AgSeCN, KSeCN/KNO$_3$/AgNO$_3$/Ag. The cell was permitted to attain equilibrium in the dark in ten to fifteen hours with the salt-bridge removed. Upon insertion of the salt-bridge, the immediate potentiometer reading was taken as the final equilibrium point owing to the rapid deposition of selenium on the silver electrode and the resultant lowering in e.m.f. Table I lists e.m.f. values observed for this cell at several concentrations of potassium selenocyanate near 0.1 *M* and the K_{sp} values that were obtained by solving the Nernst equation. The activity coefficients of potassium selenocyanate required for these calculations were taken as the mean of values for the activity coefficients of potassium bromide and iodide.[2,3] The K_{sp} values appear to be in fair agreement considering the difficulty of measurement arising from the drift in potentiometer readings as noted above.

TABLE I

K_{sp} VALUES FOR SILVER SELENOCYANATE AT 25 ± 0.1°

Expt.	*M*, KSeCN	*M*, AgNO$_3$	E.m.f., volt	K_{sp} $\times 10^{-15}$
1	0.0894	0.1363	0.7081	7.1
2	.0935	.0856	.7008	6.5
3	.0958	.3183	.7288	6.6
4	.0644	.1340	.6988	7.4

A comparison of the K_{sp} values for silver halides and halogenoids (thiocyanate and selenocyanate) as shown in Table II reveals the interesting fact that these values decrease progressively with increase in ionic weight of the anion attached to the silver ion. Points obtained by plotting ionic weights against the log of the reciprocal of K_{sp} values will be found to lie very nearly along a straight line. This would seem to be further evidence for the assumption that halide and halogenoid ions are structurally similar. The fluoride and cyanide ion which form complexes with silver ion fall outside this classification. The K_{sp} value for silver cyanate (AgOCN) is not known but might be predicted to lie between that of silver chloride and silver thiocyanate.

TABLE II

COMPARISON OF K_{sp} VALUES FOR SILVER HALIDES AND HALOGENOIDS

Anion combined with Ag$^+$	Ionic weight	K_{sp} value at 25°
Cl$^-$	35.46	1.95×10^{-10} [4]
OCN$^-$	42.02	....
SCN	58.08	1.34×10^{-12} [5]
Br$^-$	79.92	6.3×10^{-13} [4]
SeCN$^-$	104.98	6.9×10^{-15}
I$^-$	126.92	9.7×10^{-17} [4]

Experimental.—The concentration cell, held in a constant-temperature bath and away from light in a dark-room, was connected with a Type K potentiometer (Leeds and Northrup), a standard cell, a 2-volt battery, and a galvanometer. One arm of the concentration cell consisted of a standard silver nitrate solution (50 ml.) in a 100-ml. glass weighing bottle. The other side of the cell was formed in a similar fashion by dissolving a weighed sample of pure potassium selenocyanate (thrice recrystallized from absolute ethanol and dried at 100-105°) in 50 ml. of water. Silver nitrate (one drop of 0.1 *M*) was then added to the potassium selenocyanate solution and the mixture was allowed to reach equilibrium after ten to fifteen hours in the dark with occasional stirring by hand for a few minutes after every two to three hours. A thin layer of silver was flashed over the surface of the silver electrodes[6] prior to immersion in the two arms of the cell and the electrical circuit was completed by immediately setting the salt-bridge in place (saturated potassium nitrate in agar). Potentiometer readings were made within ten to fifteen seconds thereafter since the selenocyanate polarized the silver electrode in a few minutes by electrochemical deposition of an observable layer of red selenium, with the probable formation of cyanide ion and possibly some free cyanogen. In any case it is not believed that these side reactions could have seriously affected the final e.m.f. values during the short interval required for taking the readings. In the last determination (Table I) the procedure was varied by adding silver nitrate (10 ml. of 0.001 *M*) to the potassium selenocyanate solution. In this case the solubility was increased somewhat possibly owing to the colloidal nature of the precipitated silver selenocyanate.

The solubility product of silver chloride determined by the use of the above apparatus under the same experimental conditions was found to be 1.93×10^{-10} which compares favorably with the value of 1.95×10^{-10} determined by Hess and Jellinek.

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(2) Harned, THIS JOURNAL, **51**, 416 (1929).

(3) Robinson, *ibid.*, **57**, 1161 (1935).

(4) Hess and Jellinek, *Z. physik. Chem.*, **A162**, 153 (1932).

(5) (Average of four determinations) Vol. 11, p. 1182, Landolt-Börnstein "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923.

(6) Hoyt, *J. Chem. Ed.*, **14**, 185 (1937).

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Synthesis of Methyl Ketones from Diethyl Acylmalonates

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A convenient method for preparing certain methyl ketones consists in the acylation of the sodium or, preferably, the magnesiumethoxy derivative of diethyl malonate with the appropriate acid chloride, followed by hydrolysis and decarboxylation of the two ester groups of the resulting diethyl acylmalonate in the presence of acid, thus

$$\mathrm{RCOCl + C_2H_5OMgCH(COOC_2H_5)_2 \longrightarrow}$$

$$\mathrm{RCOCH(COOC_2H_5)_2 \xrightarrow[\text{Acid}]{\text{HOH}} RCOCH_3}$$

TABLE I

SYNTHESIS OF METHYL KETONES FROM DIETHYL MALONATE AND VARIOUS ACID CHLORIDES

Acid chloride	Ketone	B. p. or m. p., °C.	Over-all[a] yield, %
o-Chlorobenzoyl	*o*-Chloroacetophenone	85–87.5, 5.5 mm. 227–228 atm.[b]	81
o-Nitrobenzoyl	*o*-Nitroacetophenone	158.5–159, 16 mm.[c]	85
p-Nitrobenzoyl	*p*-Nitroacetophenone	78.5–80°(m. p.)[d]	61
Phenylacetyl	Phenylacetone	97–98.5, 13 mm. 214–215, (cor.) atm.[e]	71
2,4,6-Trimethylphenylacetic	Mesitylacetone	59.5–60.0 (m. p.)[f]	83
Hexahydrobenzoyl	Hexahydroacetophenone	64–65.5, 12 mm. 178–179 (uncor.) atm.[g]	66
Caproyl	Methyl *n*-amyl ketone	[h]	

[a] Yield of ketone is based on the acid chloride. [b] Thorpe and Brunskill, THIS JOURNAL, **31**, 1260 (1915). Oxime, m. p. 105–106°. These authors report m. p. of 104°, for oxime. [c] Camps, *Ber.*, **32**, 3232 (1899). [d] Drewsen (ref. 6) reported m. p. of 80–81°. Oxime, m. p. 170–171° (uncor.); Posner [*Ann.*, **389**, 43 (1912)] reported 172–173°. [e] Fourneau and Tiffeneau, *Compt. rend.*, **141**, 663 (1905). Semicarbazone, m. p. 187–190° (Tiffeneau and Cahnmann, *Bull. soc. chim.*, [5] **3**, 1880–1881 (1935)). [f] *Anal.* Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.16. Found: C, 81.58; H, 9.25. Holmberg [*Svensk Kem. Tid.*, **40**, 304–305 (1928)] reported the preparation of the semicarbazone (m.p. 198–199°), but was unable to isolate the free ketone. We prepared a semicarbazone m. p. 204–205° (uncor.). *Anal.* Calcd. for $C_{13}H_{19}N_3$: N, 18.00. Found: N, 18.22. (Microanalyses by Arlington Laboratories, Fairfax, Virginia.) [g] B. p. 179–180°, Darzens, *Compt. rend.*, **144**, 1124 (1907). Semicarbazone, m. p. 175–176°, Bouveault, *Bull. soc. chim.*, [3] **29**, 1051 (1903). [h] No appreciable amount of methyl *n*-amyl ketone could be isolated; instead, higher boiling products were obtained along with a considerable residue which appeared to have resulted from aldol condensations.

The method has previously been employed by several workers,[1] but its usefulness does not appear to have been widely recognized.

In the present investigation, satisfactory yields (Table I) have been obtained for *o*-chloroacetophenone, *o*- and *p*-nitroacetophenones, phenyl[2] and mesityl acetones, and hexahydroacetophenone, but not for methyl *n*-amyl ketone. We have chosen the magnesium ethoxy derivative of diethyl malonate[3] rather than the sodium derivative because we believe the former is prepared more conveniently. Although the acid chloride does not appear to react appreciably with the excess alcohol[3] used in the preparation of the magnesium-ethoxy derivative, we have employed a 10% excess of the latter in order to minimize this possible side reaction. The crude diethyl acylmalonates were hydrolyzed and decarboxylated in the presence of aqueous acetic and sulfuric acids according to the method previously employed for the ketonic cleavage of certain β-keto esters.[4]

The present method appears to be one of the best for the preparation of certain higher aliphatic or aliphatic-aromatic[5] methyl ketones, and especially for certain substituted acetophenones. Methods involving Grignard, Friedel–Crafts, or nitration reactions do not appear to be applicable to the preparation of *o*- or *p*-nitroacetophenones,[6] while the Friedel–Crafts reaction is not applicable to *o*-chloroacetophenone. These and other substituted acetophenones have been prepared by the acylation of acetoacetic ester, followed by hydrolysis and decarboxylation of the ester group and cleavage of the acetyl group. However there appears to be a greater tendency for *o*-acylation to occur with acetoacetic ester[7] than with malonic ester; moreover, in the acetoacetic ester method cleavage might occur at either acyl group, whereas, in the malonic ester method, cleavage of the two ester groups may usually be effected without appreciable cleavage of the acyl group.

An attempt to extend the malonic ester method using diethyl α-*n*-butylmalonate and *p*-nitrobenzoyl chloride has not been satisfactory under the conditions which were employed for the preparation of methyl ketones.

Experimental

General Procedure.—Diethyl acylmalonates were prepared by a modification of the procedure of Lund.[3,8] In a 500-ml. three-necked flask equipped with a mercury-sealed stirrer, dropping funnel, and reflux condenser protected by a drying tube, was placed 5.35 g. (0.22 mole) of magnesium. Five ml. of absolute ethanol and 0.5 ml. of carbon tetrachloride were added. The reaction, which started almost immediately, was allowed to proceed for a few minutes and 75 ml. of absolute ether was then added cautiously. The resulting mixture was placed on the steam bath and a solution of 35.2 g. (0.22 mole) of diethyl malonate, 20 ml. of absolute ethanol and 25 ml. of absolute ether was added at such a rate that rapid refluxing was maintained, heat being applied when necessary. The mixture was refluxed for three hours, or until the magnesium had dissolved. To the clear solution was added with vigorous

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(1) For example, Adickes [*J. prakt. Chem.*, **161**, 271–279 (1943)] prepared methyl pentadecyl ketone; Wilds and co-workers, [THIS JOURNAL, **66**, 1688 (1944), and **68**, 89 (1946)] and Johnson and Offenhauer, [*ibid.*, **67**, 1045 (1945)] have synthesized certain rather complex methyl ketones.

(2) Metzner [*Ann.*, **298**, 378 (1897)] prepared pheny acetone by this method, but no yield is reported.

(3) Lund, *Ber.*, **67B**, 935 (1934).

(4) Hudson and Hauser, THIS JOURNAL, **63**, 3136 (1941).

(5) We believe that the malonic ester method is more convenient for phenylacetone than those described in "Organic Syntheses," Coll. Vol. II, 389, 391 (1943).

(6) *p*-Nitroacetophenone has been prepared from *p*-nitrocinnamic acid [Drewsen, *Ann.*, **212**, 160 (1882)], but the method does not appear to be any more convenient than the malonic ester method.

(7) See Bouveault and Bongert, *Bull. soc. chim.*, [3] **27**, 1039 (1902).

(8) The present procedure is similar to that of Breslow, Baumgarten, and Hauser [THIS JOURNAL, **66**, 1286 (1944)] for the preparation of ethyl-*t*-butyl acylmalonates.

stirring[9] an ethereal solution of 0.20 mole of the acid chloride and the mixture refluxed for one-half hour. The reaction mixture was cooled and acidified with dilute sulfuric acid. The ether phase, with which an ether extract of the aqueous phase was combined, was washed with water and the solvent distilled.

To the crude diethyl acylmalonate was added a solution of 60 ml. of glacial acetic acid, 7.5 ml. of concentrated sulfuric acid and 40 ml. of water, and the mixture refluxed for four or five hours until the decarboxylation was complete. The reaction mixture was chilled in an ice-bath, made alkaline with 20% sodium hydroxide solution, and extracted with several portions of ether. The combined ethereal extracts were washed with water, dried with sodium sulfate followed by Drierite, and the solvent distilled. The residue containing the ketone was distilled *in vacuo* or recrystallized. The results are summarized in Table I.

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[9] In certain cases a viscous mixture was formed and unless it was stirred vigorously, lower yields were obtained.

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Cyclic Thioureas

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A number of monoformyl-diamines were prepared and cyclized to the cyclic thioureas by reaction with sulfur.[1] The by-products obtained in the preparation of two N,N′-dialkyl-alkylenediamines were identified.

Experimental[2]

N,N′-Dibutyl-ethylenediamine (I).—In the preparation of this product, b. p. 110–111° (8 mm.),[3] yield, 64%, from five moles of butylamine and one mole of ethylene dichloride,[4] the high-boiling by-product obtained was identified as N,N′,N″-tributyldiethylenetriamine (II),[5] b. p. 163–165° (8 mm.). Upon titration in acetone solution with aqueous hydrochloric acid using brom phenol blue indicator, only two nitrogens of (II) were titrated.

(I) forms an insoluble monohydrate, m. p. 48–49°, recrystallized from hexane.[6]

N,N′-Dibutyl-trimethylenediamine (III).—Prepared by the method under (I), this product boiled at 120–121° (14 mm.); yield, 72%. The linear amine, N,N′,N″-tributyl-di-(trimethylene)-triamine, b. p. 164–165° (3 mm.), obtained as a by-product, behaves as a triatomic base on titration in acetone solution with aqueous hydrochloric acid, using brom phenol blue indicator.

(III) hydrate melts at 44–45°, after pressing on absorbent paper.

Formylation of Ethylenediamine (IV).—Condensation of (IV) with 85% formic acid at reflux did not produce appreciable amounts of formyl derivatives. A 30% yield of crude N-formyl-(IV),[7] b. range 90–110° (14 mm.), was obtained by the ester acylation method.[8]

TABLE I

Derivative	Formula	Nitrogen, %	
		Calcd.	Found
N,N′-Dibutyl-ethylenediamine (I)	$C_{10}H_{24}N_2$	16.3	16.1
Hydrate of I	$C_{10}H_{26}N_2O$	14.7	14.5
N,N′,N″-Tributyl-diethylenetriamine (II)	$C_{16}H_{37}N_3$	15.5	15.3
N-Formyl-(I)	$C_{11}H_{24}N_2O$	14.0	13.7
N,N′-Diformyl-(I)	$C_{12}H_{24}N_2O_2$	12.3	12.6
(I)-Dithiocarbamate[a]	$C_{11}H_{24}N_2S_2$	11.3	11.2
1,3-Dibutyl-ethylenethiourea (VI)	$C_{11}H_{22}N_2S$	13.1	13.1[b]
N,N′-Dibutyl-trimethylenediamine (III)	$C_{11}H_{26}N_2$	15.0	14.9
Hydrate of III	$C_{11}H_{28}N_2O$	13.7	13.7
N,N′,N″-Tributyl-di-(trimethylene)-triamine	$C_{18}H_{41}N_3$	14.0	13.9
N-Formyl-(III)	$C_{12}H_{26}N_2O$	13.1	13.1
N,N′-Diformyl-(III)	$C_{13}H_{26}N_2O_2$	11.6	11.9
1,3-Dibutyl-trimethylenethiourea (VII)	$C_{12}H_{24}N_2S$	12.3	12.3
N-Formyl-(V)	$C_{15}H_{16}N_2O$	11.7	11.9
N,N′-Diformyl-(V)	$C_{16}H_{16}N_2O_2$	10.4	10.2
1,3-Diphenyl-ethylenethiourea[c]	$C_{15}H_{14}N_2S$	11.0	10.9

[a] M. p. 135–136° with effervescence. Sebrell and Clifford, ref. 3, reported 134–136°. [b] Calcd.: S, 15.0. Found: S, 14.8. [c] Recrystallized from methanol, m. p. 189–190°.

Formylation of N,N′-Dibutyl-ethylenediamine (I).—Technical 85% formic acid (108 g. or 2 moles) and 86 g. (0.5 mole) of (I) reacted by the procedure described.[1] The mixture was quenched with water, alkalinized strongly, and the water-insoluble product was separated with the aid of benzene and distilled. N-Formyl-(I), 47 g., was obtained at 153–165° (7 mm.); on redistillation, the fraction boiling at 134–135° (4 mm.) was collected. N,N′-Diformyl-(I), 40 g., was recovered at 197–199° (7 mm.).

Formylation of N,N′-Dibutyl-trimethylenediamine (III).—From the reaction of 108 g. of 85% formic acid and 93 g. (0.5 mole) of (III), N-formyl-(III) was collected at 146–155° (4 mm.), and on redistillation yielded 41.6 g. (39%) of product at 148–149° (4 mm.). N,N′-Diformyl-(III), 41.3 g. (34%), was obtained at 200–201° (4 mm.).

Formylation of N,N′-Diphenyl-ethylenediamine[9] (V).—The reaction mixture from 108 g. of 85% formic acid and 106 g. (0.5 mole) of (V) was poured into 500 cc. of water, precipitating a thick oil which hardened to a semi-solid mass on standing. The supernatant liquid was decanted, the semi-solid was air-dried for 24 hours and then treated with 150 cc. of methanol at 25°. The crystals were filtered from the methanol mother liquor, washed with 50 cc. of methanol and air-dried; yield, 54 g. (45%) of N,N′-diformyl-(V), which, after crystallization from methanol, melted at 121–122°.

The aqueous supernatant liquid obtained above was filtered, alkalinized with 80 g. of 50% sodium hydroxide solution, and cooled to 25°. The solid N-formyl-(V) precipitated was filtered off, washed with water and air-dried; yield, 19 g. (14%); m. p. 65–66°, recrystallized from methanol. The monoformyl derivative is somewhat soluble in hot water and in aqueous acids.[10]

1,3-Dibutyl-ethylenethiourea (VI).—(1) A mixture of 20 g. (0.1 mole) of N-formyl-(I) and 4.0 g. of sulfur heated

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[1] Zienty and Thielke, THIS JOURNAL, **67**, 1040 (1945).

[2] All melting points are corrected.

[3] Sebrell and Clifford, U. S. Patent 1,948,317 (February 20, 1934); *Chem. Zentr.*, **105**, II, 1695 (1934), reported the b. p. to be 185–187° (3 mm.), which obviously is in error.

[4] Kyrides, U. S. Patent 2,126,560 (August 9, 1938); *Chem. Zentr.*, **110**, I, 1107 (1939).

[5] Sebrell and Clifford, ref. 3, reported the formation of N,N′-dibutylpiperazine as the by-product when two moles of butylamine reacted with one mole of ethylene dichloride.

[6] Sebrell and Clifford, ref. 3, reported 40°.

[7] This material, heated with sulfur at 130–135°, gave ethylenethiourea, m. p. 195–196°. Ruiz and Libenson, *C. A.*, **24**, 5726 (1930), reported m. p. 195° (uncor.).

[8] Hill and Aspinall, THIS JOURNAL, **61**, 822 (1939).

[9] Prepared by the method of Bennett, *J. Chem. Soc.*, **115**, 577 (1919).

[10] These properties are similar to those of N-acetyl-N,N′-diphenyl-ethylenediamine described by Bischoff and Nastvogel, *Ber.*, **22**, 1784 (1889).