α-Diazomercurials. Synthesis and Photochemistry

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A general synthesis of alkyl- and arylmercuridiazo compounds is described. By selective control of the experimental conditions, either of two novel intermediates may be studied upon photolysis of the diazomercury compound in the liquid phase: monovalent carbon or α-mercuricarbene. The photochemistry of methylmercuridiazoacetate in methanol is briefly stated.

α-Metallodiazo compounds are of current interest owing to their use as (a) intermediates in the synthesis of substituted diazo compounds,[2] (b) precursors to monovalent carbon,[3] and (c) precursors to metalated divalent carbon.[2c,d,3b,4]

$$\mathrm{RCM} \xrightarrow[\mathrm{R'X}]{\text{(a)}} \mathrm{RCR'} + \mathrm{MX}$$
$$\mathrm{N_2} \qquad\qquad \mathrm{N_2}$$

$$\xrightarrow[h\nu]{\text{(b)}} \mathrm{RC} + \mathrm{N_2} + \mathrm{M}$$

$$\xrightarrow[h\nu]{\text{(c)}} \mathrm{RCM} + \mathrm{N_2}$$

Büchner reported the first synthesis of a diazomercurial compound, diethyl mercuribis(diazoacetate) (1).[5] Mercuration has since been extended to include many classes of diazo compounds.[2h,6]

$$2\mathrm{HCCOOEt} + \mathrm{HgO} \xrightarrow[\text{ether}]{0^\circ} \mathrm{Hg(CCOOEt)_2} + \mathrm{H_2O}$$
$$\mathrm{N_2} \qquad\qquad\qquad\qquad \mathrm{N_2}$$
$$\mathbf{1}$$

During the course of preliminary studies with carboethoxycarbyne, as produced by photolysis of **1**, it became evident that the mercuribis(diazo ester) gave several intermediates rendering mechanistic interpretation difficult. The use of monodiazomercury compounds offered to simplify the chemistry found in these photolysis reactions.

Synthesis of α-Diazomercurials.—The following one-flask synthesis was devised to prepare alkyl, or arylmercuridiazo compounds.[7]

$$\mathrm{RHgCl} \xrightarrow[\mathrm{EtOH}]{\mathrm{KOEt}} \mathrm{RHgOEt} + \mathrm{KCl} \xrightarrow[\mathrm{N_2}]{\mathrm{HCY}} \mathrm{RHgCY} + \mathrm{EtOH}$$
$$\mathrm{N_2}$$

The yields of monodiazomercury compound are high (80–99% based on RHgCl) owing to the insolubility of potassium chloride in ethanol. The method is generally applicable to a wide variety of R and Y substituents. Where RHgOH is available, it can be used directly.

$$\mathrm{RHgOH} + \mathrm{HCY} \xrightarrow{\mathrm{EtOH}} \mathrm{RHgCY} + \mathrm{H_2O}$$
$$\mathrm{N_2} \qquad\qquad \mathrm{N_2}$$

In order to assess the effect of the R group upon the photochemistry of α-mercuridiazo compounds, a series of alkyl- and arylmercury derivatives were synthesized from methyl diazoacetate. The mercurials were characterized by mass spectrum, ir, uv, and nmr. Features common to all the mass spectra were the parent (weak–medium intensity), PN_2 and RHg ions. The substitution of a mercury atom for the methine hydrogen of methyl diazoacetate increases the wavelength of both the C=N$_2$ and C=O stretch absorptions by *ca.* 0.1 μ in the infrared spectra. The mercuridiazoacetates possess two absorption bands in the ultraviolet (MeOH): 374–377 nm (ε ~44–59) and 268–274 (8600–10,000). The presence of the mercury atom induces a 20–25-nm red shift of the shorter wavelength absorption maximum and reduces the intensity by *ca.* 40%. The position of the long wavelength absorption maximum changes only slightly (2–3 nm) in the same direction but the intensity is increased threefold.

The amount of carbon–mercury bond fragmentation, as indicated by the yield of mercury precipitated during photolysis in olefin, was a function of R group, wavelength of incident light, and temperature, as shown in Table I.

$$\mathrm{RHgCCOOMe} \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} \mathrm{RHg\dot{C}COOMe} + \mathrm{N_2}$$
$$\mathrm{N_2} \qquad\qquad \mathrm{R\cdot} + \mathrm{Hg} + \mathrm{N_2} + \mathrm{\cdot\dot{C}COOMe}$$

The increase in fragmentation parallels the order of stability of the carbon radicals (R·) produced: methyl < ethyl < phenyl < isopropyl ≲ benzyl < *tert*-butyl. Second, photolysis in the more intense short-wavelength band (253.7 nm) caused the greatest amount of frag-

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(2) (a) F. Gerhart, U. Schöllkopf, and H. Schumacher, *Angew. Chem., Int. Ed. Engl.*, **6**, 74 (1967); (b) U. Schöllkolf, F. Gerhart, M. Reetz, H. Frasnelli, and H. Schumacher, *Justus Liebigs Ann. Chem.*, **716**, 204 (1968); (c) U. Schöllkopf and N. Rieber, *Angew. Chem., Int. Ed. Engl.*, **6**, 884 (1967); (d) U. Schöllkopf, D. Hoppe, N. Rieber, and V. Jacobi, *Justus Liebigs Ann. Chem.*, **730**, 1 (1969); (e) U. Schöllkopf and H. Frasnelli, *Angew. Chem., Int. Ed. Engl.*, **9**, 301 (1970); (f) U. Schöllkopf and N. Rieber, *ibid.*, **6**, 261 (1967); (g) U. Schöllkopf and N. Rieber, *Chem. Ber.*, **102**, 488 (1969); (h) H. Hartzler, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 205P; (i) M. Regitz, *Synthesis*, 351 (1972); (j) M. F. Lappert and J. S. Polland, *Advan. Organometal. Chem.*, **9**, 397 (1970).

(3) (a) T. DoMinh, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, **89**, 6785 (1967); (b) O. P. Strausz, T. DoMinh, and J. Font, *ibid.*, **90**, 1930 (1968).

(4) (a) U. Schöllkopf, B. Banhidai, and H. U. Scholz, *Justus Liebigs Ann. Chem.*, **761**, 137 (1972); (b) D. Seyferth, H. Menzel, A. W. Dow, and T. C. Flood, *J. Organometal. Chem.*, **44**, 279 (1972); (c) A. G. Brook and P. F. Jones, *Can. J. Chem.*, **49**, 1841 (1971).

(5) E. Büchner, *Ber. Deut. Chem. Ges.*, **28**, 215 (1895).

(6) (a) P. Yates and F. X. Garneau, *Tetrahedron Lett.*, 71 (1967); (b) T. DoMinh, O. P. Strausz, and H. E. Gunning, *ibid.*, 5237 (1968); (c) A. N. Wright, K. A. W. Kramer, and G. Steel, *Nature (London)*, **199**, 903 (1963); (d) R. Scheffold, private communication to P. S. Skell, June 1968; (e) J. Lorberth, *J. Organometal. Chem.*, **27**, 303 (1971); (f) D. Seyferth, R. S. Marmor, and P. Hilbert, *J. Org. Chem.*, **36**, 1379 (1971); (g) M. Regitz, A. Liedenheger, U. Eckstein, W. Martin, and W. Anschütz, *Justus Liebigs Ann. Chem.*, **748**, 207 (1971).

(7) We learned (June 1968) from R. Scheffold, Universite de Fribourg, that he also had developed synthesis of RHgOR′ and that he had employed these reagents for the replacement of active hydrogen atoms in a variety of systems, including diazo compounds.

TABLE I

MERCURY YIELDS OBSERVED IN THE PHOTOLYSES OF ALKYLMERCURIDIAZOACETATES

$RHgCCOOCH_3$ ‖ N_2	Hg yield, %[a] 253.7 nm[b]	>280 nm	>355 nm
Alkyl Group Variation			
Methyl	...	...	5
Ethyl	32	15	12
Phenyl	...	17[c]	7[d]
Isopropyl	41	26	...
Benzyl	...	27	...
tert-Butyl	64[c]	37	...
Temperature Variation			
Ethyl (−48°)	...	...	6
Ethyl (−8°)	...	...	8
Ethyl (1°)	...	...	12
Ethyl (14°)	...	...	13

[a] At 100% nitrogen evolution in refluxing *trans*-2-butene (1°). [b] Some mercury may also have come from photolysis of the mercury-containing products. [c] In cyclohexene at 14°. [d] In 2-methylpropene at −8°.

mentation with little occurring when only the long-wavelength band was irradiated ($\lambda > 335$ nm). Third, the amount of mercury obtained in a photolysis decreases slightly as the reaction temperature is lowered. Thus, photolysis of methyl methylmercuridiazoacetate with light of wavelength greater than 335 nm had the least amount of carbon–mercury bond fragmentation (*ca.* 5%). The low yield of mercury was maintained as the Y substituent attached to the methylmercuridiazo group was changed (Y = COMe, CN, CH_3, Ph) as shown in Table II. These results indicate that nearly

TABLE II

MERCURY YIELDS OBSERVED IN THE PHOTOLYSIS OF $CH_3HgC(=N_2)Y$

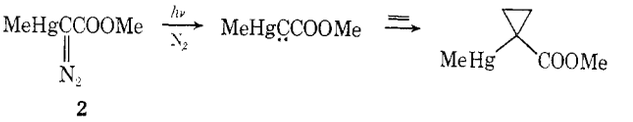
Y group	Hg yield, %[a]
$COCH_3$	5
CCH_3 ‖ O	4
C≡N	8
C_6H_5	9[b]
CH_3	10

[a] At 100% nitrogen yield in refluxing 2-methylpropene (−8°), $\lambda > 335$ nm. [b] $\lambda > 400$ nm.

quantitative production of methylmercuricarbene may be obtained upon irradiation of the long-wavelength absorption band of methylmercuridiazo compounds at temperatures below *ca.* 0°. The use of the near-visible light has the further advantage of not causing photodecompositions of the mercury containing products.

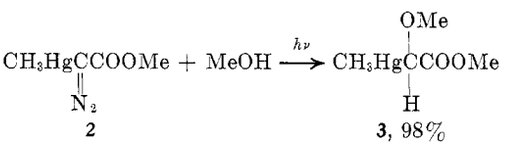
The monovalent carbon intermediate resulting from both nitrogen and mercury elimination may be better studied using a *tert*-butylmercuridiazo compound with incident light >280 nm than from the corresponding mercuribisdiazo compound with light of shorter wavelength (~253.7 nm).[8] As a precursor, the *tert*-butylmercuridiazo is superior to the mercuribisdiazo compound since the number of intermediates occurring in its decomposition are reduced and the more ready fragmentation of the carbon–mercury bond allows the use of less energetic light, thus avoiding the photodecompositions of the mercury-containing products.

Photochemistry of Methyl Methylmercuridiazoacetate in Methanol.—α-Mercuricarbomethoxycarbenes have been shown to react with olefin, yielding cyclopropane almost exclusively, in contrast to non-mercury-containing carbenes which have important competitive pathways of rearrangement and insertion.[9]



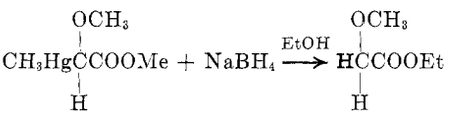
2

With a similar high selectivity, the photolysis ($\lambda > 335$ nm) of methyl methylmercuridiazoacetate (**2**) in methanol produces a quantitative yield of a single compound, methyl 2-methylmercuri-2-methoxyacetate (**3**).

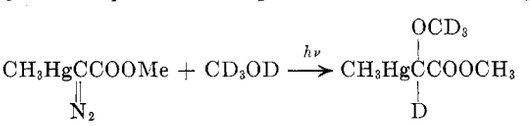


2 **3**, 98%

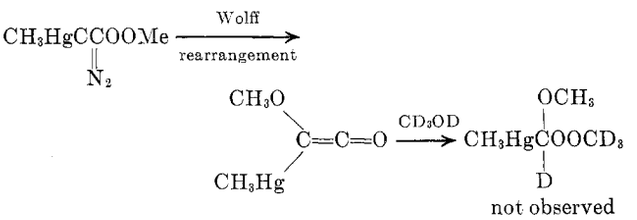
Reduction of methyl 2-methylmercuri-2-methoxyacetate with sodium borohydride in ethanol gives evidence for the position of the carbon–mercury bond. No C–H bond insertion product was detected. Use of methanol-



d_4 as substrate for the reaction shows that it is the methyl ether which comes from the alcohol, since the methyl ether proton absorption is absent in the pmr



analysis of the reaction residue. Thus, very little, if any, Wolff rearrangement occurs in the reaction.



not observed

Photolysis of mercury-free diazoacetates in alcohol gives rise to products of oxygen–hydrogen and carbon–hydrogen carbene insertion, Wolff rearrangement, and "exchange."[10,11] Thus, the substitution of a mercury

(8) G. J. A. Kennepohl, F. Garneau, T. DoMinh, B. Kim, O. P. Strausz, S. J. Valenty, and P. S. Skell, *J. Amer. Chem. Soc.*, in press.

(9) P. S. Skell and S. J. Valenty, *J. Amer. Chem. Soc.*, **95**, 5042 (1973).

(10) T. DoMinh, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **91**, 1261 (1969).

(11) In preliminary experiments, besides the O–H insertion product, a second product was observed (*ca.* 9% yield) in the photolysis of **2** in ethanol which is tentatively identified as ethyl 2-methylmercuri-2-ethoxyacetate on the basis of nmr. This product appears to result from a formal ester exchange as is obtained when methyl diazoacetate is photolyzed in ethanol.[10] Light is required for the exchange, since a "dark" reaction showed no exchange in, or product formation from, the mercuridiazo ester. Further, exchange has been shown not to occur in the products either in the dark or upon irradiation.

atom adjacent to the carbene site enhances the selectivity of the intermediate. Coupled with the nearly quantitative preparation of methylmercuridiazo compounds and this high reaction selectivity, the ready cleavage of the carbon–mercury bond by $NaBH_4$ and electrophilic reagents affords many possibilities for further synthesis.

Experimental section

General Information.—Melting points were determined in a sealed capillary tube using an electrically heated and stirred Thiele-type apparatus and are reported uncorrected. Infrared spectra were obtained with a Beckman IR-5A. Only intense or characteristic absorptions are listed with the position of the maximum reported in microns (μ). Ultraviolet and visible absorption spectra were obtained on solutions in Spectro Grade methanol (1-cm length path) using either a Cary 14 or Cary 15 spectrophotometer. Maxima are reported in wavelength units of nanometers (nm) with the molar extinctions coefficients (ε) following in parentheses. Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60A. The chemical shifts are reported on the δ scale, in parts per million (ppm), downfield from the internal standard tetramethylsilane (TMS). Values of coupling constants (*J* values) are given in hertz (Hz). Low-resolution mass spectra were obtained on an AEI MS-902 instrument. Analysis for covalently bonded mercury was done with a Perkin-Elmer Model 303 atomic absorption spectrometer (AA). Mercurial compounds were analyzed as solutions in 95% ethanol in comparison to standard diphenylmercury solutions. It is to be noted that reproducible and accurate results were obtained only when using the lower temperature flame afforded by a hydrogen (7.0 psi)–argon (9.0 psi)–entrained air mixture in place of the standard acetylene–air mixture.

Alkylmercuric Halides.—Alkylmercuric bromides were obtained from the reactions of the corresponding alkyl Grignard reagent with mercuric bromide. The *tert*-butylmercuric chloride was formed from the reaction of *tert*-butyllithium with mercuric chloride. Methylmercuric chloride was used as obtained from Alfa Inorganics, Inc. The alkylmercuric halides were characterized by comparison of their melting points with those reported in the literature and by nmr and mass spectrum.

Alkylmercuric Ethoxides.—Alkylmercuric ethoxides were made *via* a two-step synthesis from the corresponding potassium ethoxide and alkylmercuric nitrate which, in turn, was obtained by treating alkylmercuric chloride with silver nitrate in absolute ethanol. The mercuri alkoxides are strong vesicants and must be handled with care. The procedure for methylmercuric ethoxide is typical.

Methylmercuric Ethoxide.—Methylmercuric chloride (40.0 mmol, 10.0 g) was added to 150 ml of absolute ethanol freshly distilled from magnesium ethoxide in a foil-wrapped, flame-dried, and nitrogen-purged 250-ml three-necked flask. After the solution was stirred for *ca.* 15 min at 60°, powdered silver nitrate (40.0 mmol, 6.80 g) was added in one portion and the solution was allowed to stir for 3 hr at 60° before suction filtering while hot. After the solid was washed with hot ethanol (3 × 10 ml) and dried, 5.65 g (39.5 mmol, 98.8%) of silver chloride was obtained. The clear, colorless filtrate was returned to the same reaction flask. Cleaned potassium metal (40.0 mmol, 1.56 g) was added in portions to 40 ml of absolute ethanol in a 75-ml dropping funnel (attached to the reaction flask and topped by a water condenser). The potassium ethoxide–ethanol solution was added dropwise to the clear methylmercuric nitrate solution at room temperature, causing a white precipitate to form immediately. After completion of the addition, the solution was allowed to stir for an additional 30 min at room temperature before suction filtering the white solid under nitrogen atmosphere. After the solid was washed with ethanol (2 × 10 ml) and dried, 4.08 g (40.4 mmol, 101%) of potassium nitrate was obtained. The clear, colorless filtrate was evaporated to dryness on a rotary evaporator, using little external heating in the final stages, leaving an off-white, powdery solid. This solid was stirred with hot absolute ether and suction filtered. Additional washes of hot ether were added, stirred with the solid, and the solution was suction filtered until the amount of remaining solid did not appear to decrease. The ethereal solution was evaporated on the rotary evaporator with no external heating, leaving a grayish-white semisolid of methylmercuric ethoxide (9.20 g, 35.4 mmol, 88.5%): mp 24–25°; nmr ($CDCl_3$) δ 1.00 (s, symmetrically disposed ^{199}Hg–^1H doublet, J = 145 Hz, 3 H), 1.23 (t, J = 7 Hz, 3 H), 3.72 (q, J = 7.0 Hz, 2 H); AA (95% EtOH) mol wt, theory 260, found 264; mass spectrum (70 eV, ^{200}Hg) *m/e* 260 (very weak), 215, 200, 45 (very strong), 44. *Caution: strong vesicant.*

Diazo Compounds. Warning.—By their nature, diazo compounds are thermally unstable and sensitive to conditions where a local temperature rise may cause explosion. Although a wide variation in stability is noted when functional groups are changed in the simple diazo compounds, the safest procedure is to prepare, store, and use the diazo compound in an excess of solvent which will not interfere in later chemical reactions. In this study, explosions have occurred when methyl diazoacetate and diazoacetone were inadvertently heated to >150° at 1 atm. A most violent detonation occurred at room temperature when a drop from a 5-g sample of neat diazoacetonitrile was being removed with a fire-polished glass stirring rod. This sample had been handled often over a two-week period before the explosion occurred, indicating the unpredictable nature of pure diazo compounds.

The diazo compounds were prepared and characterized according to literature procedures: diazomethane,[12] diazoethane,[13] methyl and ethyl diazoacetate,[14] diazoacetone,[15] phenyldiazomethane,[16] and diazoacetonitrile.[17]

α-Mercuridiazo Compounds. Warning.—In general, the thermal stability of the mercury derivative parallels that of the parent diazo compound. The only explosion noted with this class of compounds occurred when bis(methylmercuridiazomethane) was isolated as a dry solid at room temperature. *Considering the toxic, light sensitive, and potentially explosive nature of these compounds, the routine use of gloves, shielding, and subdued light is required.*

Methyl Methylmercuridiazoacetate (2).—The synthesis of this compound is typical for the preparation of alkylmercuridiazo esters. Methylmercuric chloride (110 mmol, 27.6 g), stirred in 600 ml of absolute ethanol at 60°, was treated directly with alcoholic potassium ethoxide (110 mg-atoms, 4.3 g, of clean potassium metal in 50 ml of absolute ethanol). After 4 hr of additional stirring at 60°, the potassium chloride was filtered and washed with ethanol. Methyl diazoacetate (108 mmol, 10.8 g) was added dropwise to the clear filtrate cooled to 0°. The solution was stirred for 15 min following the completion of the addition, and the ethanol was removed with the rotary evaporator. The yellow solid residue was dissolved in refluxing dry ether (freshly distilled from lithium aluminum hydride) and gravity filtered through a fine filter. After the ether was removed on the rotary evaporator, a powder, yellow solid remained which was used without further purification (93.0 mmol, 29.2 g, 86% based on diazo ester): mp 71–72°; ir (CCl_4) 4.85 (C=N_2), 6.02 (C=O), 7.9, 8.5 μ; nmr (CCl_4) δ 0.83 (s, symmetrically disposed ^{199}Hg–^1H doublet, 150 Hz, % ^{199}Hg ~20, 3 H), 3.68 (s, 3 H); uv (MeOH) 377.0 nm (ε 44), 269.0 (10,000); mass spectrum (70 eV, ^{200}Hg) *m/e* 314, 286, 283, 243, 215, 200.

Methyl ethylmercuridiazoacetate (91% yield) was a yellow oil: ir (neat) 4.85 (C=N_2), 6.00 (C=O), 7.8 and 8.5 (conjugated ester), 13.60 μ; nmr (CCl_4) δ 1.0–1.8 (m, 5 H), 3.68 (s, 3 H), low-field portion of ^{200}Hg–C^1H_2 coupling centered at 3.0; uv (MeOH) 377.0 nm (ε 50), 272.0 (9410); mass spectrum (70 eV, ^{200}Hg) *m/e* 328, 300, 257, 229, 200.

Methyl isopropylmercuridiazoacetate (97% yield) was a yellow oil: ir (neat) 4.82, 6.01, 7.90, 8.40, 13.5 μ; nmr (CCl_4) δ 1.50 (d, J = 7.0 Hz, with symmetrically disposed pair of two doublets, $J_{^{199}HgCC^1H_2} \cong$ 194 Hz, % ^{199}Hg = 15, $J_{^1H-^1H}$ = 7.0–7.5 Hz, 6 H), 2.80 (m, 1 H), 3.65 (s, 3 H); uv (MeOH) 376.0 nm (ε 53), 274.0 (8630); mass spectrum (70 eV, ^{200}Hg) *m/e* 342, 314, 243, 228, 214, 200, 43.

Methyl *tert*-butylmercuridiazoacetate (93% yield) was a viscous, yellow oil unstable at 0°: ir (neat) 4.85, 6.0–6.1, 7.8, 8.4, 13.6 μ; nmr (CCl_4) δ 1.48 (s, with symmetrically disposed ^{199}Hg–^1H doublet, J = 173 Hz, % ^{199}Hg = 18.6, 10 H), 3.67 (s, 3 H); mass spectrum (70 eV, ^{200}Hg) *m/e* 356, 328, 300, 200, 57; uv not recorded.

(12) J. A. Moore and D. E. Reed, *Org. Syn.*, **41**, 16 (1961).
(13) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).
(14) N. E. Searle, U. S. Patent, 2,490,714; *Chem. Abstr.*, **44**, 3519e (1950).
(15) F. Arndt and J. Amende, *Ber.*, **61**, 1124 (1928).
(16) R. J. Mohrbacher and N. H. Cromwell, *J. Amer. Chem. Soc.*, **79**, 409 (1957).
(17) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2026 (1956).

Methyl benzylmercuridiazoacetate (73% yield) was a yellow oil: ir (neat) 4.81, 6.0, 7.75, 8.4, 13.5, 13.15, and 14.35 μ (monosubstituted benzene); nmr (CCl_4) δ 2.76 (s, with symmetrically disposed ^{199}Hg–^1H doublet, J = 192 Hz, % ^{199}Hg = 15, 2 H), 3.61 (s, 3 H), 7.08 (m, 5 H); uv (MeOH) 375.5 nm (ϵ 59), 271.5 (sh, 9080), 250.5 (19,000); mass spectrum (70 eV, ^{200}Hg) m/e 390, 291, 200, 91.

Ethyl methylmercuridiazoacetate[18] (84% yield) was obtained as brilliant yellow needles from Et_2O: mp 31–33°; ir (CCl_4, CS_2) 4.84, 5.99, 7.87, 8.30, 8.49, 9.47, 13.6 μ; nmr ($CDCl_3$) δ 0.80 (s, with symmetrically disposed ^{199}Hg–^1H doublet, J = 152 Hz, % ^{199}Hg = 16.9, 3 H), 1.25 (t, J = 7.0 Hz, 3 H), 4.15 (q, J = 7.0 Hz, 2 H); uv (MeOH) 377 nm (ϵ 47.7), 269 (11,000); mass spectrum (70 eV, ^{200}Hg) m/e 328, 300, 283, 215, 200.

Alkyl phenylmercuridiazoacetates were also prepared in an alternative manner by treating phenylmercuric hydroxide with the diazo ester. The following synthetic procedure is typical.

Methyl Phenylmercuridiazoacetate.—Methyl diazoacetate (30 mmol, 3.0 g) was dissolved in 50 ml of dry ether and cooled to 0°. Phenylmercuric hydroxide (30 mmol, 8.82 g, Alfa Inorganics) was added in small portions over a period of 60 min. After the addition was completed, the reaction was allowed to stir for 2 hr. The ethereal solution was filtered and concentrated to *ca.* 20 ml with the rotary evaporator, *n*-pentane was added until the solution became cloudy and the solid crystallized at −5°. After suction filtration and drying at room temperature on the filter, an 84% yield of a pale yellow powder was obtained (25.3 mmol, 7.5 g): mp 82–84°; ir (CCl_4) 4.85, 5.95, 7.9, 8.4 μ; nmr (CCl_4) δ 3.69 (s, 3 H), 7.29 (broadened s, symmetrically placed ^{199}Hg–^1H broadened doublet, J = 144 ± 10 Hz, 5 H); uv (MeOH) 376.5 nm (ϵ 59), 268.0 (10,200); mass spectrum (70 eV, ^{200}Hg) m/e 376, 354, 348, 305, 277, 200.

Ethyl phenylmercuridiazoacetate (84% yield) was a yellow oil: ir (neat) 4.85, 6.1 (broad), 7.86, 8.4, 13.6 (sh), 13.8, and 14.4 μ (monosubstituted benzene); nmr (CCl_4) δ 1.18 (t, J = 7.0 Hz, 3 H), 4.08 (q, J = 7.0 Hz, 2 H), 7.28 (broadened s, with symmetrically disposed ^{199}Hg–^1H multiplet, J = 140 ± 10 Hz, 5 H); mass spectrum and uv not recorded.

Methylmercuridiazoacetone was prepared from methylmercuric ethoxide and diazoacetone as outlined previously for methyl methylmercuridiazoacetate in 66–79% yield. The reaction was also produced a small amount of a red-yellow solid insoluble in dry ether which might have arisen from a competing mercuration of the carbon adjacent to the carbonyl function. The mercuridiazo compound was characterized as follows: pale yellow solid from ether; mp 94.5–96.0° dec; ir (CCl_4, CS_2) 4.86, 6.14, 8.47, 12.73, 13.08 μ; nmr (CCl_4) δ 0.87 (s, with symmetrically placed ^{199}Hg–^1H doublet, J = 152 Hz, % ^{199}Hg = 12, 3 H), 2.20 (s, 3 H); uv (MeOH) 360.0 nm (ϵ 71.3), 288.0 (8580), 232.5 (7280); mass spectrum (70 eV, ^{200}Hg) m/e 298, 270, 215, 200, 43; AA (95% EtOH) mol wt, theory 298, found 304.

Phenylmercuridiazoacetone was prepared in methylene chloride at 0° from phenylmercuric hydroxide and diazoacetone as outlined for the synthesis of methyl phenylmercuridiazoacetate: 85% yield; pale yellow powder from CH_2Cl_2; mp 119–120° dec; ir (CCl_4, CS_2) 4.88, 6.18, 7.78, 13.84, 14.44 μ; nmr ($CDCl_2$) δ 2.26 (s, 3 H), 7.36 (broadened s, 5 H) with symmetrically disposed ^{199}Hg–^1H multiplet ($J_{^{199}Hg-^1H} \cong$ 140 Hz); uv (MeOH) 366 nm (ϵ 79.6), 288 (8350); mass spectrum (70 eV, ^{200}Hg) m/e 360 (weak), 332, 277, 200, 77.

Methylmercuridiazoacetonitrile was prepared from methylmercuric ethoxide and diazoacetonitrile as outlined for methyl methylmercuridiazoacetate with some modification. After an ethanolic solution of methylmercuric ethoxide (20 mmol) was obtained, the ethanol was removed on the rotary evaporator. The residue was slurried with methylene chloride (20 ml) and added dropwise to a 0.1 *M* diazoacetonitrile solution in methylene chloride (200 ml) stirring at −78° under nitrogen atmosphere. The amber-colored methylene chloride solution was assumed to contain a 100% yield of methylmercuridiazoacetonitrile (0.091 *M*), stored at −78° and used without further purification. A low yield of amber crystals could be obtained upon concentration of a small volume of solution and purified by recrystallization from ether at −10°: mp 107–108° dec; ir (CCl_4, CS_2) 4.57 (C≡N stretch), 4.86 (C=N_2 stretch), 7.98, 12.80, 13.12 μ; nmr ($CDCl_3$) δ 0.95 (s with symmetrically placed ^{199}Hg–^1H doublet, J = 165 Hz, % ^{199}Hg = 15.7); uv (MeOH) 400 nm (65.1), 262 (9370), 208 (21,600); mass spectrum (70 eV, 8 eV, ^{200}Hg) m/e 281, 253, 215, 200; AA (95% EtOH) mol wt, theory 281, found 289.

Methylmercuriphenyldiazomethane was prepared from methylmercuric ethoxide and phenyldiazomethane at −78°. An ethanolic solution of methylmercuric ethoxide (1.0 *M*, 10 ml) was added dropwise over a period of 5 min to a stirring solution of phenyldiazomethane in ethanol (12 mol, 1.4 g in 10 ml) cooled at −78° and stirred for 30 min following completion of the addition. The ethanol was removed at reduced pressure (<5 mm), and the red sludge was taken up in dry ether and gravity filtered. After crystallization at −10°, blood-red crystals (7.5 mmol, 2.5 g, 75%) were obtained following suction filtration, *n*-pentane wash, and rapid vacuum drying at room temperature and must be stored at −78°. Spectral data: ir (CCl_4) 2.92, 4.97, 7.74, 8.61, 14.57, 15.00 μ; nmr ($CDCl_3$, −35°) δ 0.79 (s, with symmetrically placed ^{199}Hg–^1H doublet, J = 145 Hz, % ^{199}Hg = 16.2, 3 H), 7.17 (m, 5.6 H); uv (MeOH) 477 (31), 273 (7700), 260 (7360), ~215 (11,000, end absorption); mass spectrum (10 eV, ^{200}Hg) m/e 332, 304, 89; AA (95% EtOH) mol wt, theory 332, found 356 ± 6. All spectra indicate presence of some phenyldiazomethane impurity.

Methylmercuridiazoethane was synthesized from methylmercuric ethoxide and diazoethane at −63°. The low-temperature recrystallization vessel used in this preparation consisted of a Pyrex tube (i.d. ~40 mm) divided into two chambers of 60-ml capacity each by a medium porosity fritted glass filter. The top chamber was surmounted by a 60-ml pressure-equilibrated dropping funnel which in turn was attached to a nitrogen gas–oil bubbler. The bottom chamber was closed at its end but had a separate opening on the side just below the frit which led to a glass tube to a height approximately equal to that of the joint on the top chamber. The apparatus was flushed with nitrogen by applying a positive pressure through the side arm to the lower chamber and flame dried before cooling to −63° (chloroform–liquid nitrogen slush). Isolated methylmercuric ethoxide (11.0 mmol) was dissolved in ~15 ml of absolute ether (freshly distilled from lithium aluminum hydride) and added to the dropping funnel. The positive nitrogen pressure to the bottom chamber was adjusted such that a gentle agitation occurred. Diazoethane in ether (20.2 ml, 0.642 *M*) was then added to the top chamber and allowed to cool to −63°. The ethoxide–ether solution was added over a period of *ca.* 20 min. Since some red crystals precipitated from the deep red-orange solution, the reaction vessel was placed in a −45° bath (chlorobenzene–liquid nitrogen slush) and these crystals were dissolved with vigorous agitation. The reaction mixture was force filtered into the lower chamber by applying a positive pressure to the top, leaving a fine gray layer on the frit. The red-orange solution (−45°) was poured out of the vessel through the side arm of the lower chamber into a tared photolysis vessel cooled at −63° under a nitrogen atmosphere. Crystallization of the red solid began at this temperature and was completed at −78° (60 min) and −120° (30 min). After the orange supernatant (−120°) was poured off, the remaining crystals were washed with 10 ml of trichlorofluoromethane at −78° and excess solvent was removed by evacuation at −45° (<1 mm) for a short time. The reaction vessel was quickly reweighed and the weight of the red crystals obtained was 2.1 g (7.8 mmol, 71% yield based on ethoxide). The mercuridiazoethane is thermally unstable at >−45° and should be stored at −78°. Spectral data: ir ($CFCl_3$), 4.98 μ (C=N_2 stretch); nmr ($CDCl_3$, −45°) δ 0.72 (s, with symmetrically placed ^{199}Hg–^1H doublet, J = 138 Hz, % ^{199}Hg = 13, 1.0 H), 2.16 (s, 0.8 H); uv (Et_2O, −57°, partial) 465 (10–20), low point in valley between short- and long-wavelength absorptions is at 355 nm.

Bis(methylmercuridiazomethane) was prepared from methylmercuric ethoxide and diazomethane in absolute ether at −96°.[19] The same general reaction procedure and apparatus described for the preparation of methylmercuridiazoethane was used here with some modification. A solution of methylmercuric ethoxide (5.0 mmol) in absolute ether (10 ml) was added slowly to a gas-agitated solution containing an excess of diazomethane (5.0 mmol in 20 ml of Et_2O) in the vessel's top chamber at −96° (acetone–liquid nitrogen slush). A brilliant yellow solid formed immediately. The reaction was agitated for 10 min following the completion of the addition and then allowed to stand without agitation for 30 min before pressure filtering the solution through the frit. The clear, yellow filtrate was poured out through the

(18) This compound has also been prepared by an alternative route.[6c]

(19) This compound has also been prepared by alternative routes.[6c,7]

side arm, the solid was washed once with ether, and the side arm was closed off with a clamped gum rubber hose. The reaction vessel was evacuated (<1 mm) and warmed to −45° for 15 min. The bright yellow crystals were transferred to a tared vial at −78° and weighed (2.42 mmol, 1.14 g, 96.8% based on ethoxide), mp 99–100° (lit.[6e] mp 98–100°). The solid decomposes rapidly at room temperature and a sample exploded when left on the bench to dry. It is best stored moist with reaction solvent at −78°. At 0°, bis(methylmercuridiazomethane) is insoluble or only slightly soluble in $CHCl_3$, CCl_4, $CFCl_3$, DME, CH_3NO_2, and *p*-dioxane, slightly more soluble in Et_2O, and moderately soluble in DMF and pyridine. Spectral data: ir (CCl_4–pyridine) 5.05 μ (C=N_2 stretch); nmr ($CDCl_3$, −20°) δ 0.75 (s, with symmetrically disposed ^{199}Hg–^{1}H doublet, J = 136 Hz; nmr (acetone-d_6, −10°) 0.54 (s, 150 Hz), (pyridine, −35°) 0.52 (s, 146 Hz, % ^{199}Hg = 15); mass spectrum (70 eV, 20 eV, ^{200}Hg) 442 (parent −N_2), 427, 230, 215, 200, no molecular ion at 470; micro N_2 analysis, mol wt observed 466 ± 4, theory 470. In several reactions, yellow or yellow-green crystals melting at 82–85° were obtained as well as yellow crystals melting at 99–100°. Both sets of crystals had the same nmr and ir (C=N_2) absorptions.

Monomethylmercuridiazomethane could not be synthesized by these methods. In the many attempts to prepare this compound, only bis(methylmercuridiazomethane) was isolated. Two typical preparation attempts are presented below.

Methylmercuric ethoxide (5.0 mmol) in absolute ethanol (20 ml) was added very slowly over a 50-min period to excess diazomethane (50.0 mmol, 88 ml of a 0.569 *M* solution in ether) cooled to −96° under a nitrogen atmosphere. A bright yellow solid (1.5 g) was obtained following suction filtration, washing with −96° ether (twice), and vacuum drying (−45°, 1 mm): mp 83–85°; ir (pyridine) 5.07 (C=N_2 stretch); nmr (pyridine, −35°) δ 0.52 (s, with symmetrically placed ^{199}Hg–^{1}H doublet, 146 Hz, % ^{199}Hg = 20); micro N_2 analysis, mol wt 466 (two determinations). Thus, the product was identical with bis(methylmercuridiazomethane).

Methylmercuric ethoxide (5.0 mmol) in absolute ethanol (20 ml) was added slowly to an equimolar amount of diazomethane (5.0 mmol, 8.58 ml of a 0.583 *N* solution in ether) cooled at −96°. A bright yellow solid [1.14 g, 2.42 mmol, 48.8% yield for bis(methylmercuridiazomethane) based on diazomethane] was obtained following suction filtration, washing with −96° ether, and vacuum drying (−45°, 1 mm). The yellow filtrate and ether wash were distilled into a cooled receiver (−110°) at reduced pressure until there was no yellow coloration remaining in the pot. The yellow solution in the receiver was treated with a known amount of benzoic acid and back titrated with standardized sodium hydroxide. Diazomethane was recovered in 42% yield (2.10 mmol).

Photolysis of Methyl Methylmercuridiazoacetate in Methanol.—**2** (10.0 mmol, 3.14 g) was dissolved in absolute methanol (250 ml distilled from magnesium methoxide) and photolyzed for 80 min at 13–14° with the soft glass-filtered light of a 1000-W A-H6 high-pressure Hg lamp. Nitrogen gas (10.4 mmol, 100 + %) and elemental mercury (0.0342 g, 0.017 mg-atom, 1.7%) were evolved. After distillation of the volatiles (80–100 mm, 25°), a heavy, yellow-brown oil remained (3.12 g). Quantitative nmr analysis of the methylmercury and methyl ester region indicate a *ca.* 100% yield of only one compound, **3**. The compound has the following spectral characteristics: nmr ($CDCl_3$) δ 0.65 (s, with symmetrically placed ^{199}Hg–^{1}H doublet, J = 124 Hz, % ^{199}Hg = 17, 3 H), 3.49 (s, 3 H), 3.78 (s, with symmetrically placed ^{199}Hg–^{1}H doublet, 5 Hz, 3 H), 4.08 (s, with symmetrically placed ^{199}Hg–^{1}H doublet, 137 Hz, 1 H); nmr (100 MHz, $CDCl_3$) δ 0.63 (s, ^{199}Hg–^{1}H doublet, 125 Hz), 3.46 (s), 3.74 (s, with shoulders), 4.04 (s, ^{199}Hg–^{1}H doublet, 137 Hz), the methylmercury absorption at δ 0.65 appears to be composed of two closely spaced signals; ir (neat) 3.42, 5.86, 6.98, 7.49, 7.99, 8.55, 9.10, 10.67, 11.04, 12.83 μ; mass spectrum (70 eV, ^{200}Hg) *m/e* 318, 303, 259, 215, 200.

The addition of sodium borohydride (6.0 mmol, 0.23 g) to a portion of the oil (3.00 mmol, 0.95 g) dissolved in *ethanol* gave an exothermic reaction precipitating elemental mercury (1.91 mg-atom, 0.382 g, 64%). Quantitative glc analysis (Auto-Prep, Carbowax 1000, 12.5 ft × 0.25 in., 116°, 115 ml/min He) of the residue left after solvent distillation at 1 atm showed only the presence of ethyl methoxyacetate (1.28 mmol, 43%). Ethyl methoxyacetate was prepared independently by the reaction of methoxyacetyl chloride and absolute ethanol.

The postphotolysis solution of a small amount of methyl methylmercuridiazoacetate (0.25 mmol, 0.0792 g) in methanol-d_4 (1.0 g, 0.8 ml) gave an nmr spectrum in which the methyl ether (δ 3.49) and methine (δ 4.08) singlets are absent. It is interesting to note that the methyl ester absorption (δ 3.78) is not a singlet but a multiplet with an intensity pattern very similar to that of the partially deuterated methanol-d_4 methyl pattern (δ 3.37). Upon addition of the product obtained from the photolysis in methanol-h_4, the singlet absorption at δ 3.49 "grew" in while the central absorption of the methyl ester multiplet increased in amplitude as did the methylmercury singlet.

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Registry No.—**2**, 41580-12-5; **3**, 41580-13-6; methylmercuric ethoxide, 41580-14-7; methylmercuric chloride, 115-09-3; methyl diazoacetate, 6832-16-2; methyl ethylmercuridiazoacetate, 41580-16-9; methyl isopropylmercuridiazoacetate, 41580-17-0; methyl *tert*-butylmercuridiazoacetate, 41580-18-1; methyl benzylmercuridiazoacetate, 41580-19-2; ethyl methylmercuridiazoacetate, 31787-45-8; methyl phenylmercuridiazoacetate, 41580-21-6; phenylmercuric hydroxide, 100-57-2; ethyl phenylmercuridiazoacetate, 41580-22-7; methylmercuridiazoacetone, 41580-23-8; diazoacetone, 2684-62-0; phenylmercuridiazoacetone, 41580-24-9; methylmercuridiazoacetonitrile, 41580-25-0; diazoacetonitrile, 13138-21-1; methylmercuriphenyldiazomethane, 41580-27-2; phenyldiazomethane, 766-91-6; methylmercuridiazoethane, 41580-28-3; diazoethane, 1117-96-0; bis(methylmercuridiazomethane), 31787-47-0; diazomethane, 334-88-3.