2-butenylbenzene, and greater in diethyl ether than in dioxane. At a catalyst concentration of 0.083 moles per litre in diethyl ether, the rate of isomerization of α -methylallylbenzene is 700 times greater with $K^+O(CH_2CH_2O)_{7-8}CH_3$ than with $K^+OC(CH_3)_3$ as catalyst. The ratio of catalytic activity of the two types of catalyst increases with increasing concentration. The results indicate that the catalytic activity of the methoxy-polyglycolates is only slightly affected by the solvent, while the solvent exerts a marked effect on the catalytic activity of potassium *t*-butylate. It is suggested that the catalytically active species of the methoxy-polyglycolates are intramolecularly polarized ion-pairs. The results do not allow any certain conclusions as to the reactive species in the case of potassium *t*-butylate.

The catalytic effect of potassium *t*-butylate on the migration of double bonds in olefinic hydrocarbons has been shown to be greatly increased by solvents such as dimethyl sulfoxide and dimethyl formamide.¹⁻⁴ The polyethylene glycol dimethyl ethers of the general formula $CH_3(OCH_2CH_2)_nOCH_3$ also give remarkably high rates of isomerization, whether used together with more inert solvents, or as the only solvent.^{5,6} The effect of the polyethylene glycol dimethyl ethers increased markedly when the chain length of the polyglycol was increased. The effect of the polyethers was attributed to their ability to solvate the potassium ion by a combined action of oxygen atoms within the same molecule. The concept of a self-solvating catalyst, characterized by having the catalytically active RO^- group and the K^+ solvating oxygen atoms in the same molecule, and having the general formula $CH_3(OCH_2CH_2)_nO^-K^+$, was presented in a previous note.⁷ The catalytic

activity of these catalysts in the isomerization of linolenic acid methyl ester was compared with that of potassium *t*-butylate. At a catalyst concentration of 0.1 mole per litre in diethyl ether solution the rate of isomerization was about 600 times higher with $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{7-8}\text{O}^-\text{K}^+$ than with $(\text{CH}_3)_3\text{CO}^-\text{K}^+$ as catalyst.

In the present paper the catalytic activity of the self-solvating catalysts is compared with the activity of potassium *t*-butylate on the isomerization of α -methylallylbenzene and 2-butenylbenzene in both diethyl ether and dioxane solutions.

The reactions are:



The equilibrium is far to the right for both reactions.

EXPERIMENTAL

Procedure

Most of the isomerization reactions were carried out in 25 ml glass-stoppered Erlenmeyer flasks with a side arm. A micro beaker containing 50 mg of the unsaturated compound was placed in the side arm and 5 ml of catalyst solution was pipetted into the bottom of the flask. The entire procedure was carried out in an atmosphere of nitrogen. The temperature of the reaction flask was adjusted to 17°C in a constant temperature bath. The reaction was started by tipping the micro beaker into the catalyst solution and shaking the flask vigorously. After a given time the reaction was stopped by adding methanol, and the mixture was diluted further with methanol to a suitable concentration for spectrophotometric analysis. Four to eight separate runs with varying reaction times were carried out to determine each rate constant.

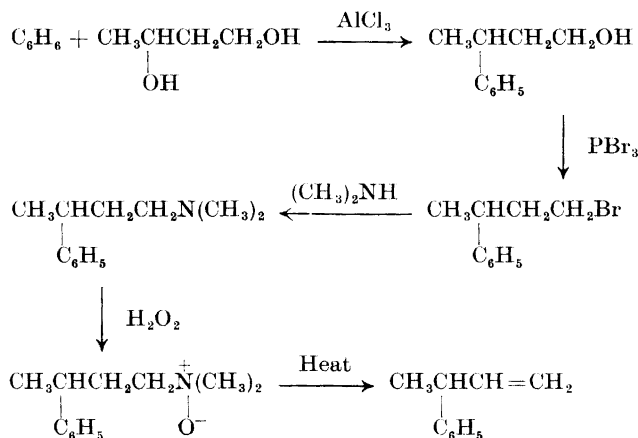
The procedure described above did not give satisfactory results with longer reaction times in diethyl ether, because the silicone grease used on the glass joint of the reaction flask did not withstand ether vapour for many hours. Better results in these cases were obtained by using a flask containing 10 times more catalyst solution. Thus the relatively slow isomerization of α -methylallylbenzene with potassium *t*-butylate in diethyl ether solution was carried out in a 100 ml flask containing 50 ml catalyst solution at the start. Five aliquots of 5 ml were withdrawn after different times in the course of 8 h. Each aliquot was immediately added to methanol. The transfer operations were carried out inside transparent plastic bags filled with nitrogen.

Because of the very long reaction times required for the isomerization of 2-butenylbenzene with potassium *t*-butylate in diethyl ether solution at 17°C, these reactions were carried out in sealed glass ampules.

The conjugated compounds corresponding to α -methylallylbenzene and 2-butenylbenzene have characteristic absorption maxima at 245 m μ and 250 m μ , respectively. The extinction coefficients at these maxima were determined with a Hilger & Watts H 999 Ultrascan spectrophotometer.

Reagents

α -Methylallylbenzene was prepared by the five step synthesis shown in the chart below.⁸



3-Phenyl-1-butanol was prepared by the method of Losev and Smirnova.⁹ 320 g of 1,3-butanediol (99 %; from Dr. Theodor Schuchardt GmbH) was reacted with 1000 ml of dry benzene (*p.a.* quality from E. Merck AG.) in the presence of 950 g of aluminium chloride (*purum* quality from Fluka AG.). Distillation and redistillation of the crude product gave 240 g of pure 3-phenyl-1-butanol, $n_D^{25}=1.5190$, b.p. 120–122°C/20 mm.

The subsequent sequence is similar to that employed by Cram¹⁰ and Bonner *et al.*¹¹ for the preparation of 3-phenyl-1-butene (α -methylallylbenzene) uncontaminated by 2-phenyl-2-butene.

The 3-phenyl-1-butanol was converted to 3-phenyl-1-brombutane by the method of Rupe and van Walvaren.¹² The crude product was distilled *in vacuo* and 156 g of the pure bromide was obtained. The bromide was reacted in dioxane solution with 200 g of dimethylamine (*purum* quality from Fluka AG.) in a steel bomb at 100°C for 18 h. The product was isolated and purified by the method of Cram¹⁰ giving 79 g of 1-*N,N*-dimethylamino-3-phenylbutane, b.p. 100–103°/8 mm, $n_D^{25}=1.4936$. The amine was converted to its oxide by stirring with 120 g of 30 % hydrogen peroxide solution for 24 h.¹⁰ The excess of hydrogen peroxide was decomposed by stirring with a suspension of 5 g platinum black (prepared by the procedure of Feulgen¹³) in 200 ml of water. The suspension was added slowly, and the reaction flask was cooled in an ice bath. The solution was filtered, and water was removed at low pressure (temperature below 40°C). To remove more water from the amine oxide 250 ml of absolute ethanol was added and carefully distilled off under reduced pressure.

The amine oxide was then heated in a Claisen flask in an oil bath under a pressure of about 1 mm. The temperature was gradually increased to 125°C. The crude olefin product which distilled was collected in a dry ice-acetone trap. This distillate was shaken with a mixture of pentane and water. The pentane layer was washed with dilute hydrochloric acid, dilute sodium carbonate solution, and finally with water. After drying over sodium sulphate the solvent was distilled off, and the residue fractionally distilled under reduced pressure, giving as the main fraction, 36 g of α -methylallylbenzene, b.p. 40–42°C/10 mm. $n_D^{25}=1.5053$ (Ref. 10 gives $n_D^{25}=1.5055$). The product gave a single peak when checked by gas chromatography.

2-Butenylbenzene (from Dr. Theodor Schuchardt, GmbH) was used without further purification. Three gas chromatograms, using different columns, all showed a single peak. The IR spectrum showed a strong absorption at 10.4 μ , indicating the presence

of the *trans* isomer. Absence of the *cis* isomer could not be shown from this spectrum, but that the compound was essentially one isomer was supported by the kinetic studies.

Diethyl ether. Commercial diethyl ether was treated with lithium aluminium hydride and distilled into a flask containing liquid potassium-sodium alloy from which the ether was distilled once more. The distillations were carried out in an atmosphere of nitrogen. B.p. 34–35°C.

1,4-Dioxane "zur Analyse" from E. Merck AG. A potassium iodide test showed that the dioxane contained some peroxides which were removed by reduction with sodium and small amounts of water. The dioxane was refluxed with sodium for 48 h, then distilled under an atmosphere of nitrogen, b.p. 100–101°C.

t-Butanol "für die Chromatographie" from E. Merck AG.

Triethylene glycol monomethyl ether. The "pract." quality from Fluka AG.

Polyethylene glycol monomethyl ether with average molecular weight between 335 and 365 ("Carbowax 350") from Union Carbide Co.

Potassium from Riedel de Haën AG.

Methanol "zur Analyse" from E. Merck AG.

Nitrogen "highly purified" from Norsk Hydro. Nitrogen and argon content higher than 99.99 %, water content less than 0.001 %.

Preparation of catalyst solutions. The potassium alcoholates were prepared by reacting the corresponding alcohols at a concentration of 0.5–1.0 mole per litre in 1,4-dioxane solution with an excess of potassium metal. To complete the reaction the mixture was refluxed for 48 h. Traces of hydroxide were allowed to settle and the clear solution of potassium alcoholate was used to prepare the catalyst solutions required. The 1,4-dioxane solutions were prepared by dilution with purified 1,4-dioxane. The ether solutions were prepared by removing the dioxane by distillation under reduced pressure and adding purified diethyl ether. The preparation of the catalyst solutions was carried out in an atmosphere of nitrogen.

RESULTS AND DISCUSSION

The isomerization reactions of α -methylallylbenzene and 2-butenylbenzene were found to follow first order kinetics at constant catalyst concentration. The integrated form of the rate expression may be written as

$$\ln \frac{\epsilon_E}{\epsilon_E - \epsilon} = k' t \quad (1)$$

where ϵ is the extinction coefficient at the time t , ϵ_E is the extinction coefficient at equilibrium, and k' is the first order rate constant.

In Fig. 1 are shown the results of the isomerization of 2-butenylbenzene with $K^+O(CH_2CH_2O)_{7-8}CH_3$ in 1,4-dioxane solution. The first order rate constant was evaluated from the slope of the straight line. The rate constants for other systems were evaluated from similar plots. The molar extinction coefficient ϵ_E was found to be about 12 600 for α -methylallylbenzene and 17 500 for 2-butenylbenzene. For the isomerization products from α -methylallylbenzene Cram¹⁴ reported a molar extinction coefficient of 12 100 at 243 $m\mu$ for *cis*-2-phenyl-2-butene (methyl groups in *cis* position) and 8160 at 235 $m\mu$ for the *trans* isomer. Cram *et al.*¹⁵ found that the isomerization of α -methylallylbenzene with potassium *t*-butylate in *t*-butanol at 75°C produced a ratio of *cis* to *trans* 2-phenyl-2-butene of about 60:1. This was explained by the higher energy of the transition state leading to the *trans* allylic anion, owing to the greater steric inhibition of coplanarity of the conjugated system in the *trans* anion compared to the *cis* allylic anion. Applied to the isomeriza-

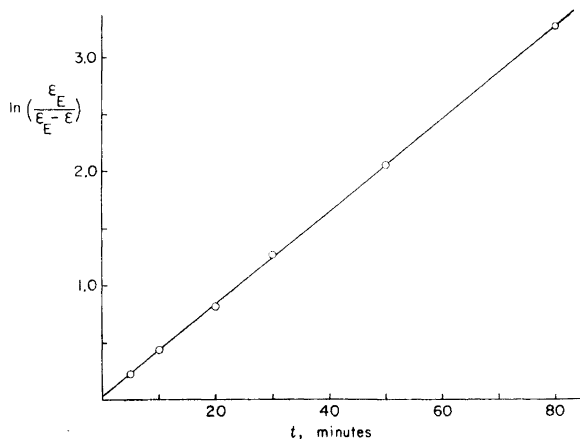


Fig. 1. First-order plot for the isomerization of 2-butenylbenzene with $\text{K}^+\text{O}(\text{CH}_2\text{CH}_2\text{O})_{7-8}\text{CH}_3$, 0.083 M in 1,4-dioxane solution. Temperature 17°C.

tion of 2-butenylbenzene the same argument predicts the formation of only a minor proportion of *cis*-1-butenylbenzene (see Fig. 2.). According to Cram *et al.*¹⁵ the kinetic ratio between *cis* and *trans* isomers in the product formed during the isomerization does not necessarily have the same value as the *cis*-to-*trans* ratio in the equilibrium mixture. Thus the ϵ_E given in the above equation may not be the true equilibrium value, but in our cases we expect ϵ_E to be close to the true equilibrium value.



Fig. 2. *trans*-2-Phenyl-2-butene and *cis*-1-butenylbenzene.

The results of the isomerization of α -methylallylbenzene and 2-butenylbenzene are given in Tables 1 and 2. The marked effect of the solvent on the catalytic activity of potassium *t*-butylate which has been reported previously^{1,5,6} is also observed in the present work. The rate of isomerization of α -methylallylbenzene with potassium *t*-butylate is about 9 times higher in dioxane than in diethyl ether. For 2-butenylbenzene the rate is about 18 times higher in dioxane than in diethyl ether.

The superior catalytic activity of the self-solvating catalysts compared to that of potassium *t*-butylate is obvious by comparing the data given in Tables 1 and 2. Furthermore it is seen that the catalytic activity of the self-solvating catalysts increases markedly with increasing chain length of the polyglycol. Table 3 gives the rates of isomerization of α -methylallylbenzene

Table 1. Isomerization of α -methylallylbenzene. Temperature 17°C.

Catalyst	Solvent	Catalyst conc. C_T moles/l	First order rate constant k' min ⁻¹
$K^+OC(CH_3)_3$	Diethyl ether	0.084	1.63×10^{-3}
	1,4-Dioxane	0.083	1.52×10^{-2}
	»	0.042	1.20×10^{-2}
	»	0.021	0.95×10^{-2}
$K^+O(CH_2CH_2O)_3CH_3$	1,4-Dioxane	0.084	0.105
	»	0.042	0.048
	»	0.021	0.025
$K^+O(CH_2CH_2O)_{7-8}CH_3$	Diethyl ether	0.083	1.14
	1,4-Dioxane	0.083	1.16
	»	0.044	0.56
	»	0.021	0.28

Table 2. Isomerization of 2-butenylbenzene. Temperature 17°C.

Catalyst	Solvent	Catalyst conc. C_T moles/l	First order rate constant k' min ⁻¹
$K^+OC(CH_3)_3$	Diethyl ether	0.165	9.09×10^{-5}
	»	0.083	7.25×10^{-5}
	»	0.021	4.63×10^{-5}
	1,4-Dioxane	0.083	1.33×10^{-3}
$K^+O(CH_2CH_2O)_3CH_3$	Diethyl ether	0.083	4.00×10^{-3}
	1,4-Dioxane	0.083	3.68×10^{-3}
$K^+O(CH_2CH_2O)_{7-8}CH_3$	1,4-Dioxane	0.083	4.05×10^{-2}

and 2-butenylbenzene with the self-solvating catalysts in dioxane solution relative to the rate with potassium *t*-butylate. The difference in catalytic activity between the two types of catalysts is seen to be considerably less for 2-butenylbenzene than for α -methylallylbenzene.

It is seen from Tables 1 and 2 that the activity of the self-solvating catalyst is nearly the same in diethyl ether and dioxane, a result which confirms the minor effect of the solvent on the catalytic activity of the self-solvating catalyst previously reported.⁷ This fact of course also implies that the ratio of the catalytic activity of the self-solvating catalysts to that of potassium *t*-butylate is considerably higher in diethyl ether than in dioxane. Another striking difference between the two types of catalyst follows from the results in Tables 1 and 2. The reaction order with respect to potassium *t*-butylate is found to be about 1/3 both in dioxane solution with α -methylallylbenzene and in diethyl ether solution with 2-butenylbenzene. In the case of the self-solvat-

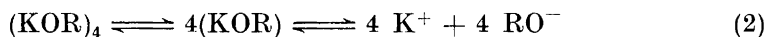
Table 3. Relative catalyst activity in 1,4-dioxane. Temp. 17°C. Catalyst concentration 0.083 moles/l.

Catalyst	α -Methylallylbenzene	2-Butenylbenzene
$K^+{}^-OC(CH_3)_3$	1	1
$K^+{}^-O(CH_2CH_2O)_3CH_3$	6.9	2.8
$K^+{}^-O(CH_2CH_2O)_{7-8}CH_3$	76.4	30.5

ing catalysts the reaction appears to be approximately first order with respect to the catalyst.

The low order with respect to potassium *t*-butylate is consistent with an association of the ion pairs. From ebullioscopic measurements in tetrahydrofuran and 1,2-dimethoxyethane Bessonov *et al.*¹⁶ found an average degree of association of about 4 for potassium *t*-butylate in the concentration range 0.03 to 0.15 moles per litre. Isopiestic measurements carried out in our laboratory with potassium *t*-butylate in diethyl ether solution also showed an average association number of about 4 in the same range of concentrations. From electrical conductivity measurements of potassium *t*-butylate in tetrahydrofuran Bessonov *et al.*¹⁶ concluded that the concentration of free ions is very low in ethereal solutions. It may be expected, however, that the catalytic activity of the free butylate ion is very much higher than that of the neutral ion pair.

If it is assumed that the free butylate ion is the only catalytic species, the order of reaction observed in the present case cannot be explained by a dissociation of the simple form



This would give an order of 1/8 with respect to the catalyst while the experimental result is about 1/3. This result might therefore suggest that neutral ion pairs of various degrees of association make a considerable contribution to the catalytic activity. At the relatively high concentration of catalyst employed there may, however, be formed different ionic associates, which may explain the high order with respect to the catalyst even if the free butylate ions are the only active species. Thus the formation of triple ions of the type $(K_2OR)^+$ would remove K^+ ions from the solution and thereby tend to increase the concentration of free RO^- ions more with increasing concentration of catalyst than expected from the simple dissociation equilibrium (2). Kinetic investigations over a wider concentration range, including measurements at much higher dilution of catalyst would be necessary before any conclusion about the nature of the actual reactive species in the case of potassium *t*-butylate can be reached. Such investigations are in progress. The higher catalytic activity of potassium *t*-butylate in dioxane compared to the diethyl ether solution is explained by a stronger primary solvation of the potassium ion in the former solvent.

The first order with respect to the catalyst which was found in the case of the self-solvating catalyst suggest that this catalyst exists completely in the form of single ion pairs. The high reactivity of these ion pairs probably results from an intramolecular solvation of the potassium ion by a combined action of the ethereal oxygen atoms in the same molecule as the catalytically active RO^- group. This may lead to a reduction of the anion-cation interaction, and thereby to an increase in the catalytic activity of the ion pair. In anionic polymerization reactions a similar enhanced reactivity is experienced for the solvent-separated ion pairs.¹⁷ The relative solvent-independence of the catalytic activity of the self-solvating catalysts is also in accordance with the assumption of intramolecularly solvated ion pairs as the reactive species.

The fact that the ratio of the catalytic activity between the self-solvating catalyst and potassium *t*-butylate is considerably higher for the isomerization of α -methylallylbenzene than for 2-butenylbenzene seems to indicate that the catalytically active species of potassium *t*-butylate is more active than that of the self-solvating catalyst. This would seem to be in accordance with the assumption that free butylate ions are the catalytically active species. The higher rate in the case of the self-solvating catalyst would therefore have to be explained as resulting from a higher concentration of active species.

The above argument may be explained simply as follows. Let us assume that free butylate ions are the only reactive species in the case of potassium *t*-butylate. These anions are assumed to be formed from dissociation equilibria of ion pairs and higher neutral and ionic associates. The experimental first order rate constant k_b' may then under the experimental conditions be expressed as

$$k_b' = k_b C_b = k_b K_x C_{Tb}^{1/3} \quad (3)$$

where k_b is the specific catalytic constant of the free butylate ions, C_b is the concentration of free butylate ions, C_{Tb} is the total concentration of potassium *t*-butylate and K_x may be considered as a constant in the region where the experimental order is about 1/3. The experimental first order rate constant for the self-solvating catalyst k_s' is given by

$$k_s' = k_s C_{Ts} \quad (4)$$

where k_s is the specific catalytic constant for the intramolecularly solvated ion pairs and C_{Ts} is the total concentration of the self-solvating catalyst. If $C_{Ts} = C_{Tb} = C_T$ the ratio of the experimental first order rate constants of the self-solvating catalyst and potassium *t*-butylate may be expressed by the Brønsted relation as

$$\frac{k_s'}{k_b'} = \frac{k_s}{k_b} \cdot \frac{C_{Ts}}{C_b} = \left\{ \frac{K_{Bs}}{K_{Bb}} \right\}^\beta \cdot \frac{1}{K_x} \cdot C_T^{2/3} \quad (5)$$

where K_{Bs} and K_{Bb} are the base constants of the self-solvating catalyst and the free butylate ion, respectively, β is a constant characteristic for the reaction and has a value between zero and unity. The value of K_{Bb} is certainly much higher than that of K_{Bs} . The ratio k_s'/k_b' therefore increases when the value of β decreases. The results in Table 3 suggest that the value of β is

higher for the isomerization of 2-butenylbenzene than for the faster isomerization of α -methylallylbenzene. This is to be expected in the present case where the rate determining step consists of a simple proton abstraction. As more energy is required for the proton abstraction the base strength becomes more important.

The advantage of the self-solvating catalysts is more pronounced in solvents of low dissociating capacity. Their advantage in inert solvents is further emphasized by their very high solubility compared to normal alcoholates. As discussed above the results further suggest that the advantage of the self-solvating catalysts decreases as proton abstraction becomes more difficult.

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REFERENCES

1. Price, C. C. and Snyder, W. H. *J. Am. Chem. Soc.* **83** (1961) 1773.
2. Schriesheim, A., Hoffmann, J. E. and Rowe, C. A., Jr. *J. Am. Chem. Soc.* **83** (1961) 3731.
3. Ugelstad, J., Jenssen, B. and Mørk, P. C. *Acta Chem. Scand.* **16** (1962) 323.
4. Schriesheim, A. and Rowe, C. A., Jr. *J. Am. Chem. Soc.* **84** (1962) 3160.
5. Ugelstad, J., Rokstad, O. A. and Skarstein, J. *Acta Chem. Scand.* **17** (1963) 208.
6. Ugelstad, J. and Rokstad, O. A. *Acta Chem. Scand.* **18** (1964) 474.
7. Ugelstad, J., Mørk, P. C. and Jenssen, B. *Acta Chem. Scand.* **17** (1963) 1455.
8. See *Acknowledgement*.
9. Losev, I. P. and Smirnova, O. V. *J. Gen. Chem. USSR* **28** (1958) 965.
10. Cram, D. J. *J. Am. Chem. Soc.* **74** (1952) 2146.
11. Bonner, W. A., Stehr, C. E. and Jefferson, R. D. A. *J. Am. Chem. Soc.* **80** (1958) 4734.
12. Rupe, H. and van Walvaren, F. *Helv. Chim. Acta* **13** (1930) 369.
13. Feulgen, R. *Ber.* **54** (1921) 360.
14. Cram, D. J. *J. Am. Chem. Soc.* **71** (1949) 3883.
15. Cram, D. J. and Uyeda, R. T. *J. Am. Chem. Soc.* **86** (1964) 5466.
16. Bessonov, V. A. et al. *J. Gen. Chem. USSR* **37** (1967) 96.
17. Shimomura, T., Smid, J. and Szwarc, M. *J. Am. Chem. Soc.* **89** (1967) 5743.

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