[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mercuration of Ketones and Some Other Compounds with Mercuric Nitrate

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A number of ketones have been mercurated with mercuric nitrate, mercuric oxide and anhydrous calcium sulfate. Acetone gives an excellent yield of acetonylmercuric iodide after conversion of the original mercuric nitrate salt by reaction with potassium iodide. The compounds made by this new method have been converted to thiazole derivatives for characterization. The method was unsuccessful with ethyl acetate and ethyl isobutyrate but did give a product with ethyl acetoacetate. Cyclohexene gives a small yield of a trioxane. Toluene is mercurated more readily than benzene but the isomeric products are difficult to separate. Isobutylene yields no substitution product.

A mixture of three salts—mercuric nitrate, mercuric oxide and calcium sulfate (Drierite)—has previously[1] been found to be excellent for the mercuration of benzene and has now been found to be effective with ketones, in fact, the only method known for preparing a monomercury compound directly from aliphatic ketones. The hitherto most successful attempt at mercuration of acetone led to "diacetone hydrate" products[2] of uncertain composition and the formation of acetonylmercuric chloride had been achieved only indirectly from butyl isopropenyl ether.[3] Acetophenone was the only ketone which has been reported[4] as mercurated with mercuric acetate to give a simple α-mercurated product.

The roles of the three salts in the present reaction are made clear by the equations for acetone

$$2Hg(NO_3)_2 + 2CH_3C(O)CH_3 \longrightarrow 2CH_3C(O)CH_2HgNO_3 + 2HNO_3$$

$$HgO + 2HNO_3 \longrightarrow Hg(NO_3)_2 + H_2O$$

$$2CaSO_4 + H_2O \longrightarrow 2CaSO_4\cdot{}^1/_2H_2O$$

Each reaction was carried out in the ketone as a solvent and the mixture was stirred thoroughly with the high-speed stirrer.[5] The product was isolated as the mercuric iodide after reaction with potassium iodide. The yields and melting points are recorded in Table I. Replacement in the methyl group of acetone is easiest of all. In methyl isopropyl ketone substitution is at the tertiary hydrogen and not at all at a primary one. In methyl ethyl ketone, however, both α-positions are attacked.

TABLE I

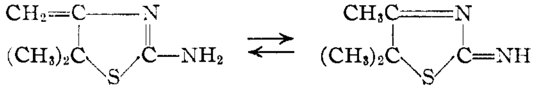
YIELDS OF MERCURIC IODIDE COMPOUNDS FROM VARIOUS KETONES

No.	Ketone	Mercuric iodide product R in RHgI	Yield,[a] %	M.p., °C.
1	Acetone	$CH_3C(O)CH_2-$	78	98–100
2	Methyl ethyl ketone	$C_2H_5C(O)CH_2-$	19	101–103
3		$CH_3C(O)CH(CH_3)-$	7	72.5–75.5
4	Methyl isopropyl ketone	$CH_3C(O)C(CH_3)_2-$	30	72.5–75.5
5	Pinacolone	$(CH_3)_3CC(O)CH_2-$	33	up to 77.5
6	Acetophenone	$C_6H_5C(O)CH_2-$	24	163–170
7		$(C_6H_5C(O)CH_2)_2-$[b]	100	168–170
8	Ethyl acetoacetate	$CH_3C(O)CH(CO_2C_2H_5)-$	47	......[c]

[a] Yields are calculated from the total mercury used. [b] The product was diphenacylmercury instead of the phenacylmercuric iodide because excess potassium iodide was used. [c] Not isolated. The yield is based on a thiazole derivative.

The mercury in these compounds is regarded as attached to carbon rather than oxygen. The solubility in organic solvents and the specific melting points accorded with the view that the bond is covalent, not polar. Infrared absorption (Fig. 1) of acetonylmercuric iodide shows that the band at 5.9 microns for the carbonyl group is present and that the one at 6.15 microns for a carbon–carbon double bond produced by enolization is absent.

The carbon to which the mercury is attached was determined by replacement of the iodomercuri group with iodine, followed by treatment with thiourea to give a thiazole derivative. The majority of these thiazole derivatives were new and authentic samples had to be prepared for comparisons. The thiazoline derived from methyl isopropyl ketone might have either of the two structures



Its hydrated benzoyl derivative is unique in that it is insoluble in neutral aqueous medium but is soluble in aqueous acid or alkali, and less change would be involved therein if such a derivative came from the amino form. The product also seemed more resistant to hydrolysis than would be expected of an imide.

Other less general characterizations of the mercuric iodide compounds were used where possible. For example, excess potassium iodide caused the phenacyl compound to undergo "symmetrization,"[6] as shown below, but this reaction was not satisfactory with acetonylmercuric iodide.

$$2C_6H_5C(O)CH_2HgI + 2KI \longrightarrow (C_6H_5C(O)CH_2)_2Hg + K_2HgI_4$$

Also alkali easily attacks acetonylmercuric iodide to give a yellow green amorphous product, possibly according to the equation below because acetone

$$2CH_3C(O)CH_2HgI + 2NaOH \longrightarrow CH_3C(O)CH_3 + C_3H_4O_2Hg_2 + 2NaI + H_2O$$

is formed when this reaction was carried out in the presence of benzaldehyde which reacted *in situ* to give dibenzalacetone.

Mercuration of ethyl acetate and methyl isobutyrate did not occur, although the red color of

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[1] Morton, Magat, Marshall and Elden, THIS JOURNAL, **69**, 908 (1947).

[2] Sand and Gessler, *Ber.*, **36**, 3704 (1903).

[3] Nesmeyanov, Lutsenko and Vereshchagina, *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 63 (1947); *C. A.*, **42**, 4149 (1948).

[4] Dimroth, *Ber.*, **35**, 2870 (1902).

[5] Morton and Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

[6] Eskin and Nesmeyanov, *Bull. acad. sci. U. R. S. S. Classe sci. chim.*, 116 (1942); *C. A.*, **38**, 4583 (1945).

mercuric oxide disappeared, a sure sign in the case of ketones and benzene that mercuration had taken place. Even the keto ester, ethyl acetoacetate, gave no soluble mercury derivative which could be isolated easily. However, treatment of the solid mixture of mercury salts and Drierite with iodine, followed by thiourea in the usual manner, did give in good yield the expected thiazole, 2-amino-4-methyl-5-carbethoxythiazole, isolated as the picrate, and this fact implies that the mercury was attached to the enol form as a polar salt which reacted with iodine to give the expected iodo product.

Cyclohexene is not metalated in a substitution process, although large amounts of an unstable addition compound, probably $C_6H_{10}(HgNO_3)(NO_3)$-1,2, is sometimes formed. The most interesting feature, however, is the formation of a very small amount of easily isolable material which contains no mercury and has properties which corresponded with the trimer of cyclopentyl aldehyde, 2,4,6-tricyclopentyl-1,3,5-trioxane or $(C_5H_9CHO)_3$. In the presence of acid this material decomposes to the aldehyde, the derivatives of which were identical with those from an authentic sample. The yield of this trimer was very low and repeated attempts with variation of temperature and proportions of reagents failed to raise the amount above 0.7 g. (usually 0.5 g.) from a single experiment. The presence of an impurity was suspected but the removal of all peroxide and the reuse of cyclohexene from a previous experiment failed to alter the quantity. Actually the use of unpurified commercial cyclohexene or of cyclohexene which had been treated with oxygen to form peroxides led to the oily addition product mentioned above. This effect of peroxides corresponds with Wright's[7] observation that the addition of mercuric salts to cyclohexene in alcohol is peroxide catalyzed.

Although cyclohexene oxide has been known[8] to give cyclopentyl aldehyde, this oxide showed little evidence of being an intermediate in this formation of the trimer. With the mercurating mixture in cyclohexane, it yielded only a trace of the trimer. The main product was a hydroxy nitrate which had properties to accord with 2-nitratocyclohexanol $C_6H_{10}(OH)(ONO_2)$-1,2.

Toluene was mercurated under these conditions in larger amount (58%) than benzene (50%) but the product was a mixture which proved exceedingly difficult to separate. Evidence for *p*-substitution was obtained by isolation of some ditolylmercury and *p*-iodotoluene, after treatment with potassium iodide and iodine, respectively. Previously reported work[9] with the mercuric acetate method likewise yielded products which were difficult to isolate.

Isobutylene is one of the most easily metalated olefins[10] but no indication of mercuration by substitution was found with this mixture of salts.

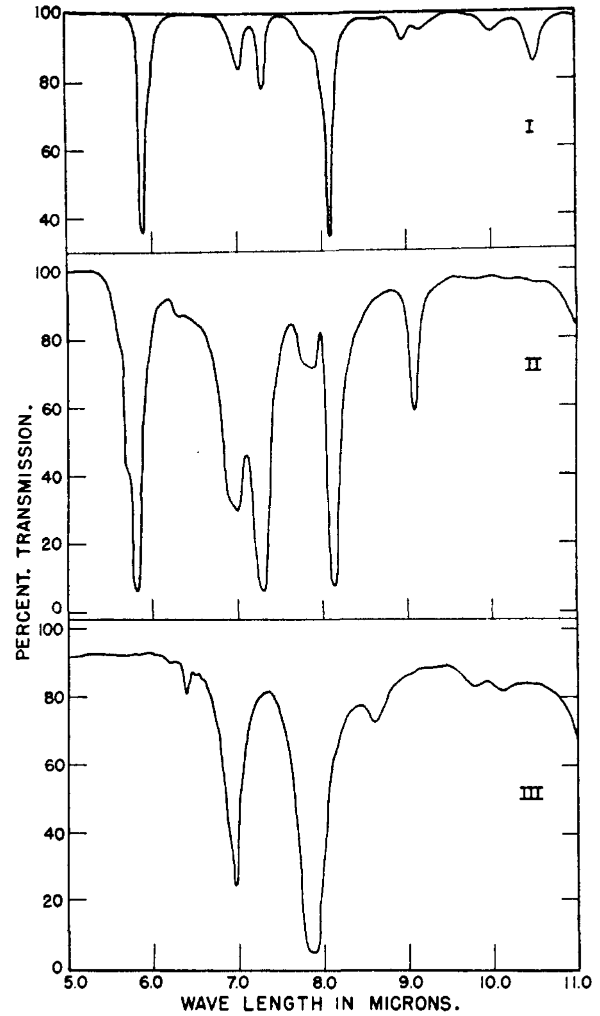

Fig. 1.—Infrared absorption of I, acetonyl-mercuric iodide; II, acetone and III, methylene chloride solvent.

The sole product was an unstable oil which changed to an amorphous solid.

The mercuration of acetone was tried with several different combinations of salts and in different solvents. The original mixture of mercuric nitrate, mercuric oxide and calcium sulfate proved best (see Table II). The use of acetone as a solvent was also best. When a mixture of acetone and benzene was used the reaction seemed to be largely with benzene, although benzene separately gave a lower yield of mercurated product and required a higher temperature than did acetone. In brief, benzene inhibited the mercuration of acetone, while acetone improved the mercuration of benzene.

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Experiments

General Procedure.—All experiments were carried out in the high-speed stirring apparatus,[5] usually in a 500-ml. flask under an atmosphere of dry nitrogen. The mercuric nitrate and oxide were Merck and Co., Inc., reagent grade. Unless otherwise noted the compound to be mercurated was used as the solvent. Usually mercuric oxide and Drierite were added first. After five or ten minutes of vigorous stirring

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(7) Romeyn and Wright, THIS JOURNAL, **69**, 697 (1947).

(8) Bedos, *Compt. rend.*, **189**, 256 (1929); Bedos and Ruyer, *ibid.*, **188**, 964 (1929).

(9) Kobe and Barduhn, *Ind. Eng. Chem.*, **38**, 247 (1946); Coffey, *J. Chem. Soc.*, **127**, 1029 (1925).

(10) Morton and Lyons, THIS JOURNAL, **72**, 3785 (1950).

(10,000 r.p.m.) the mercuric nitrate was added. A water-bath around the flask retarded the temperature rise, which required about one hour. The reaction was rapid where the red color of the oxide disappeared and the temperature was maintained there for about one-half longer.

The cooled mixture was usually filtered to remove the inorganic salts. The mercury product was assumed to be soluble and the filtrate was accordingly evaporated at reduced pressure to give the nitrate salt or, more commonly, was treated bit by bit with potassium iodide until no more potassium nitrate precipitated. Observation of this point was facilitated by a coincidental yellowing, possibly related to symmetrization. The mixture was stirred for 15 or 30 minutes longer and then filtered. Evaporation of the filtrate yielded the stable iodomercuri product which could be recrystallized usually from acetone, alcohol, pentane, benzene or mixtures of these.

Insoluble mercury compounds were probably present also with the residue but the only successful attempt to isolate them was in the preparation from ethyl acetoacetate.

All melting points were corrected.

Acetone.—A mixture of 396 g. or 6.83 moles of Merck and Co., Inc., reagent grade acetone, 20 g. or 0.092 mole of mercuric oxide, 55 g. or 0.4 mole of Drierite and 30 g. or 0.092 mole of mercuric nitrate had a reaction temperature of 56°. With 25 g. of potassium iodide 55 g. of the iodomercuriacetone was obtained as colorless plates. It was recrystallized twice from acetone and twice from benzene.

Anal. Calcd. for C_3H_5OHgI: C, 9.35; H, 1.31; I, 33.00. Found: C, 9.61; H, 1.36; I, 33.09.

This compound was hydrolyzed by aqueous acetic acid, aqueous sodium acetate and even by water, but preferably by combination of 2 g. of acetic acid and 0.5 g. of sodium acetate per 20 ml. of aqueous solution which quantitatively hydrolyzed 0.42 g. after three hours on the steam-bath. In 30 ml. of alcohol, 0.2575 g. (or 0.000669 mole) of the compound required 0.000662 mole of alcoholic iodine solution which contained 0.02001 mole of iodine per liter.

One gram of the iodomercuri compound with 25 ml. of a saturated alcoholic sodium hydroxide solution gave, at first, an oil and, in a few minutes, a yellow green solid which was insoluble in water, alcohol, acetone, ethylene glycol, acetic acid, acetic anhydride or nitrobenzene. After being successively washed with alcohol, acetone, water and acetone, 0.4 g. (m.p. 235° dec.) was obtained.

Anal. Calcd. for $C_3H_4O_2Hg_2$: C, 7.61; H, 0.85. Found: C, 7.71; H, 0.97.

The same reagents but with excess benzaldehyde were warmed to boiling and left overnight. The mixture was again heated and then filtered. The filtrate was evaporated to 15 ml. and cooled on solid carbon dioxide. The 0.1 g. (33%) of dibenzalacetone which separated was crystallized from alcohol and melted at 111–113°, identical with an authentic sample.

Attempts to prepare derivatives of the iodomercuri compound with 2,4-dinitrophenylhydrazine, hydroxylamine or semicarbazide led to simultaneous hydrolysis and formation of the derivatives of acetone.

2-Amino-4-methylthiazole picrate was made from 3.0 g. of the iodomercuri product with a slight excess of alcoholic iodine followed by warming of the solution (after removal of the mercuric iodide by filtration) with 1 g. of thiourea until dissolved. To the clear red solution was added 1.5 g. of picric acid in 25 ml. of hot alcohol. The yellow crystals (2.1 g. or 78.5% yield) were crystallized three times from alcohol. They melted at 241.5 to 242.5°, identical in a mixture with a sample made from iodoacetone which, in turn, had been made by the method of Scholl and Matthaipoulos.[11]

Anal. Calcd. for $C_{10}H_9O_7N_5S$: C, 34.99; H, 2.64; N, 20.40. Found: C, 34.81; H, 2.90; N, 20.31.

Methyl Ethyl Ketone.—The nitrate product from the reaction of 250 ml. of the ketone, 17 g. of mercuric oxide, 55 g. of Drierite and 25 g. of mercuric nitrate at 55° consumed 18 g. of potassium iodide. The crude iodomercurimethyl ethyl ketone was washed with 40 ml. of acetone and then weighed 11.5 g. (18.7%). After being recrystallized from benzene–pentane and benzene–ligroin this fraction melted at 101–103°.

Anal. Calcd. for C_4H_7OHgI: C, 12.05; H, 1.77; I, 31.84. Found: C, 11.87; H, 1.67; I, 32.00.

Six grams of this compound was converted to a thiazole hydroiodide which was dissolved in water, treated with sodium hydroxide and extracted with ether. Evaporation of the dried (over magnesium sulfate) extract left an oil which was dissolved in 5 ml. of pyridine and treated dropwise with 2 ml. of benzoyl chloride. After one-half hour on the steam-bath, the mixture was cooled and poured into 100 ml. of aqueous sodium bicarbonate. The oily product was dried in ether solution and yielded 0.4 g. (11.5%) of 2-benzamido-4-ethylthiazole. When crystallized from benzene–ligroin and aqueous alcohol, it melted at 131.5–133°.

Anal. Calcd. for $C_{12}H_{12}ON_2S$: C, 62.04; H, 5.21; N, 12.06. Found: C, 62.22; H, 5.51; N, 11.93.

This thiazole was assumed to be a 4-ethyl compound because it was different from the only possible isomer which was already well authenticated.

The isomeric methyl iodomercuriethyl ketone was obtained from the acetone wash, mentioned before, of the crude crystals. From a parallel experiment a solid (4.1 g. or 6.7%) separated from this fraction after three days at −72°. When recrystallized from benzene it melted at 72.5–75.5°.

Anal. Calcd. for C_4H_7OHgI: C, 12.05; H, 1.77. Found: C, 11.74; H, 1.39.

The original acetone wash was converted to a mixture (22.3 g.) of thiazole picrates, equivalent to 40% more yield of mercury compounds than calculated from the iodomercurimethyl ethyl ketone isolated. This mixture was difficult to separate, hence a 4.5-g. portion was suspended in ether and treated with 2 g. of lithium hydroxide[12] in 25 ml. of water. The ethereal solution was then washed with water until colorless, dried over magnesium sulfate and evaporated to give 0.6 g. of a yellow oil which was dissolved in 3 ml. of pyridine and treated with 1 ml. of benzoyl chloride. 2-Benzamido-4,5-dimethylthiazole (0.18 g.) was eventually isolated and was recrystallized from dilute alcohol (m.p. 149–150.5°).

Anal. Calcd. for $C_{12}H_{12}ON_2S$: C, 62.04; H, 5.21; N, 12.06. Found: C, 62.18; H, 5.46; N, 12.01.

An authentic sample of this thiazole was prepared from 5 g. of methyl bromoethyl ketone[13] in alcohol with 2.5 g. of thiourea. The mixture was warmed to dissolve the solid and then boiled for five minutes. A crystalline hydrobromide separated from the cooled solution. This material was converted to the free base (m.p. 76–80°, recorded[14] 82–83°). The benzamido derivative melted at 150–151° and was identical with the product derived from methyl iodomercuriethyl ketone.

Methyl Isopropyl Ketone.—A mixture of 250 ml. of the ketone with 17 g. of the oxide, 45 g. of Drierite and 25 g. of the nitrate reacted at 51° and then required 15 g. of potassium iodide to form methyl iodomercuriisopropyl ketone. The crude mixture (15 g.) of oil and solid was taken up in 20 ml. of acetone, filtered and kept at −72° for four days. The crystalline solid (7 g.) obtained melted at 72.7–75.5°, after recrystallization from benzene–ligroin.

Anal. Calcd. for C_5H_9OHgI: C, 14.55; H, 2.20; I, 30.76. Found: C, 14.51; H, 2.08; I, 30.38.

This iodomercuri compound was converted to 2-amino-4-methylene-5,5-dimethylthiazole picrate in 82% yield, which, after two crystallizations, melted at 215–216° dec. An authentic sample was made from 1.1 g. of methyl bromoisopropyl ketone[15] and 0.5 g. of thiourea in 10 ml. of alcohol. The mixture was warmed to dissolve the thiourea, then boiled for three minutes. A hot solution of 1.3 g. of picric acid in 8 ml. of alcohol caused the formation of 1.0 g. (40%) of the yellow plates of the thiazoline picrate which melted, after recrystallization, at 215–216° dec.

Anal. Calcd. for $C_{12}H_{13}O_7N_5S$: C, 38.81; H, 3.53; N, 18.86. Found: C, 39.00; H, 3.62; N, 18.88.

The identity of these two products was confirmed by calculations from X-ray diffraction patterns of the interplanar spacings in the crystals.[16]

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[11] Scholl and Matthaipoulos, *Ber.*, **29**, 1558 (1896).

[12] Burger, THIS JOURNAL, **67**, 1615 (1945).

[13] The authors are greatly indebted to Dr. T. E. Lesslie for a sample of this ketone.

[14] Jensen and Thorsteinson, *Dansk Tids. Farm.*, **15**, 41 (1941); *C. A.*, **35**, 5109 (1941).

[15] Catch, Hey, Jones and Wilson, *J. Chem. Soc.*, 276 (1948).

[16] The authors are greatly indebted to Dr. William O. Statton for the comparison.

A portion (6.5 g.) of this picrate was converted to the free 2-amino-4-methylene-5,5-dimethylthiazoline by aqueous lithium hydroxide. The ethereal solution was washed and dried (magnesium sulfate) and the ether evaporated to give 2.5 g. of a yellow oil which had the odor of musty potatoes. A portion was distilled (98–103° 1 mm.) and had n^{25}_D 1.5600.

Anal. Calcd. for $C_6H_{10}N_2S$: C, 50.67; H, 7.09; N, 19.70. Found: C, 50.83; H, 7.27; N, 19.64.

The thiazoline with benzoyl chloride gave the hydrate of a benzoyl derivative which lost a trifle over one mole of water when heated at 110° under reduced pressure.

Anal. Calcd. for $C_{13}H_{14}ON_2S$: C, 63.39; H, 5.73; N, 11.38. Found: C, 63.97; H, 6.35; N, 10.80.

The picrate of this benzoyl derivative melted sharply at 169–171°.

Anal. Calcd. for $C_{19}H_{17}O_8N_5S$: C, 48.00; H, 3.61. Found: C, 47.90; H, 3.91.

A 25-mg. portion of the benzoyl hydrate was suspended in 1 ml. of water. It dissolved when 1 ml. of 6 *N* aqueous sodium hydroxide was added. Dilute hydrochloric acid was then added dropwise. At the neutral point (litmus) a crystalline product separated. A few more drops of acid caused solution. Cautious addition of alkali would reverse the above effects.

Pinacolone.—The reaction of 100 ml. of pinacolone with 85 g. of oxide, 22.5 g. of Drierite and 12.5 g. of nitrate was carried out at 63°. Potassium iodide, 8.0 g., gave iodomercurimethyl *t*-butyl ketone, which was difficult to obtain pure because of decomposition and formation of some red mercuric iodide. Eventually 10.8 g. (33%) of product was obtained which melted over a range up to 77.5°.

A portion (5.3 g.) was dissolved in 10 ml. of alcohol, treated with iodine (this product is strongly lachrymatory) and thiourea (1.5 g.) and warmed on the steam-bath for 15 minutes. An ethereal solution of this hydroiodide was treated with ammonium hydroxide, the solution dried and the ether removed at reduced pressure. The oily product was then treated with 3 ml. of acetic anhydride and a quarter drop of sulfuric acid. This mixture was warmed, the acid was removed by bicarbonate, and the 2-diacetylamino-4-*t*-butylthiazole was recrystallized from benzene, ligroin and combinations of these solvents until the melting point remained at 190–191°.

Anal. Calcd. for $C_{11}H_{16}O_2N_2S$: C, 54.98; H, 6.71; N, 11.66. Found: C, 54.73; H, 7.27; N, 11.39.

Acetophenone.—The mixture of 500 ml. of acetophenone, 38 g. of oxide, 93 g. of Drierite and 50 g. of nitrate reacted at 71.5°. After treatment with 50 g. of potassium iodide and filtration, the solid was washed with 500 ml. of benzene and the washings added to the filtrate. An aliquot portion of the filtrate and washings was evaporated at low pressure at 50° for five days. The semi-solid residue was digested with 50 ml. of acetone. The dissolved portion with iodine and thiourea gave 2-amino-4-phenylthiazole, which was first obtained as an impure picrate and then converted again to 2.5 g. of crude thiazole. After alternate crystallizations from benzene–ligroin and dilute aqueous alcohol, the crystals melted at 149–150° (recorded[17] 147°). This amount corresponded to a yield of 8.2% of phenacylmercuric iodide from the original reaction mixture. The solid iodomercuriacetophenone (12 g. or 15.8%) left after the above digestion melted from 163 to 170°, after crystallizations from benzene and acetone.

Anal. Calcd. for C_8H_7OHgI: C, 21.51; H, 1.58; I, 28.41. Found: C, 21.57; H, 1.54; I, 27.84.

One gram of this iodomercuri product was dissolved in 30 ml. of warm acetone and treated with 0.2 g. of potassium iodide. After one-half hour the mixture was filtered and the filtrate cooled to −72°. Crystals (0.55 g.) of diphenacylmercury precipitated, which, after being crystallized from benzene, melted at 168–170°.

Anal. Calcd. for $C_{16}H_{14}O_2Hg$: C, 43.78; H, 3.22. Found: C, 43.84; H, 3.29.

This compound was sensitive to diffused light and was kept in an amber colored bottle.

Ethyl Acetate and Methyl Isobutyrate.—These esters were treated with the mercurating mixture in much the same way as for acetone. A striking feature was the instantaneous decoloration of the oxide, but no product could be isolated by the treatment given the acetone reactions. Mercuric oxide with the ester or the nitrate alone did not lose its color.

Ethyl Acetoacetate.—In a mixture of 100 ml. of the keto ester (Eastman Kodak Co. pure grade refractionated), 6.7 g. of oxide, 20 g. of Drierite and 10 g. of nitrate, the red color disappeared within five or ten minutes. An additional 6.7 g. of the oxide was almost instantly decolorized, as were two more portions of 6.7 g. each added later. After 45 minutes at a maximum temperature of 32°, the mixture was stirred for 15 minutes more with 10 g. of potassium iodide. The liquid was separated from the solid in a centrifuge but contained no material that was readily characterized as a simple iodomercuri product, although 4.0 g. of residue which began to decompose at 205° was obtained. The solid left by the centrifuge was shaken in alcohol with successive small quantities of iodine until a color showed that a slight excess was present. Thiourea was added to the filtrate from this treatment and the mixture warmed until no lachrymating effect was perceptible. An 85-ml. portion of this solution with 8 g. of solid picric acid then gave 9.0 g. of crystals after 24 hours. Four grams of the crude product was treated with lithium hydroxide to recover the free base in ether. The dried (over magnesium sulfate) layer was evaporated on a steam-bath. When the ether was nearly gone 2-amino-4-methyl-5-carbethoxythiazole solidified with a crackling and popping like pop-corn in a yield of 0.3 g. (16.6%). The melting point was 173–175° (recorded[18] 175°).

Cyclohexene.—A typical experiment used 250 ml. of cyclohexene, 45 g. of Drierite, 25 g. of mercuric nitrate and 17 g. of mercuric oxide for thirty minutes at a maximum temperature of 70°. No potassium iodide was used. If the cyclohexene had been freed from peroxide by treatment with ferrous sulfate or had been well fractionated or recovered from a previous experiment, the filtrate from the reaction left a residue after evaporation which crystallized (0.5 g.) from acetone. The compound was almost too soluble in pentane to be crystallized well. Repeated crystallizations from acetone and pentane failed to raise the melting point above 119.5–123.5°.

Anal. Calcd. for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27; mol. wt., 294. Found: C, 73.57; H, 10.37; mol. wt., 315.

A portion (0.25 g.) of this trimer was treated with 0.5 g. of 2,4-dinitrophenylhydrazine in 15 ml. of alcohol. Seven drops of concentrated hydrochloric acid was added and the mixture boiled for ten minutes. The crystals, which separated when the solution was cooled, were crystallized six times from alcohol and from benzene–pentane and melted at 160.5–161.5°. The recorded[19] value for the 2,4-dinitrophenylhydrazone of cyclopentylaldehyde is 158.7°.

Another portion (0.1 g.) was steam distilled from a 60% (by volume) sulfuric acid solution. Some unchanged trimer was removed from the distillate and the filtrate was then treated with a solution of 0.2 g. dimethone in 4 ml. of alcohol. The mixture stood for 24 hours and was then heated at 70° for eight hours. About 0.1 g. of crystals separated from the cooled mixture. When recrystallized from dilute alcohol by means of a Craig[20] tube, the crystals melted at 162.5–164.5°. The recorded[21] value for the dimethone of cyclopentyl aldehyde is 162–163°. The material was identical (mixed melting point) with an authentic sample from the aldehyde prepared from *trans*-cyclohexandiol-1,2 by the method of Tiffeneau and Tchoubar.[22]

When the cyclohexene was not purified, evaporation of the filtrate from the reaction mixture left an oil (24 g. or more) which did not crystallize. When titrated with iodine the amount consumed was equivalent to a molecular weight of 425. The calculated value for $C_6H_{10}(ONO_2)(HgNO_3)$-1,2 is 407. Conversion to $C_6H_{10}(ONO_2)I$-1,2 was assumed. The corresponding bromide made by treatment of the oil with a chloroform solution of bromine was distilled at low vacuum. One fraction which came over at 58–63° (3–4 microns) and had n^{25}_D 1.5210 had a composition indicative of 1-bromo-2-nitratocyclohexane.

Anal. Calcd. for $C_6H_{10}O_3Br$: C, 32.1; H, 4.45; Br, 35.7. Found: C, 34.7; H, 4.95; Br, 36.6.

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[17] Traumann, *Ann.*, **249**, 38 (1889).

[18] Zuercher, *Z. Chem.*, **11**, 327 (1868).

[19] Dunbar and Adkins, THIS JOURNAL, **54**, 442 (1934).

[20] Craig and Post, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 413 (1944).

[21] Newman, THIS JOURNAL, **57**, 732 (1935).

[22] Tiffeneau and Tchoubar, *Compt. rend.*, **199**, 1626 (1934).

Cyclohexene oxide[23] (7.5 g.) in 250 ml. of olefin-free cyclohexane was treated with 17 g. of mercuric oxide, 40 g. of Drierite and 25 g. of mercuric nitrate for one and one-half hours at a temperature of 65° as a maximum. The usual change in color did not take place. The filtrate from the reaction mixture was evaporated at reduced pressure. The yellow oily residue (9 g.) had properties which agreed with those expected for the mono-nitrate ester of cyclohexandiol $C_6H_{10}(OH)(ONO_2)$-1,2. A fraction distilled at 84.5° (1 mm.) and had $n^{25}D$ 1.4769.

Anal. Calcd. for $C_6H_{11}O_4N$: C, 44.71; H, 6.88; N, 8.69. Found: C, 44.89; H, 6.71; N, 8.67.

A diphenylamine test gave a deep blue color. A solid urethan derivative melted, after crystallization twice from carbon tetrachloride and five times from benzene–ligroin, at 145.5–146.5°.

Anal. Calcd. for $C_{17}H_{18}O_5N_2$: C, 61.81; H, 5.49; N, 8.48. Found: C, 62.08; H, 5.73; N, 8.38.

Benzene and Toluene.—Thiophene-free benzene (250 ml.) was mercurated with 15 g. (0.046 mole) of mercuric nitrate, 8 g. of mercuric oxide (0.037 mole) and 40 g. (0.294 mole) of Drierite. After one hour the temperature was 65° but little change in color had occurred. During the next hour, the temperature was raised to 81°. The filtrate from this mixture was concentrated at reduced pressure to 50 ml. Pentane, 100 ml., was then used to precipitate 14.5 g. (50.3% based on the total mercury) of the phenylmercuric nitrate which melted at 127.5–131.5°.

Sulfur-free toluene (500 ml.) was mercurated with 60 g. (0.184 mole) of mercuric nitrate, 45 g. (0.21 mole) of mercuric oxide and 105 g. (0.77 mole) of Drierite. The temperature was slowly increased to 80° within two hours and the reaction there continued for 2.25 hours more. One-half of the filtrate from the mixture, when evaporated at reduced pressure, left a residue of 38.3 g. or 58.5% based on the total mercury used. This mixture was not separated by crystallization. A sample, once precipitated, could not be completely dissolved a day later, probably because of the formation of a basic salt. A 16.3-g. portion was, however, dissolved in 775 ml. of acetone and treated with 7.5 g. of potassium iodide. The mixture was shaken mechanically for 30 minutes and left overnight. The solid was then recovered by filtration, was digested with 100 ml. of boiling acetone, and this solution was cooled to −72°. Crystals of di-*p*-tolylmercury (0.4 g.) separated. They were recrystallized six times (ligroin, alcohol, benzene–petroleum ether). Slow evaporation of an alcohol solution over two months proved the best method. The yield was 0.11 g.; m.p. 241.3–243.0°, recorded[24] 238°.

The other half of the filtrate was treated with 20.25 g. (a slight excess) of iodine dissolved in toluene. The inorganic mercury salts were removed by filtration and the filtrate fractionated. A mixture of iodotoluenes, 17.8 g., was collected from 45–49° (1–2 mm.). No high boiling residue remained in the flask. This mixture was dissolved in 20 ml. of pentane and shaken with 3% sodium thiosulfate to remove the red color. The organic layer was cooled to −72°. The crystals obtained in this manner, after some recrystallization, melted at 32–33.5°. The recorded[25] value for *p*-iodotoluene is 35°. The total amount of this compound was 1.72 g. or 21% of the mixture.

Isobutylene.—The reaction was carried out in 200 ml. of thiophene-free benzene with 5 g. of isobutylene, 14.5 g. of mercuric nitrate, 10 g. of mercuric oxide and 25 g. of Drierite. During the first hour the temperature rose from 15 to 38° where the reaction was continued for 1.5 hours longer. The red color disappeared but the filtrate from the mixture gave only a small amount of a dark oil.

Variation of Mercurating Conditions.—Table II shows the variety of salts and solvents used in these tests.

TABLE II

EFFECT OF DIFFERENT SALTS AND SOLVENTS ON MERCURATION

Salt,[a] g.	Oxide[b] or equivalent, g.	Drierite, g.	Solvent,[c] ml.	Max. temp., °C.	Time, hr.	Yield,[d] %
N 30	Hg 20	55.0	A. 500	55	1.5	78
N 12.5	Hg 8.5	22.5	EA. A.[e] } −100	55	1.5	46
N 12.5	Mg 3.0	20.0	A. 125	55	1.5	17
N 25.0	Ba[f] 9.0	30.0	A. 250	55	1.5	0
Ac. 24.5	Hg 17.0	45.0	A. 250	55	1.5	0
S 22.8	Hg 17.0	45.0	A. 250	55	1.5	0
N 12.5	Hg 8.5	22.5	AB.[g]	65	2.0	60
N 12.5	Hg 8.5	25.0	EA. B } −110	55	0.5	13
N 15.0	Hg 8.0	40.0	B 250	81	1.5	50

[a] N, Ac. and S refer, respectively, to the nitrate, acetate and sulfate. [b] Hg, Mg and Ba refer, respectively, to mercuric oxide, magnesium oxide and barium carbonate. [c] A., EA., and B. refer, respectively, to acetone, ethyl acetate and benzene. [d] In all cases, the product was acetonylmercuric iodide except in the last three where phenylmercuric iodide was obtained. [e] Equal volumes of these two solvents were used. [f] A steady stream of gas was evolved from 34 to 55° for one hour. [g] This experiment was a competitive one with equal moles of acetone and benzene present. The product was expected to be largely acetonylmercuric iodide, although no decoloration took place at 55° where normally acetone is mercurated. The cooled reaction mixture was treated with 7.7 g. of solid potassium iodide and the filtrate from this mixture evaporated. The oily residue was then titrated to a slight excess of iodine. The mercuric iodide thus formed was 22.75 g., equivalent to 65% of all the mercury used in the reaction. The iodo compound thus obtained was expected to be largely acetonylmercuric iodide but yielded only 1.3 g. of 2-amino-4-methylthiazole picrate equivalent to 7.6% of the mercurated product or 5% of the total mercury used. The residues were collected and iodobenzene shown to be present by careful fractionation. Nitration of a portion gave *p*-nitroiodotoluene which was identical with an authentic sample.

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(24) Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co. (Reinhold Publishing Corp.), New York, N. Y., 1921, p. 181.

(25) Korner, *Z. Chem.*, 11, 327 (1868).