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MERCURY DERIVATIVES OF α-DIAZO KETONES

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Oxidation of the monohydrazones of α-diketones with yellow mercuric oxide in the presence of base is a well-known method for the preparation of α-diazo ketones (1). Some years ago, the interesting observation was made (2) that when this reaction was applied to I, the hydrazone of an α-ketoaldehyde, the crude product showed in its infrared spectrum two bands in the "diazo stretching" region [4.7 - 5.0 μ (3)]. One of these (4.76 μ) was shown to be due to the expected product, the α-diazo ketone II, but the nature of the product giving rise to the second band (4.82 μ) was not determined. It was found, however, that this second product was not formed when I was oxidized with activated manganese dioxide (4).

$$\mathrm{RCOCH{=}NNH_2} \xrightarrow[\mathrm{OH^-}]{\mathrm{HgO}} \mathrm{RCOCHN_2}$$

I, $R = 2,4,6\text{-}(CH_3)_3C_6H_2$ II, $R = 2,4,6\text{-}(CH_3)_3C_6H_2$

We have now found that the second product can be prepared in high yield by treatment of the diazo ketone II in petroleum ether with yellow mercuric oxide. Elemental analysis shows that it has the composition, $C_{22}H_{22}N_4O_2Hg$*; the presence of mercury was confirmed by the formation of mercuric iodide on treatment with iodine. Its infrared and ultraviolet spectra resemble those of II, while its n.m.r. spectrum significantly differs from that of II in lacking the one-proton singlet at δ 5.40 ppm due to the proton of the $-COCHN_2$ group (2). Treatment with hydrogen sulfide in aqueous dioxane gives the diazo ketone II and mercuric sulfide. On the basis of these observations we assign structure III to this compound.

$$RCOCHN_2 \xrightarrow{HgO} (RCOCN_2)_2Hg$$

II, R = 2,4,6-$(CH_3)_3C_6H_2$
IV, R = $(CH_3)_3C$
VI, R = C_6H_5
VIII, R = $C_6H_5CH_2$

III, R = 2,4,6-$(CH_3)_3C_6H_2$
V, R = $(CH_3)_3C$
VII, R = C_6H_5
IX, R = $C_6H_5CH_2$

In like manner, the mercury derivatives V, VII, and IX have been obtained from the α-diazo ketones, IV, VI, and VIII, respectively. The following is a typical procedure: To a solution of IV (2.00 g.) in petroleum ether (b.p. 40-60°; 200 ml.) was added yellow mercuric oxide (3.43 g.). The mixture was stirred in the dark at room temperature for 4 hours. The yellow solid was collected by gravity filtration and was extracted several times with

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* Satisfactory elemental analytical data for C, H, and N have been obtained for all new compounds.

diethyl ether followed by chloroform. The combined extracts were evaporated under reduced pressure to give V (2.89 g.; 81%) as yellow crystals, m.p. 128-128.5°; recrystallization from carbon tetrachloride raised the m.p. to 130.5-131°. This product and VII were shown to regenerate their parent diazo ketones on treatment in aqueous dioxane with hydrogen sulfide. As anticipated, ethyl 2-diazoacetoacetate and diazocamphor failed to give mercury derivatives.

The yields and m.p.'s of the mercury derivatives are listed in Table 1. Their spectroscopic properties are listed in Table 2 together with comparison data for the parent diazo ketones.

TABLE 1

Mercury Derivatives of α-Diazo Ketones

Compound	Yield(%)[1]	M.p.[2]		Recryst. Solvent
		Crude	Recryst.	
III	80	135-137°	138-139.5°	$CH_3CO_2C_2H_5$
V	81	128-128.5°	130.5-131°	CCl_4
VII	97	144.5-145.5°[3]	148-149.5°[4]	CH_2Cl_2
IX	55	107-111°	118-118.5°	C_6H_6

[1] Yield of crude product [2] All products melt with decomposition [3] Partial decomposition at 124.5-125.5° [4] Partial decomposition at 126-128°

TABLE 2

Spectroscopic Data for the Mercury Derivatives and their Parent Diazo Ketones[1]

$CHCl_3$ λ_{max}, μ		EtOH λ_{max}, mμ (log ε)		$CDCl_3$ δ, ppm[2]	
III	II	III	II	III	II
4.82	4.76	242(4.29)	240(4.01)	2.28, 2.32(9H)	2.30(9H)
6.27	6.20	278(4.27)	276(4.01)	-	5.40(1H)
				6.87(2H)	6.92(2H)
V	IV	V	IV	V	IV
4.80,[3] 4.87	4.75	254(4.04)	251(3.95)	1.26	1.15(9H)
6.29	6.14	284(4.02)	265(3.91)[3]	-	5.46(1H)
VII	VI	VII	VI	VII	VI
4.80,[3] 4.84	4.73	241(4.32)	251(4.05)	-	5.92(1H)
6.27	6.19	304(4.26)	297(4.09)	~7.55[4]	~7.62(5H)[4]
IX	VIII	IX	VIII	IX	VIII
4.81, 4.84[3]	4.74	253(4.04)	251(4.02)	3.66(2H)	3.60(2H)
6.26	6.14	293(4.02)	273(3.89)[3]	-	5.11(1H)
				~7.23(5H)[4]	7.26(5H)

[1] Compounds II-IX are yellow crystalline solids, except IV, which is a yellow liquid [2] Singlets unless otherwise specified [3] Shoulder [4] Multiplet

A corresponding reaction of diazoacetic esters was discovered many years ago by Buchner (5); however, there appears to have been no previous report of the formation of mercury derivatives of α-diazo ketones.

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