The Reaction of Carbon Monoxide with Organometallic Compounds. IX. The Syntheses of Cyclic Ketones and Polyketones by the Reaction of Carbon Monoxide with Polymethylene Dilithiums*[1]

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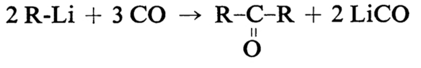
In the preceding paper[2] of this series, it was reported that carbon monoxide reacted with organolithium compounds in an ether solution at −70°C, producing corresponding symmetrical ketones in good yields. In these reactions, it was assumed that carbon monoxide attacked organolithium compounds nucleophilically and abstracted the lithium as lithium carbonyl, producing symmetrical ketones (Eq. 1):



$$2\,\text{R-Li} + 3\,\text{CO} \rightarrow \text{R-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-R} + 2\,\text{LiCO} \qquad (1)$$

As this new method is simple and can be extended to similar reactions in good yields, the present authors carried out the reaction of carbon monoxide with polymethylenedilithiums by applying this reaction to a

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* Part VIII: This Bulletin, 37, 341 (1964).

[1] This work was presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

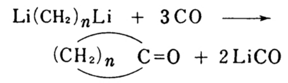
[2] M. Ryang and S. Tsutsumi, This Bulletin, 35, 1121 (1962).

TABLE I.

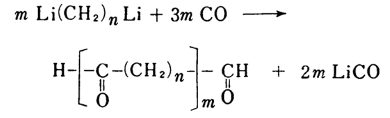
	$Li(CH_2)_4Li$			$Li(CH_2)_5Li$			$Li(CH_2)_6Li$	
	1	2	3	1	2	3	1	2
$Br(CH_2)_nBr$ (mol.)	0.1	0.025	0.025	0.1	0.1	0.1	0.1	0.1
Li (g. atom)	0.5	0.13	0.13	0.5	0.5	0.5	0.5	0.5
Ethyl ether (ml.)	200	200	400	150	180	250	200	300
Product (g.)								
a) Polymer	5.0	0.5	0.4	5.8	7.8	6.6	7.5	5.7
b) Cyclic ketone	0.2	0.2	0.8	0	0.1	0.2	0.3	0.6
c) Dialdehyde	0.6	0.1	0.2	0.8	0.1	0.2	0.2	0.3
d) Trimer	1.6	0.1	0.1	0.7	0.5	0.3	0.3	1.2
e) Tetramer	0.1	0.1	0.2	0	0	0	0.2	0.4
f) Acid	0.6	0	0	0.5	0.4	0.3	0.6	0.4

synthetic method of cyclic ketones (by intramolecular ketonization) and poly-ketones (by intermolecular ketonization).

The polymethylenedilithiums (tetramethylenedilithium, pentamethylenedilithium and hexamethylenedilithium) were prepared by the reaction of the corresponding polymethylenedibromide with methallic lithium in an ether solution at $-10\sim-5°C$.[3] Then pure, dry carbon monoxide was bubbled into the solution at $-70°C$. Thus cyclic ketones (Eq. 2) (cyclopentanone, cyclohexanone and cycloheptanone) and several poly-ketones (Eq.3) were synthesized :



$$\mathrm{Li(CH_2)}_n\mathrm{Li} + 3\mathrm{CO} \longrightarrow \mathrm{(CH_2)}_n\,\mathrm{C{=}O} + 2\mathrm{LiCO} \qquad (2)$$



$$m\,\mathrm{Li(CH_2)}_n\mathrm{Li} + 3m\,\mathrm{CO} \longrightarrow \mathrm{H}-\left[-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-(\mathrm{CH_2})_n-\right]_m-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} + 2m\,\mathrm{LiCO} \qquad (3)$$

$n=4$, 5 and 6.

The synthesis of poly-ketones by the reaction of ethylene and carbon monoxide under high carbon monoxide pressure was exclusively studied by Hanford, Brubaker and Coffman.[4] Brubaker, Coffman and Hoehn[5] have reported detailed studies of the formation condition and structure of the poly-ketone. These reactions were carried out under high carbon monoxide pressure and the carbonyl groups were irregularly inserted, while the authors' method can be used at low temperatures under atmospheric pressure and the carbonyl groups in poly-ketones are regularly inserted.

Also, we have undertaken a study of the effect of dilution with a solvent (diethyl ether) on the yields of cyclic ketones; it has been found that the yields of cyclic ketones are considerably increased by the high dilution of polymethylenedilithium with a solvent.

Results and Discussion

The results of the reactions of carbon monoxide with polymethylenedilithiums are summarized in Table I.

Poly-ketones. — The poly-ketones (products a) were obtained as an ether-insoluble precipitate after the hydrolysis of the reaction mixtures with dilute hydrochloric acid and purification by the ordinary method.[5]

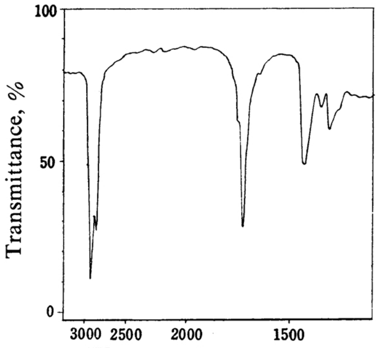


Fig. 1. Infrared spectrum of poly-ketone, $-[-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-(-\mathrm{CH_2})_5-]_n-$

TABLE II. THE EFFECT OF DILUTION WITH A SOLVENT

	1	2	3
$Br-(CH_2)_4-Br$ (mol.)	0.1	0.025	0.025
Diethyl ether (ml.)	200	200	400
The degree of dilution	1	4	8
Cyclopentanone, yield* (%)	2.5	10	40
Poly-ketone, yield* (%)	56	24	19

* The calculations of yields are based on the amount of tetramethylenedibromide used.

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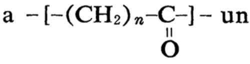
[3] R. West and E. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

[4] H. Gilman, *Organic Chemistry: An Advanced Treatise*, Vol. IV, 1025—1042.

[5] M. M. Brubaker, D. D. Coffman and H. H. Hoehn, *J. Am. Chem. Soc.*, **74**, 1509 (1952).

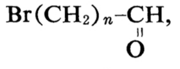
TABLE III.

Fraction		$Li(CH_2)_4Li$	$Li(CH_2)_5Li$	$Li(CH_2)_6Li$
(1)	b. p.	60~ 90°C/70 mmHg	60~ 80°C/30 mmHg	65~ 85°C/12 mmHg
(2)	b. p.	110~150°C/17 mmHg	140~160°C/25 mmHg	100~125°C/17 mmHg
(3)	b. p.	155~160°C/ 3 mmHg	150~170°C/ 3 mmHg	155~164°C/17 mmHg
(3)	b. p.	~180°C/ 3 mmHg		~160°C/ 3 mmHg

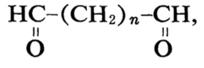
The infrared spectra of the poly-ketones showed the presence of methylene and a carbonyl group (1690~1700 cm^{-1}) ; the elementary analysis of these poly-ketones are correct for $C_{n+1}H_{2n}O$ (n=4, 5, 6,), which indicates that these poly-ketones have a  $-[-(CH_2)_n-\underset{\underset{O}{\|}}{C}-]-$ unit as a monomer unit. Typical infrared spectra of poly-ketone are reproduced in Fig. 1.

Cyclic Ketones. — Cyclic ketones (products b) were obtained by the distillation of the neutral part under reduced pressure, and their structures were determined by ordinary methods, such as elementary analysis, mixed-melting-point measurements of their 2, 4-dinitrophenylhydrazones, and infrared spectra measurements. It was found that dilutions of polymethylenedilithiums with diethyl ether lead to increasing yields of cyclic ketones and decreasing yields of poly-ketones. (Cf., for example, Table II.) This method of synthesizing cyclic ketones under high dilution with a solvent seemed to be the simplest way to prepare cyclic ketones from aliphatic compounds. (Earlier methods may be seen in the literature cited in Ref. 6.)

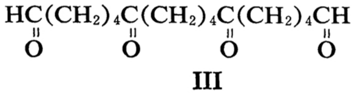
Other Products. — Various by-products were produced by these reactions. Among these by-products, the following compuuds (I—III) were isolated; their structures were assumed on the basis of the results of elementary analyses, infrared spectra measurements and molecular weight measurements.


$Br(CH_2)_n-\underset{\underset{O}{\|}}{C}H$,

I


$H\underset{\underset{O}{\|}}{C}-(CH_2)_n-\underset{\underset{O}{\|}}{C}H$,

II


$H\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}H$

III

These products are thought to be the precursors to the poly-ketones.

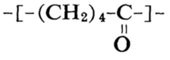
Experimental

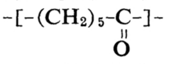
Materials.—Commercial polymethylenedibromides were purified by fractional distillation: tetramethylenedibromide (b. p. 113~115°C/60 mmHg), pentamethylenedibromide (b. p. 118~119°C/34 mmHg, n_D^{15} 1.5146), and hexamethylenedibromide (b. p. 138~139°C/34 mmHg, n_D^{15} 1.5111).

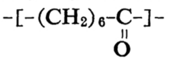
The Preparation of Polymethylenedilithiums.—Into a 500 ml. four-necked flask equipped with a mechanical stirrer, a low temperature thermemoter, a reflux condenser protected from moisture, a gas bubbler and a dropping funnel, 50 ml. of anhydrous diethyl ether (dried over sodium) were placed; after the apparatus had been swept with dry oxygen-free nitrogen, 3.5 g. (0.5 g. atom.) of lithium in the form of small pieces of thin coil was added. A solution of polymethylenedibromide (0.1 mol.) in 100 ml. of anhydrous diethyl ether was stirred in via the dropping funnel over a period of 1 hr., while the internal temperature was maintained at −10~−5°C.

The Reaction of Carbon Monoxide with Polymethylenedilithium.—After the addition had been completed, the stirring was continued for another hour, after which the reaction mixture was cooled to −70°C with a dry ice-methanol bath kept at −78°C. Dry pure carbon monoxide was then introduced from the gas bubbler at a rate of 0.5 l./min. for 1 hr. The reaction mixture was then decomposed with 50 ml. of 95% ethanol and, further, with 100 ml. of 6 N hydrochloric acid. Then poly-ketone was precipitated as an ether-insoluble solid and was filtered off under reduced pressure. The organic layer separated from the filtrate was treated with three succesive 50-ml. portions of saturated aqueous potassium carbonate and divided into (1) the organic layer and (2) the potassium carbonate solution.

Poly-ketones. — The precipitate was dissolved in hot benzene, and then this solution was added to methanol by means of a vigorous agitation. The polymer, separated as a powder, was filtered; this procedure was repeated three times, and then the polymer was dried to a constant weight. The elementary analysis of these poly-ketones are:


$-[-(CH_2)_4-\underset{\underset{O}{\|}}{C}-]-$ polymer. Found: C, 70.99; H, 8.93. Calcd. for C_5H_8O: C, 71.39; H. 9.53%


$-[-(CH_2)_5-\underset{\underset{O}{\|}}{C}-]-$ polymer. Found; C, 74.40; H, 10.80. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27%.


$-[-(CH_2)_6-\underset{\underset{O}{\|}}{C}-]-$ polymer. Found: C, 76.59; H, 10.83. Calcd. for $C_7H_{12}O$: C, 75.00; H, 10.78%.

The organic layers containing neutral compounds were washed with water and dried over anhydrous sodium sulfate. The brownish residual oils obtained after the removal of the solvent were distilled under reduced pressure to give the following fractions (Table III).

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6) L. Ruzicka et al., *Helv. Chim. Acta*, **9**, 249, 499 (1926); J. C. Sauer, *J. Am. Chem. Soc.*, **69**, 2448 (1947); J. Heer and K. Miescher, *Helv. Chim. Acta*, **31**, 1289 (1948); Monsanto Chemical Co., *Chem. & Eng. News*, **1957**, 85; K. Ziegler et al., *Ann.*, **504**, 94 (1933).

Cyclic Ketones.—Fraction 1 was assumed to be mainly cyclic ketones, which were identified by mixed-melting-point measurements of their 2, 4-dinitrophenylhydrazones and by elementary analysis. The yields of cyclic ketones were calculated from the results of gas chromatographic analysis (Column-SiDC 550, 2 m. ; or P. E. G. 6000, 2 m.; carrier gas, H_2).

Cyclopentanone. — 2, 4 - Dinitrophenylhydrazone (m. p. 144°C, recrystallized from ethanol).

Found : C, 49.62 ; H, 4.25. Calcd. for $C_{11}H_{12}O_4N_4$: C, 49.80 ; H, 4.53%.

Cyclohexanone. — 2, 4 - Dinitrophenylhydrazone (m. p. 157.5∼158°C, recrystallized from ethanol).

Found : C, 52.16 ; H, 5.09. Calcd. for $C_{12}H_{14}O_4N_4$: C, 51.80 ; H, 5.07%.

Cycloheptanone. — 2, 4 - Dinitrophenylhydrazone (m. p. 146.5∼147°C, recystallized from ethanol).

Found : C, 53.13 ; H, 5.32. Calcd. for $C_{13}H_{16}O_4N_4$: C, 53. 42 ; H, 5.52%.

From fraction 1 (from hexamethylenedilithium), 6-bromohexamethylenealdehyde was also isolated. 2, 4-Dinitrophenylhydrazone (m. p. 227∼228°C, recrystallized from ethylacetate).

Found: C, 42.20; H, 4.83. Calcd. for $C_{13}H_{17}O_4N_4Br$: C, 41.83 ; H, 4.60%.

Dialdehyde. — Fraction 2 was assumed to be dialdehyde, $HCO(CH_2)_nCHO$; $n=4,5,6$. Pimeloaldehyde (II) was identified from the results of the mixed-melting-point measurement of its 2, 4-dinitrophenylhydrazone (m. p. 183∼184°C, recrystallized from ethanol-ethylacetate).

Found : C, 46.32 ; H, 3.98, Calcd. for $C_{19}H_{20}O_8N_8$: C, 46.74 ; H, 4.09%.

Ketoaldehyde (trimer).—Fraction 3 was assumed to be ketoaldehyde (trimer) from the results of its infrared spectra and molecular weight measurements. For example, tetradeca-5, 10-dione-1, 14-dialdehyde (III) ;

Found : C, 70.21 ; H, 9.74. Mol. wt. (in benzene). 285. Calcd. for $C_{16}H_{24}O_4$: C, 68.05 ; H ; 9.28%. Mol. wt. 282.

IR Spectrum.—1680 cm^{-1} and 1700 cm^{-1}.

Other Products.—The sublimable brownish crystals obtained from fraction 3 (in tetramethylenedilithium) were recrystallized from benzene to give yellowish crystals, m. p. 202°C ; mol. wt. 145 ; elementary analysis : C, 72.98 ; H, 7.56% ; IR spectrum 1670 cm^{-1}). However, the structure of these crystals has not yet been determined. The acidic parts were not examined.

Summary

The reactions of carbon monoxide with tetramethylenedilithium, hexamethylenedilithium and pentamethylenedilithium at −70°C have yielded the corresponding poly-ketones (monomer unit : $-CO(CH_2)_n-$, $n=4, 5$ and 6) and cyclic ketones (cyclopentanone, cyclohexanone and cycloheptanone). In these reactions, high dilutions of polymethylenedilithiums with a solvent (diethyl ether) lead to the formation of cyclic ketones in good yields. For example, cyclopentanone has been obtained in a 40% theoretical yield.

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