in pentane (300 ml.) solvent was carried out according to the procedure described for the dichloro ester. The final organic solution was distilled. The material boiling at 62–67°/115 mm. (92 g., n_D^{25} 1.4372) was redistilled to give 72 g. (b.p. 67°/115 mm., n_D^{25} 1.4468, 55.5% yield) of pure 1,1-dichloro-2,2-dimethylcyclopropane (II). The yield of di-*t*-butyl carbonate (148 g., b.p. 89°/65–70 mm., m.p. 38–40°) was 91%.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Synthesis of Medium- and Large-Ring Ketones *via* the Dieckmann Condensation

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The Dieckmann cyclization of a series of α,ω-diesters, diethyl suberate through diethyl thapsate, has been carried out with potassium *t*-butoxide in xylene under high dilution conditions with high speed stirring in a nitrogen atmosphere, and some medium- and large-ring monoketones and large-ring diketones, with carbonyl groups diametric, have been obtained. The relative yields have been compared with those of the corresponding carbocyclic ketones and diketones obtained by other methods.

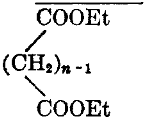
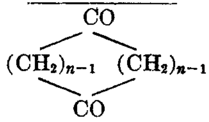
The concept has been generally held that the Dieckmann cyclization of diesters is applicable only to the formation of the classical rings of five, six, and seven members, as originally employed.[1] With the conviction that suitable conditions could extend the usefulness of this reaction and in the interest of providing an additional route to larger cyclic ketones, we have examined the relative proportions of monoketones and diketones obtainable following the cyclization of a series of α,ω-diesters with potassium *t*-butoxide in xylene under high dilution conditions in a nitrogen atmosphere.

These cyclization conditions were employed originally for the synthesis of an eight-membered ring aminoketone by Sentz[2] in this laboratory, who also suggested their application to the formation of cycloakanones of greater ring size than seven members. Potassium *t*-butoxide has been used successfully for the cyclization of various aminodiesters to eight-[3–7] and ten-membered[6] ring aminoketones and sixteen-[6] and twenty-membered[6] ring diaminodiketones. Sodium hydride, which Blicke and his co-workers[8] employed for the synthesis of cyclooöctanone *via* a Dieckmann condensation, has also been used for the preparation of eight-membered[6,9,10] ring aminoketones and sixteen-membered[9] ring diaminodiketones.

In the present investigation we have carried out the Dieckmann cyclization of the esters (I), diethyl suberate through diethyl thapsate, under identical conditions, employing potassium *t*-butoxide in xylene, under high dilution conditions with high speed stirring in a nitrogen atmosphere. A uniform isolation procedure was used and the monoketones (II) and diketones (III) were collected and identified, while no attempt was made to characterize any triketones or polymeric products. The yields of mono- and diketones are given in Table I. It will be observed that the conditions employed are useful for obtaining the cyclic 14- and 15-membered monoketones and the 18-, 20-, 22-, and

TABLE I

YIELDS OF KETONES PRODUCED BY THE DIECKMANN CYCLIZATION

	Actual Yield, %	
Diester (I)	Monoketone (II)	Diketone (III)
	$(CH_2)_{n-1}CO$	
$n =$ 7	47	0
8	15	11
9	0	28
10	0	12
11	0.53	23
12	0.47	16
13	24	19
14	32	2.2
15	48	0.94

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[1] (a) W. Dieckmann, *Ber.*, **27**, 102 (1894); (b) W. Dieckmann, *Ann.*, **317**, 27 (1901).

[2] R. C. Sentz, Ph.D. thesis, University of Illinois, 1952.

[3] N. J. Leonard and R. C. Sentz, *J. Am. Chem. Soc.*, **74**, 1704 (1952).

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[6] N. J. Leonard, M. Ōki, and S. Chiavarelli, *J. Am. Chem. Soc.*, **77**, 6234 (1955).

[7] N. J. Leonard, D. F. Morrow, and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 5476 (1957).

[8] F. F. Blicke, J. Azuara, N. J. Doorenbos, and E. B. Hotelling, *J. Am. Chem. Soc.*, **75**, 5418 (1953).

[9] N. J. Leonard and M. Ōki, *J. Am. Chem. Soc.*, **77**, 6241 (1955).

[10] N. J. Leonard and M. Ōki, *J. Am. Chem. Soc.*, **77**, 6245 (1955).

TABLE II

HIGHEST YIELD METHODS FOR THE SYNTHESIS OF KETONES

Compound II	Method	Yield,[a] %
Cycloheptanone	Ziegler's cyclization of dinitrile	96[11]
Cycloöctanone	Ziegler's cyclization of dinitrile	89[11]
Cyclononanone	Diazomethane on cycloöctanone or	61[12]
	Acyloin condensation; reduction	27[13]
Cyclodecanone	Acyloin condensation; reduction	ca. 50,[14] 54[13]
Cyclohendecanone	Acyloin condensation; reduction	53[13]
Cyclododecanone	Acyloin condensation; reduction	68[13]
Cyclotridecanone	Acyloin condensation; reduction	59[13]
Cyclotetradecanone	Acyloin condensation; reduction	75[13]
Cyclopentadecanone	Ziegler's cyclization of dinitrile	60[11]
III		
1,8-Cyclotetradecanedione	Blomquist's diketene reaction	10[15]
1,9-Cyclohexadecanedione	Blomquist's diketene reaction	ca. 33[16]
1,10-Cycloöctadecanedione	Dieckmann reaction or	28[17]
	Ziegler's cyclization of dinitrile	28[11]
1,11-Cycloeicosanedione	Blomquist's diketene reaction or	26[18]
	Ziegler's cyclization of dinitrile	25[11]
1,12-Cyclodocosanedione	Ziegler's cyclization of dinitrile	60[11]
1,13-Cyclotetracosanedione	Dieckmann reaction	16[17]
1,14-Cyclohexacosanedione	Dieckmann reaction	19[17]
1,15-Cycloöctacosanedione	Dieckmann reaction	2.2[17]
1,16-Cyclotriacontanedione	Ziegler's cyclization of dinitrile	18[19]

[a] From precursor specified or obviously assumed from the steps mentioned.

24-membered diketones. Diethyl azelate and diethyl tetradecanedioate provided approximately equimolar quantities of the corresponding mono- and diketones. In the range of lowest (or negligible) monoketone yield (II—9, 10, 11, 12), where the steric repulsion of the alkylene chains suppresses the closure of the medium-size rings, intermolecular condensation followed by intramolecular cyclization of the longer chains resulted in diketone formation (III—9, 10, 11, 12). In selected cases where the yield of monoketone was appreciable, it was improved in ratio to diketone by operating under higher dilution conditions, that is, by extending the addition time for the diester from 24 hr., which was taken as the standard, to a longer period.

While the Dieckmann reaction, even as here modified, has uneven utility in synthesizing carbocyclic ketones from straight-chain diesters, its addition to the storehouse of synthetic tools for preparing many-membered rings is significant. The steps from ester to carbalkoxyketone involve the use of a strong base, a base which acts practically irreversibly for best results, but since the hydrolysis and decarboxylation steps may not require strong acid treatment, the latter feature may direct the use of the Dieckmann condensation for the closure of a ring containing a labile group. The intermediate carbalkoxyketone may also provide the means of bringing about the attachment of other substituents on the large ring.

Finally, a comparison of yields of carbocyclic ketones obtained by various methods leads to the conclusion that there is no one reaction which is perfect for the synthesis of the entire spectrum of cyclic ketones. The methods which give the highest yield of ketone in each case, irrespective of ease or expense of synthesis and ease of purification of product, are summarized in Table II. It will, of course, be recognized that not all of the possible methods may have been applied to the synthesis of each compound; nevertheless, this table is intended as a useful guide and as an indication of our present state of experience based on published, detailed methods.

Blomquist, Prager, and Wolinsky[16] have provided a method for the reduction of diametric diketones to monoketones, so that compounds of type III may be considered to be precursors of large-ring carbocyclics of type II.

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(11) K. Ziegler and R. Aurnhammer, *Ann.*, **513**, 43 (1934).

(12) E. P. Kohler, M. Tischler, H. Potter, and H. T. Thompson, *J. Am. Chem. Soc.*, **61**, 1057 (1939).

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(14) *Org. Syntheses*, **36**, 79, 14 (1956).

(15) A. T. Blomquist and R. D. Spencer, *J. Am. Chem. Soc.*, **70**, 30 (1948).

(16) A. T. Blomquist, J. Prager, and J. Wolinsky, *J. Am. Chem. Soc.*, **77**, 1804 (1955).

(17) Present work.

(18) A. T. Blomquist and R. D. Spencer, U.S. Patent 2,584,664 (Feb. 5, 1952).

(19) K. Ziegler, H. Eberle, and H. Ohlinger, *Ann.*, **504**, 94 (1933).

EXPERIMENTAL[20]

General procedure for the Dieckmann cyclizations. The Dieckmann cyclizations were all run using the special apparatus previously described.[3–6,9] A 2-l. Morton flask was equipped with a Morton high speed stirrer[21] and a cyclic high dilution apparatus[3,22,23] which carried a dropping funnel and a reflux condenser with stopcock attached.[3] Nitrogen was admitted through the lower end of the stirrer shaft and passed out through a drying tube which protected the top of the reflux condenser. A third joint of the flask was used for the admission of reactants to the flask. The dry apparatus was flushed with nitrogen, and 1.2 l. of dry xylene was added to the flask. Two hundred milliliters of xylene were distilled from the flask at the stopcock on the reflux condenser. This insured removal of any moisture which might have resisted preliminary drying. Refluxing was discontinued and nitrogen passage was accelerated. Twelve molar equivalents of distilled *t*-butyl alcohol and 4.8 atomic equivalents of potassium were added to the flask. After the potassium *t*-butoxide had been formed, the excess *t*-butyl alcohol and about 100 ml. of xylene were distilled from the flask. One molar equivalent of diethyl ester (I) dissolved in 250 ml. of xylene was then introduced dropwise over a period of approximately 24 hr. During this period a nitrogen atmosphere was retained, stirring and refluxing were continued, and an ethanol-xylene mixture was removed by distillation at approximately the same rate as liquid was being added. After all of the ester had been added stirring and refluxing were continued for an hour; then the reaction mixture was allowed to cool to room temperature.

The reaction mixture was made acidic by adding glacial acetic acid in excess. The reaction mixture was washed three times with 50 ml. of water. The xylene solution was filtered to remove insoluble polymeric ketones, and the filtrate was concentrated to a small volume by distillation at reduced pressure. To the residue was added a dilute solution of hydrochloric acid (*ca.* 3*N*); hydrolysis and decarboxylation were effected by refluxing overnight. In several cases ethanol was added to the decarboxylation medium to promote solubility of the ketoesters. In these cases the unreacted starting material was recovered as diester instead of as acid. The reaction mixture was extracted with ether, and the combined ether extracts were extracted with a 10% aqueous solution of sodium bicarbonate. The bicarbonate extracts, when acidified, yielded unreacted starting material as dicarboxylic acid.

The ethereal solution was distilled and the ketones and ester were collected. The ketones were characterized by the close similarity of their physical properties with those previously reported: boiling point or melting point, n_D, and melting point of a suitable derivative. The infrared carbonyl maxima (5% solutions in carbon tetrachloride) for the diketones are given for the first time. The yields appear in Table I.

Cycloheptanone.[24]

Cycloöctanone,[24] and 1,9-cyclohexadecanedione, m.p. 83–85°,[25] ν_{max} 1713 cm.$^{-1}$

1,10-Cycloöctadecanedione, m.p. 95–97°,[25] ν_{max} 1716 cm.$^{-1}$

1,11-Cycloeicosanedione, m.p. 49–51°,[25] ν_{max} 1715 cm.$^{-1}$

Cyclohendecanone; semicarbazone, m.p. 202–204°,[26] and 1,12-cyclodocosanedione, m.p. 54–55.5°,[25] ν_{max} 1715 cm.$^{-1}$

Cyclododecanone, m.p. 58–61°,[25] and 1,13-cyclotetracosanedione, m.p. 62–63.5°,[25] ν_{max} 1716 cm.$^{-1}$

Cyclotridecanone, m.p. 26–29°;[25] semicarbazone, m.p. 205–206° (dec.),[26] and 1,14-cyclohexacosanedione, m.p. 65–68°,[25] ν_{max} 1715 cm.$^{-1}$

Cyclotetradecanone, m.p. 55.5–56°,[25] and 1,15-cyclooctacosanedione, m.p. 72–73.5°,[25] ν_{max} 1716 cm.$^{-1}$

Cyclopentadecanone, m.p. 64–66°,[25] and 1,16-cyclotriacontanedione, m.p. 76–78°,[15] ν_{max} 1716 cm.$^{-1}$

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(20) Melting points are corrected. Infrared spectra were recorded by Mr. James Brader and his associates in this laboratory.

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(22) A. C. Cope and E. C. Herrick, *J. Am. Chem. Soc.*, **72**, 983 (1950).

(23) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5884 (1952).

(24) Compared with commercially available material.

(25) L. Ruzicka, M. Stoll, H. W. Huyser, and H. A. Boekenoogen, *Helv. Chim. Acta*, **13**, 1152 (1930). Reported melting points are close or identical.

(26) L. Ruzicka, M. Stoll, and H. Schinz, *Helv. Chim. Acta*, **9**, 249 (1926). Reported melting points are close or identical.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD RESEARCH INSTITUTE, AND THE ETHYL CORP.]

Uncatalyzed Addition of Bromotrichloromethane to Ethylene and Substituted Ethylenes. I. Nature and Scope of the Reaction[1]

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The uncatalyzed addition of bromotrichloromethane to ethylene and various substituted ethylenes has been found to give good yields of the 1:1 adducts. The adducts are the same as those obtained from the peroxide-, light-, or gamma radiation-induced additions. The reaction is believed to be a thermally initiated free radical chain reaction.

Numerous workers[3–15] have studied the catalytic addition of bromotrichloromethane to ethylene and substituted ethylenes. These reactions have been initiated by the use of peroxides, gamma radiation,

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(1) The work reported herein was supported in part by the Ethyl Corp., Baton Rouge, La., and by Stanford Research Institute, Menlo Park, Calif.

(2) Stanford Research Institute, Menlo Park, Calif.

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(4) M. S Kharasch, U. S. Patent **2,464,869** (March 22, 1949).

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