technique and a standardized solution of methylsulfinyl carbanion.

Experimental

Methylenetriphenylphosphorane. General Procedure.—Sodium hydride (0.10 mole as a 55% dispersion in mineral oil) in a 300-ml. three-necked flask was washed with several portions of *n*-pentane to remove the mineral oil. The flask then was equipped with rubber stopples, a reflux condenser fitted with a three-way stopcock, and a magnetic stirrer. The system was alternately evacuated and filled with nitrogen; 50 ml. of dimethyl sulfoxide was introduced *via* syringe, and the mixture was heated at 75–80° for *ca.* 45 min., or until the evolution of hydrogen ceased. The resulting solution of methylsulfinyl carbanion[2] was cooled in an ice–water bath, and 35.7 g. (0.10 mole) of methyltriphenylphosphonium bromide[3] in 100 ml. of warm dimethyl sulfoxide was added. The resulting dark red solution of the ylide was stirred at room temperature for 10 min. before use.

Methylenecyclohexane.—Freshly distilled cyclohexanone, 10.8 g. (0.11 mole), was added to 0.10 mole of methylenetriphenylphosphorane, and the reaction mixture was stirred at room temperature for 30 min. followed immediately by distillation under reduced pressure to give 8.10 g. (86.3%) of methylenecyclohexane, b.p. 42° (105 mm.) which was collected in a Dry Ice trap. [lit.,[3] b.p. 99–101° (740 mm.)].

Methoxymethylenecyclohexane.—To a solution of 0.02 mole of methoxymethylenetriphenylphosphorane was added 1.96 g. (0.02 mole) of cyclohexanone, and the mixture was stirred for 1 hr. at room temperature. The resulting mixture was then distilled under reduced pressure; the fraction of b.p. 70–80° (30–35 mm.) was collected in a flask cooled at −20°, washed with aqueous potassium carbonate, extracted with *n*-pentane, and dried over anhydrous magnesium sulfate. Removal of the pentane and distillation of the residual oil gave 1.70 g. (67.6%) of methoxymethylenecyclohexane, b.p. 70–71° (37 mm.).[4]

The infrared spectrum showed bands at 5.90 and 11.10 μ.

2-Methylenebornane.—(+)-Camphor, 6.08 g. (0.04 mole), in 20 ml. of dimethyl sulfoxide was added to a solution of 0.05 mole of methylenetriphenylphosphorane, and the reaction mixture heated at 50° for 1 hr., at which time 5 ml. of *n*-pentane was introduced to wash down any sublimed camphor. Heating was continued for 16 hr. at a bath temperature of 56°; the solution was cooled and poured into 40 ml. of water The aqueous phase (containing some precipitated triphenylphosphine oxide) was extracted three times with 100-, 75-, and 50-ml. portions of *n*-pentane, respectively. The triphenylphosphine oxide and dimethyl sulfoxide layer were further extracted with two 75-ml. portions of pentane. The pentane fractions were combined and washed with 100 ml. of a 1:1 water–dimethyl sulfoxide solution, and then with 200 ml. of a 50% saturated sodium chloride solution. The pentane layer was dried over anhydrous magnesium sulfate and passed through 25 g. of neutral alumina (activity 1). The alumina was eluted with pentane until a negative tetranitromethane test was obtained. All eluents were combined, and the pentane was distilled using a Vigreux column. The residual oil was sublimed to give 4.40 g. (73.4%) of 2-methylenebornane,[5] m.p. 68–70°. The infrared spectrum was in agreement with expectations and with that given by Zeiss and Zwanzig[5]; the n.m.r. spectrum showed three sharp methyl peaks at 0.75, 0.90, and 0.92 p.p.m. downfield from tetramethylsilane, multiplets due to seven protons at 1.0 to 2.5 p.p.m. and two olefinic protons as a multiplet with center at *ca.* 4.6 p.p.m. downfield from tetramethylsilane.

3-Methylenecholestane.—A solution of 3-cholestanone, 0.357 g. (1.0 mmole), in 5 ml. of tetrahydrofuran (distilled from calcium hydride) was added to a solution of 1.5 mmoles of methylenetriphenylphosphorane, followed immediately by the addition of 20 ml. more of tetrahydrofuran to redissolve any precipitated cholestanone. The reaction mixture then was stirred at a bath temperature of 50° for 22 hr., poured into 150 ml. of water, and the aqueous solution was extracted with 75-, 50-, and 25-ml. portions of *n*-pentane. The pentane extracts were washed with 100 ml. of water, dried over anhydrous magnesium sulfate, and passed through 5.0 g. of neutral alumina (activity I). Elution with pentane and evaporation and recrystallization from methanol gave 0.266 g. (69%) of 3-methylenecholestane,[6] m.p. 64–65°.

Methyl 4-(*p*-Anisyl)-4-pentenoate.—To a solution of 0.013 mole of methylenetriphenylphosphorane was added 2.22 g. (0.10 mole) of methyl 3-*p*-anisoylpropionate. After keeping at room temperature for 23 hr., the solution was poured into 250 ml. of water and the product was extracted with pentane. The greenish yellow pentane extracts were combined, washed with 100 ml. of a 1:1 water–dimethyl sulfoxide solution and then with 200 ml. of water, dried, and filtered through 5 g. of neutral alumina (activity 3). The product was eluted with 300 ml. of pentane, the colorless eluents combined, and the pentane removed on a steam bath. The semisolid remaining was crystallized from methanol–water at low temperatures. The yield of crude product was 1.77 g. (80.5%), m.p. 26–28°. The infrared spectrum was entirely free from the ketone absorption at 5.93 μ, and showed the characteristic methylene bands at 3.12 μ, 6.12 μ (both appeared as shoulders), and 11.12 μ. An analytical sample was prepared by evaporative distillation at 0.10 mm., bath temperature, *ca.* 135°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.70; H, 7.28.

Spiro(cyclopropane-1,9-fluorene).—To a solution of 0.04 mole of methylenetriphenylphosphorane was added 1.80 g. (0.01 mole) of 9-fluorenone in 20 ml. of dimethyl sulfoxide. The reaction mixture was stirred at a bath temperature of 55° for 3 days and the resulting deep greenish blue solution was poured into 100 ml. of water followed by extraction with 75-, 50-, and 25-ml. portions of *n*-pentane. The yellow pentane extracts were combined, and the total volume reduced to *ca.* one-fourth the original. An excess of a 30% hydrogen peroxide solution was added to the pentane and the heterogeneous mixture stirred for 3 hr. to ensure the oxidation of all triphenylphosphine present. The pentane layer was separated, washed with water, dried, and passed through 15 g. of neutral alumina (activity 1). Elution with pentane was continued until no further solid was obtained on evaporation of the eluent. Recrystallization from methanol gave 0.565 g. (29.4%) of spiro(cyclopropane-1,9-fluorene), m.p. 69–70° (lit.,[7] m.p. 70–71°).

1,1-Diphenylpropen-1.—A solution of sodium methylsulfinyl carbanion was prepared under nitrogen from 0.03 mole of sodium hydride and 20 ml. of dimethyl sulfoxide. The solution was cooled in a cold water bath and stirred during the addition of 11.1 g. (0.03 mole) of ethyl triphenylphosphonium bromide in 60 ml. of dimethyl sulfoxide, whereupon the deep red color of the ethylidenephosphorane was produced. After stirring at room temperature for 15 min., 4.55 g. (0.025 mole) of benzophenone in 10 ml. of dimethyl sulfoxide was added and stirring continued for 3 hr. at room temperature and 1.5 hr. at 60°. The reaction mixture was cooled and poured into 200 ml. of cold water in a round-bottomed flask. The mixture of solid and liquid was shaken with five 100-ml. portions of pentane which were decanted, combined and washed once with water, dried over anhydrous sodium sulfate, evaporated to a volume of 50 ml., and filtered through 50 g. of Merck alumina, using 1 l. of pentane to elute the product. Evaporation of the pentane left 4.73 g. (97.5%) of the product as a white crystalline solid, m.p. 46–49°. Recrystallization from 95% ethanol gave colorless plates, m.p. 49° (lit.,[8] m.p. 52°; 46–48°).

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[4] S. G. Levine, *J. Am. Chem. Soc.*, **80**, 6150 (1958), reports isolation, in 40% yield, of the 2,4-dinitrophenylhydrazone of cyclohexane carboxaldehyde from this reaction.

[5] H. H. Zeiss and F. R. Zwanzig, *ibid.*, **79**, 1733 (1957), report the preparation of 2-methylenebornane, m.p. 62.5–64°, by a different route.

[6] F. Sondheimer and R. Mechoulam, *ibid.*, **79**, 5029 (1957).

[7] E. Mechoulam and F. Sondheimer, *ibid.*, **80**, 4386 (1958).

[8] L. Horner, H. Hoffmann, and H. G. Wippel, *Ber.*, **91**, 61 (1958).

Synthesis of Trichloromethylmercury Derivatives

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Two groups of Russian workers recently have reported that dichlorocarbene undergoes an insertion reaction into the mercury–chlorine bond of mercuric chloride and derivatives thereof to give the corresponding trichloromethylmercury derivatives.

$$:CCl_2 + RHgCl \longrightarrow RHgCCl_3\ [R = Cl\ (I),\ CH_2{=}CHCH_2{-},\ C_6H_5{-},\ Ar{-}]$$

Reutov and Lovtsova[1] treated chloroform with potassium *t*-butoxide in the presence of the mercuric chloride derivative to obtain their products, while Razuvaev and co-workers[2] utilized the pyrolysis of sodium trichloroacetate as the (presumed) dichlorocarbene source.

Seyferth and Burlitch[3] have presented evidence which suggests that the reaction of phenylmercuric bromide with potassium *t*-butoxide and chloroform proceeds by way of a simple nucleophilic displacement by the trichloromethide ion to give phenyltrichloromethyl mercury.

The purpose of this Note is to present the results of our independent experiments which suggest that the related nonaromatic trichloromethylmercurials are also formed by a displacement reaction and not by a carbene insertion mechanism. Furthermore, we wish to present full experimental details on the sodium trichloroacetate procedure, since it is an unusually simple route to these interesting compounds and it can be used to prepare bis(trichloromethyl)mercury, which may not be accessible by the haloform-base procedure.

Following Reutov's procedure,[1b] mercuric bromide reacted with potassium *t*-butoxide and chloroform to give, as the only organomercurial, a low yield (1.2%) of trichloromethylmercuric bromide (II), identified by mercury and chlorine analyses, molecular weight determination, and melting point similarity to the same compound prepared by Nesmeyanov and co-workers.[4] Since dichlorocarbene insertion should yield bromodichloromethylmercuric bromide, identification of the product as II favors the displacement mechanism.

The low yield of II and difficulties experienced in obtaining it pure by Reutov's procedure prompted our investigation of the sodium trichloroacetate (III) pyrolysis route, originally described by Wagner[5] and later adapted to the synthesis of mercurials by Razuvaev.[2] Heating mercuric bromide and III in monoglyme (see Experimental) gave II, readily isolated as the only water insoluble material from the reaction. A single crystallization from chloroform gave pure II, m.p. and mixture m.p. with II prepared by the Reutov procedure, 160–161°, identified as discussed previously. The simplicity of this procedure makes this a preferred route to this and related compounds. In Table I are listed the pertinent data for the compounds that we have prepared to date by this method.

It is of interest to note that the reaction of a 1:1 ratio of III to mercuric chloride leads to trichloromethylmercuric chloride as the only product, whereas use of a 2:1 ratio of III to either mercuric chloride or acetate leads to bis(trichloromethyl)mercury (IV) as the sole product.

TABLE I

PREPARATION OF TRICHLOROMETHYLMERCURY DERIVATIVES FROM SODIUM TRICHLOROACETATE (III)

Reactant	Ratio, III/reactant	Product[a]	Pure product % Yield[b]	Pure product M.p.°C.
$HgCl_2$	1:1	Cl_3CHgCl	76	193–194
$HgCl_2$	2:1	$(Cl_3C)_2Hg$[c]	71	140–141
$Hg(OAc)_2$	2:1	$(Cl_3C)_2Hg$[c]	54	140–142
$HgBr_2$	1:1	Cl_3CHgBr	44	160–161
$HgBr_2$	2:1	Cl_3CHgBr	69	160–161
C_6H_5HgCl	1:1	$C_6H_5HgCCl_3$[c]	77	111.5–112.5

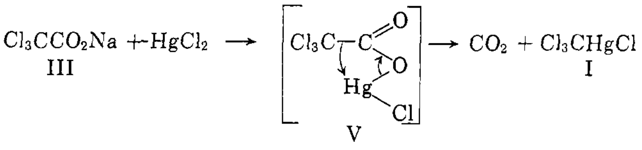
[a] All products were quantitatively analyzed for mercury and chlorine by X-ray fluorescence and shown to agree satisfactorily with calculated values. Molecular weight determinations (cryoscopic benzene method) also agreed with calculated values within 2–5%. [b] All yields are based on the assumption that the sodium trichloroacetate is 100% pure. [c] These compounds were tested for antimicrobial activity and shown to be comparable to phenylmercuric acetate.

$$\underset{\text{III}}{2Cl_3CCO_2Na} + HgX_2 \longrightarrow \underset{\text{IV}}{(Cl_3C)_2Hg} + 2NaX + 2CO_2$$

X = Cl or OAc

It was demonstrated that I reacts with another molecule of III to give IV. Regardless of the stoichiometry employed with mercuric bromide, however, only II (and none of IV) could be isolated.

It was demonstrated that the presence of mercuric salts increases the rate of carbon dioxide evolution in the trichloroacetate pyrolysis. This might suggest that the reaction proceeds through the intermediate formation of V, which could then decompose by a concerted mechanism to give the observed product.



However, Razuvaev[2] claims to have synthesized V by an undisclosed route and found it to be stable under these pyrolysis conditions. Our attempts to isolate V and/or mercuric trichloroacetate were unsuccessful, as reported by other workers.[6]

If these mercurials are formed by a "free" trichloromethide ion displacement of chloride from the original mercuric chloride derivative, then displacement is faster than chloride loss to give dichlorocarbene. This was demonstrated by carrying out the pyrolysis in the presence of a large excess of cyclohexene and showing, by gas chromatographic analysis, that no dichloronorcarane had been formed.

As reported by Seyferth and co-workers[7] for phenyltrihalomethylmercury compounds, we found that pyrolysis of both I and IV in the presence of olefins led to dichlorocycylopropanes. For example, 1,1-dichlorodecylcyclopropane (VI) was obtained in 24% yield from 1-dodecene and IV by extended heating at 170–190°. Identification was made by infrared and gas chromatographic comparison with an authentic sample[8]

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(1) (a) O. A. Reutov and A. N. Lovtsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, 1716 (1960); (b) *Dokl. Akad. Nauk SSSR*, **139**, 622 (1961); *Chem. Abstr.*, **56**, 1469 (1962).

(2) G. A. Razuvaev, N. S. Vasileiskaya, and L. A. Nikitina, *Tr. po Khim. i Khim. Tekhnol.*, **3**, 638 (1960); *Chem. Abstr.*, **56**, 15116d (1962).

(3) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962).

(4) A. N. Nesmeyanov, R. Kh. Freidlina, and F. K. Velichko, *Dokl. Akad. Nauk SSSR*, **114**, 557 (1957); *Chem. Abstr.*, **52**, 296d (1958).

(5) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

(6) W. G. Bateman and D. B. Conrad, *J. Am. Chem. Soc.*, **37**, 2553 (1915); M. S. Kharasch and F. W. Staveley, *ibid.*, **45**, 2961 (1923); also, references cited in these papers.

(7) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(8) T. J. Logan, *Tetrahedron Letters*, 173 (1961).

prepared by the method of Doering and Hoffmann.[9] We were not able to demonstrate whether VI was formed by a dichlorocarbene–olefin addition or a two-step addition-elimination reaction of the mercurial with the olefin. With the goal of obtaining a product which would yield dichlorocyclopropanes when mixed with olefins at room temperature or below, several attempts were made to prepare trichloromethyl derivatives of other metals, including Pb, Cu, Ag, and Zn, using the trichloroacetate pyrolysis procedure. All these attempts were unsuccessful.

Experimental

The inorganic mercuric salts used in this study were commercial materials, reagent grade. The monoglyme (1,2-dimethoxyethane) was obtained from Matheson, Coleman and Bell. Purification was achieved by refluxing over lithium aluminum hydride, followed by distillation and subsequent storage over sodium ribbon. Sodium trichloroacetate was prepared by the careful neutralization of commercial trichloroacetic acid, followed by freeze-drying until no more water could be removed. This product was then forced through a 100-mesh sieve and thoroughly mixed, under nitrogen, to ensure uniformity.

The potassium *t*-butoxide was used as received from the MSA Research Corporation.

All melting points are uncorrected and were obtained in open capillary tubes on a MEL-Temp apparatus.

Trichloromethylmercuric Bromide (II) *via* Haloform–Base Route.—Into a 500 ml., three-necked flask equipped with stirrer, thermometer, and condenser were placed 150 ml. of benzene, 108.1 g. (0.3 mole) of mercuric bromide, and 11.9 g. (0.1 mole) of chloroform. While stirring rapidly, 11.2 g. (0.1 mole) of potassium *t*-butoxide was added in small portions through Gooch tubing over a period of 30 min. while cooling with an ice bath. Stirring was continued an additional 50 min. before pouring the mixture into 1 l. of water. The water was then extracted with diethyl ether and the ether was subsequently washed with water, dried, and evaporated on a rotary evaporator to give 0.5 g. (1.2% yield) of product, m.p. 160–161°, after recrystallization from chloroform. As indicated in Table I, mercury and chlorine analyses, and molecular weight determinations were in satisfactory agreement with calculated values. The mother liquor was carefully examined for other organomercurials but none were found.

Preparation of II *via* Sodium Trichloroacetate Route.—Into a flask equipped with reflux condenser and exit tube were placed mercuric bromide, 36.04 g. (0.1 mole), 18.5 g. (0.1 mole) of III, and 150 ml. of monoglyme. The exit tube led to an inverted graduated cylinder used to measure carbon dioxide evolution by water displacement. Heat was applied with a mantle and in 15 min., 2.5 l. of carbon dioxide had been collected from the refluxing solution. Reflux was continued an additional 1 hr., but no further gas evolution could be detected. The contents of the flask were then poured into water to give a heavy brown oil that was separated by ether extraction. The extract was water-washed, dried over magnesium sulfate, and the solvent removed on a rotary evaporator. Recrystallization from chloroform gave 17.8 g. (44.5%) of product, m.p. and m.m.p. with II above, 160–161°.

Use of a 2:1 ratio of III/mercuric bromide gave the same product in 69% yield (recrystallized).

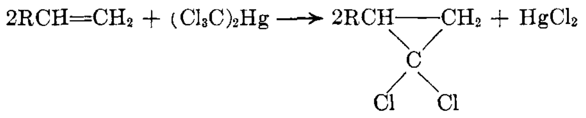
Bis(trichloromethyl)mercury (IV) from Mercuric Chloride and III.—Into the same apparatus as described above was placed 27.2 g. (0.1 mole) of mercuric chloride, 37.0 g. (0.2 mole) of III and 150 ml. of monoglyme. The solution was refluxed for 1 hr. and 4.3 l. of gas was collected (4 l. in first 25 min.). The contents of the flask were poured into 1 l. of water to give a dense white oil which was separated by ether extraction and treated as described above. Recrystallization from chloroform gave 31.2 g. (71.5%) of product, m.p. 140–141°.

The same product was obtained in 54% yield (recrystallized) by an identical procedure utilizing 31.9 g. (0.1 mole) of mercuric acetate in place of mercuric chloride.

All other mercurials were obtained by identical procedures and the pertinent data is shown in Table I.

Preparation of IV from I and Sodium Trichloroacetate.—Into the same apparatus as described previously were placed 8.9 g. (0.025 mole) of I, 4.6 g. (0.025 mole) of sodium trichloroacetate, and 100 ml. of monolyme. After 1 hr. of reflux, 1 l. of gas had been collected. Product isolation as described above gave 7.5 g. (67.5% yield) of IV, m.p. and m.m.p. with IV above, 140–141°.

Preparation of 1,1-Dichlorocyclopropanes from Olefins and I or IV.—Into a nitrogen-flushed 100-ml. flask equipped with condenser and magnetic stirring bar were placed 4.37 g. (0.01 mole of IV and 16.8 g. (0.1 mole) of 1-dodecene. This mixture was heated in an oil bath at 170–190° for 2.5 hr. Petroleum ether (50 ml.) was added to precipitate unchanged IV and I (identified by recrystallization and m.p. comparison with known I) and this filtered, clear layer was water-washed, dried, and distilled to separate 1-dodecene from the product fraction, b.p. 98–120° (0.5 mm.). The dichlorocyclopropane product was identified by comparisons with the same compound[8] prepared from chloroform, potassium *t*-butoxide, and olefin.[9] The yield of product was 24%, by gas chromatographic analysis, based on the following stoichiometry.



$$2RCH{=}CH_2 + (Cl_3C)_2Hg \longrightarrow 2RCH{-}CH_2(CCl_2) + HgCl_2$$

A 25% yield of dichloronorcarane was obtained by heating IV with cyclohexene for 15 min. at 200° in an autoclave.

Heating I with cyclohexene for 15 min. at 250° in an autoclave gave a 36% yield of dichloronorcarane.

Acknowledgment.—The author is indebted to Dr. K. T. Knapp for the X-ray fluorescence analysis of these compounds.

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[9] Wm. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

A New Synthesis of Perfluoroalkylmagnesium Halides

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Although perfluoroalkyl Grignard reagents have been known for some time, direct formation of the organometallics from the corresponding halides and magnesium has been possible only with perfluoroalkyl iodides. Perfluoropropylmagnesium bromide was prepared[2] by a metathetical reaction of phenylmagnesium bromide with perfluoropropyl iodide and not by the conventional Grignard technique. 1,1,2,2,3,3,3-Heptafluoropropane was obtained[3] upon hydrolysis of the reaction mixture between perfluoropropyl bromide and magnesium in ether; thus it is possible that a Grignard reagent was present, although no other reactions were described. The experimental difficulties connected with the preparation of trifluoromethylmagnesium iodide[4] and the ready availability of trifluoromethyl bromide led us to explore the feasibility of converting the latter into the corresponding Grignard reagent.

No reaction occurred upon treatment of the bromide with sublimed magnesium in anhydrous ether. How-

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[1] Taken from part of a thesis submitted by Robert D. Battershell to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] O. R. Pierce, A. F. Meiners, and E. T. McBee, *J. Am. Chem. Soc.*, **75**, 2516 (1953).

[3] T. J. Brice, W. H. Pearlson, and J. H. Simons, *ibid.*, **68**, 969 (1946).

[4] R. N. Haszeldine, *J. Chem. Soc.*, 1273 (1954).