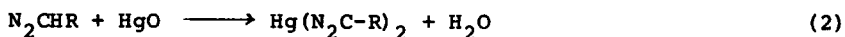
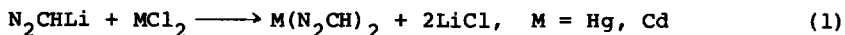


SYNTHESIS OF DIAZOMERCURIALS

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Recent interest in the chemistry of carbynes¹ and metal carbenes^{1,2} generated by photochemical decomposition of metal diazo compounds has prompted us to attempt the synthesis of some unknown variety of this type of structure. We have shown that photolysis of mercurydiazoacetate for instance, may lead to the formation of a carbyne or a mercurycarbene¹ intermediate, depending on the wavelengths of radiation. Schollkopf and coworkers have demonstrated that these same materials may be utilized as excellent reagents to prepare α -halo³, tin and silcondiazoesters² which are precursors of the corresponding carbenes. Over half a century ago Buchner⁴ discovered the reaction of mercuric oxide and diazoacetic esters, and described the first examples of diazomercurials, the methyl and ethyl derivatives. Recently Yates and Garneau reported the synthesis of similar structures from diazoketones⁵. We now have been able to add to this list a number of new diazomercurials and to extend the applicability of this synthetic reaction to those compounds which possess analogous activating groups such as cyano and trifluoromethyl. The reaction is described by equation 2,



The diazomercurials reported here include,

I, R = CF₃; II, R = CN; III, R = COMe; IV, R = COEt;

V, R = COiPr; VI, R = CO₂iPr; VII, R = CO₂All;

VIII, R = CO₂tBu, and IX, R = CO₂Ph.

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A. Synthesis of Mercurybis(trifluorodiazaoethane), I, and 1,1,1-Trifluorotriiodoethane.

2,2,2-Trifluorodiazaoethane was prepared by diazotization of 2,2,2-trifluoroethylamine hydrochloride.⁶ The freshly distilled ether solution (300 ml, 0.1M) was treated with yellow mercuric oxide (3.5g, 0.016 mole). The reaction mixture was stirred at 0° in the dark for 5 hours at which time most of the mercuric oxide was dissolved. After drying over anhydrous sodium sulfate and filtering, the intensely yellow ether solution was evaporated under reduced pressure to give essentially pure I (6.0g, 95% yield). Compound I exhibits a UV spectrum similar to its parent compound (Table II). The IR spectrum shows strong bands at 2070 cm⁻¹ (Hg-Diazo) and 1100-1300 (C-F) with no absorption above 3000 (C-H). While trifluorodiazaoethane exhibits a quartet (J = 4 cps) at 5.62τ in the NMR due to F¹⁹ coupling, I gives no signal. F¹⁹-NMR however, produces a singlet at 51.1ppm with C₆F₆ as internal reference (A-56/60-A). Combustion analysis data are commensurate with the formula C₄F₆N₆Hg, (Calcd: C, 11.49; N, 13.40. Found: C, 11.94; N, 13.64). High resolution mass spectrometer data (MS-9) gave a molecular weight of 420, a base peak at m/e 81 (C₂F₃⁺) and mass fragments characteristic of isotopic mercuries.

Mercurybis(trifluorodiazaoethane) is a supercooled yellow liquid (mp ~ 35°) at room temperature. In pure form it is relatively unstable, highly sensitive to heat and light, but in ether solution it may be stored for several weeks at 0° without appreciable decomposition. Attempts to purify it by distillation caused an explosion. As an example of its synthetic utility, the compound provides an efficient synthesis of the heretofore unknown 1,1,1-trifluorotriiodoethane. To prepare this material, an ether solution of I (0.05M, 10ml) was titrated with iodine in carbon tetrachloride. Mercuric iodide was filtered and the solvents were evaporated. The residue was distilled under reduced pressure (bp 58-60°/13mm) to give a violet liquid (150 mg, yield 70%). This compound gave IR bands at 1170 and 1196 cm⁻¹ (C-F) and a mass spectrometric molecular weight of 461.7092 (Calcd. for C₂F₃I₃ 461.7093). The F¹⁹-NMR shows a singlet at δ_{CFC1₃} 78.0 ppm.

B. Synthesis of Mercurybisdiazoacetonitrile, II.

Diazoacetonitrile was prepared by diazotization of aminoacetonitrile hydrosulfate according to a modified method of Curtius⁷. Mercuric oxide in slightly less than the theoretical amount was gradually added with stirring to the red liquid diazoacetonitrile. When the reaction mixture became a yellow viscous mass and mercuric oxide was no longer dissolved, ether was added to extract the unreacted material and soluble impurities. The yellow crude product was dried in vacuum. It appeared to be unusually stable in the absence of light, but decomposed at $\sim 150^\circ$ and exploded during combustion analyses. The IR spectrum consists of two intense sharp bands at 2180 (nitrile) and 2080 cm^{-1} (Hg-Diazo). The mass spectrum shows a parent ion at m/e 334 in agreement with the formula $\text{C}_4\text{N}_6\text{Hg}$ (202). The yield was $\sim 70\%$.

C. Synthesis of Mercurybisdiazoacetone, III.

Compound III was prepared in 83% yield under similar conditions as II, except the reaction was conducted under nitrogen atmosphere with occasional cooling to remove excessive heat of reaction which could cause fire. The reaction mixture was washed with n-pentane, dissolved in ether or chloroform, filtered, dried over sodium sulfate and recrystallized in carbon tetrachloride, (mp $121-2^\circ$). Compounds IV - IX were all satisfactorily prepared using procedure (C), with the exception of V which was most conveniently obtained by method (A) in n-pentane. Some relevant data related to these new compounds are given in Table I. Their spectroscopic data are summarized in Table II along with those of the parent compounds, some of which have not been previously reported.

TABLE I
New Diazomercurials

Hg(N ₂ C-R) ₂ R	Yield(%)	Mp	Recrystallization Solvent	Method
CF ₃ (I)	95	~ 35°	n-Pentane	A
CN (II)	80	150° dec.	crude	B
CO ₂ Me (III)	83	120-1°	CCl ₄	C
CO ₂ Et (IV)	65	69-70°	n-Pentane-Et ₂ O	C
CO ₂ iPr (V)	75	38-40°	crude	A
CO ₂ iPr (VI)	50	83-4.5°	n-Pentane-Et ₂ O	C
CO ₂ All (VII)	98	oil	passed over silica gel	C
CO ₂ tBu (VIII)	64	143-4°	n-Pentane-CHCl ₃	C
CO ₂ Ph (IX)	79	116-7°	n-Pentane-CHCl ₃	C

D. Synthesis of Mercury and Cadmiumbisdiazomethane.

Among the family of monovalent carbon intermediates, only methyne (CH) is known to exist in nature⁸. For this reason the synthesis of mercury and cadmium derivatives of diazomethane as potential sources of methyne has prominent significance. It has been reported by Wright and coworkers that this compound among others may be prepared in 5% yield by the reaction of diazomethane and mercuric acetate⁹. Unfortunately our many attempts to reproduce this reaction under a wide variety of conditions, including the use of reagents such as dimethoxymercury, mercuric oxide and halides etc., have not been successful. Exchange between diazomethyl lithium¹⁰ and mercuric halides in THF or ether at -70° was somewhat encouraging (Equation 1). A yellow color developed at low temperature, but when the reaction mixture was allowed to warm up it became colorless and no diazo product was detected. Only when cadmium chloride was used, a yellow oil with IR band at 2090 cm⁻¹ was isolated in low yield by low

TABLE II
Spectroscopic Data of Diazo Compounds and their Mercury Derivatives

R	N ₂ CH-R			Hg(N ₂ C-R) ₂			
	λ_{max} EtOH $\log \epsilon_{\text{max}}$	ν_{max} CHCl ₃ cm ⁻¹	δ_{max} CDCl ₃ τ	λ_{max} EtOH $\log \epsilon_{\text{max}}$	ν_{max} CHCl ₃ cm ⁻¹	δ_{max} CDCl ₃ τ	MS (Hg ₂ O ₂) M ⁺ at m/e
CF ₃	248 390	3120(w) 2110(s) 1110-	5.62(Q), J=4cps δ_{max} CFCl ₃ 56.7ppm(D)	250(3.83) 400(1.93)	2070(w) 1100-	δ_{max} CFCl ₃ 51.1 ppm	420 C ₄ F ₆ N ₄ Hg
CN	205(3.73) 248(4.09) 328(3.33)	3110(w) 2220(w) 2100(s)	5.50(S)	210(4.10) 258(4.04) 400(1.22)	2180(m) 2080(s)		334 C ₄ N ₆ Hg
COMe	250(4.96) 273(4.99) 350(1.36)	3120(w) 2100(s) 1650(s)	7.90(S, 3H) 4.60(S, 1H)	252(4.15) 278(4.19) 378(2.06)	2080(s) 2050(sh) 1580(s)	7.72(S)	368 C ₆ H ₆ N ₄ O ₂ Hg
COEt	246(3.93) 275(3.89) 352(1.37)	3120(w) 2105(s) 1650(s)	8.87(T, 3H) 7.65(Q, 2H) 4.70(S, 1H)	248(4.10) 272(4.00)	2045(s) 2100(sh) 1610(s)	8.87(T, 3H) 7.45(Q, 2H)	396 C ₈ H ₁₀ N ₄ O ₂ Hg
COiPr	250(3.86) 272(3.79) 354(1.43)	3110(w) 2110(s) 1650(s)	8.87(D, 6H) 7.50(H, 1H) 4.70(S, 1H)	285(4.06)	2050(s) 1600(s)	8.90(D, 6H) 7.14(H, 1H)	424 C ₁₀ H ₁₄ N ₄ O ₂ Hg
CO ₂ Me	250(4.38) 380(1.14)	3130(w) 2120(s) 1710(s)	6.35(S, 3H) 5.15(S, 1H)	265(4.34) 380(2.30)	2080(s) 1670(s)	6.30(S)	400 C ₆ H ₆ N ₄ O ₄ Hg
CO ₂ Et	250(4.13) 380(1.15)	3120(w) 2115(s) 1700(s)	8.75(T, 3H) 5.85(Q, 2H) 5.32(S, 1H)	264(4.39) 380(2.03)	2070(s) 2100(sh) 1670(s)	8.75(T, 3H) 5.81(Q, 2H)	428 C ₈ H ₁₀ N ₄ O ₄ Hg
CO ₂ iPr	248(4.12) 378(1.15)	3110(w) 2110(s) 1700(s)	8.74(D, 6H) 4.89(H, 1H) 5.20(S, 1H)	268(4.30) 382(2.06)	2070(s) 2100(sh) 1640(s)	8.75(D, 6H) 4.88(H, 1H)	456 C ₁₀ H ₁₄ N ₄ O ₄ Hg
CO ₂ All	247(4.22) 375(1.16)	3114(w) 3080(w) 2110(s) 1700(s)	5.55(D, 2H) 5.35(S, 1H) 4.90(Q, 2H) 3.90(M, 1H)	264(4.29) 375(1.96)	3080(w) 2080(s) 2085(sh) 1675(s)	5.50(D, 2H) 4.80(Q, 2H) 3.80(M, 1H)	452 C ₁₀ H ₁₀ N ₄ O ₄ Hg
CO ₂ tBu	280(3.30) 378(0.98)	3130(w) 2110(s) 1690(s)	8.55(S, 9H) 5.40(S, 1H)	278(3.69) 380(1.98)	1650(m) 2070(s) 1660(s)	8.52(S)	484 C ₁₂ H ₁₈ N ₄ O ₄ Hg
CO ₂ Ph	278(3.48) 365(1.18)	3120(w) 2112(s) 1720(s)	5.20(S, 1H) 2.80(M, 5H)	282(3.62) 370	2075(s) 1680(s)	2.80(M)	524 C ₁₆ H ₁₀ N ₄ O ₄ Hg

temperature vacuum distillation. Our current results indicates that diazomethane may not form a mercury derivative with mercuric oxide, because the hydrogens may not be sufficiently activated by the diazo group alone. But failure to isolate mercurybisdiazomethane from an exchange reaction involving diazomethylithium suggests an unusual instability of this compound, at least under our experimental conditions. **

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After submission of this communication, Dr. H. D. Hartzler of E.I. duPont de Nemours has kindly called our attention to his recent work (H.D. Hartzler, Abstracts of the 155th ACS Meeting, San Francisco, April, 1968, No.P205) and sent us an unpublished manuscript describing the synthesis and chemistry of other diazomercurials.