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SYNTHESIS OF α-ACETYLENIC KETONES BY ACYLATION OF MERCURY ACETYLENIDES

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In this paper, the possibility of preparing mercury acetylenides in a series of functionally substituted acetylenes, diacetylenes, and allenylacetylenes is studied, and the reactivity of these organomercury compounds with respect to chlorides and anhydrides of aliphatic, aromatic, and unsaturated carbocylic acids is investigated.

Three methods for preparation of Hg derivatives from acetylenic hydrocarbons have been described [1]. The only attempt to prepare a derivative of functionally substituted acetylene, namely, dimethylethynylcarbinol, ended in failure [1]. We were able to prepare two functionally substituted mercury acetylenides (Id) and (Ie) and also Hg derivatives of representatives of the class of diacetylenes (Ic) and allenylacetylenes (If) (Table 1) by selecting for each the most suitable of the known preparation methods [1]. Table 1 includes mercury acetylenides which we investigated in acylation, both previously known ones (Ia, b) and ones synthesized for the first time (Ic-f). The preparation method giving the best results is indicated for each compound.

Mercury acetylenides are high-melting solid substances easily purifiable by recrystallization, resistant to air, water, and bases, and freely soluble in dioxane, CH_2Cl_2, and, with heating, also in hydrocarbons. Mercury acetylenides are an acetylene-component source convenient for synthesis, especially in the case of unstable diacetylenes and acetylenes. Acetylenides (Ia-c) react easily with AcBr and AcCl during boiling of the reagent mixture in heptane, forming the corresponding ketones in yields of 40-70%. In addition, unlike in the case of dialkylmercury [3], both acetylene radicals bonded to the Hg atom are acylated, and the reaction proceeds easily in the absence of a catalyst (see also [4] and [5]):

$$\underset{(Ia-c)}{(RC{\equiv}C)_2Hg} + 2CH_3COX \rightarrow \underset{(IIa-c)}{2RC{\equiv}CCOCH_3} + HgX_2$$

$$R = C_6H_5\ (a),\ C_4H_9\ (b),\ C_4H_9C{\equiv}C\ (c);\ X = Cl,\ Br.$$

Addition of acetylenides (Id-f) (see Table 1) to this reaction did not give the desired results. Thus, the reaction of the acetylenide of dimethylethynylcarbinol (Id) with AcBr gave a mixture of unidentified products. During boiling with AcBr in heptane, the acetylenides of 3-(diethylamino)-1-propyne (Ie) and 5-methyl-3,4-hexadien-1-yne (If) were resinified.

The halides of benzoic acid are less active in this reaction than the halides of aliphatic acids. Thus, C_6H_5COCl did not react at all, and C_6H_5COBr required longer heating than AcBr. Moreover, in this reaction, only one of the acetylenide radicals of mercury acetylenide was acylated, apparently because of the formation of an insoluble intermediate organomercury compound

$$\underset{(Ia,\,c)}{(RC{\equiv}C)_2Hg} + C_6H_5COBr \rightarrow \underset{(IIIa,\,c)}{RC{\equiv}CCOC_6H_5} + \underset{(IVa,\,c)}{RC{\equiv}CHgBr}$$

Acetic, benzoic, crotonic, and tetrolic anhydrides were also investigated as acylating agents. It was found that all these anhydrides per se were inert with respect to mercury acetylenides, but in the presence of $AlBr_3$, acetic, benzoic, and crotonic anhydrides easily acylated mercury acetylenides to α-acetylenic ketones in 50-70% yields. The reaction proceeded in CH_2Cl_2 for 15 min at -20°C:

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TABLE 1. Mercury Acetylenides $(RC \equiv C)_2Hg$ (Ia-f)

Acetylenide	R	Preparation method*	Yield, %	Empirical formula	Found/Calculated, % C	H	N	IR spectrum, ν, cm⁻¹ (compacted KBr)	mp, °C (solvent)
(Ia)	C_6H_5	C	90					214	124 [1]
(Ib)	C_4H_9	B	80					2135	87–88 [2] (methanol)
(Ic)	$C_4H_9C\equiv C$	A	45					2130	156 (heptane—benzene)
		B	60	$C_{16}H_{18}Hg$	47,00/46,77	4,74/4,41		2230	
(Id)	$(CH_3)_2C(OH)$	A	58	$C_{10}H_{14}HgO$	32,40/32,74	4,15/3,84		2150 3400	79–80 (benzene)
(Ie)	$(C_2H_5)_2N_2CH_2$	A	31	$C_{14}H_{24}HgN$	39,93/39,49	6,09/5,74	6,80/6,65	2130	64–65 (acetone)
(If)†	$(CH_3)_2C{=}C{=}CH$	B	65	$C_{14}H_{14}Hg$	43,72/43,91	4,04/3,69		1960 2110 2150	128 (benzene)

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*Methods for preparation of mercury acetylenides [1]: A) Grignard reaction, $HgCl_2$; B) $Hg(OAc)_2$ in an amine medium; C) $HgCl_2$, KI in an alkaline medium.

†The reaction proceeds very fast: a mixture of precooled components is stirred for 2-3 min and poured into a cooled acid solution.

$$(RC\equiv C)_2Hg + 2\,(R'CO)_2O \xrightarrow[CH_2Cl_2]{AlBr_3} 2RC\equiv CCOR' + Hg(OCR')_2$$

$$\text{(II), (III), (V)}$$

$$R' = CH_3\ \text{(II)},\ C_6H_5\ \text{(III)},\ CH_3CH{=}CH\ \text{(V)}.$$

The reaction proceeded with tetrolic anhydride, as indicated by isolation of the corresponding mercury salt, but it was not possible to isolate the resulting diacetylenic ketone, probably because of its easy polymerization in the presence of $AlBr_3$. Therefore, tetrolic anhydride cannot be an acylating agent in the above-described reaction. Under the reaction conditions, functionally substituted acetylenides (Id) and (Ie) were resinified, and acetylenide (If) formed a ketone in 10% yield, also probably because of easy polymerization.

Thus, the high reactivity of the mercury acetylenides which we observed in acylation reactions opens up a new method for preparation of α-acetylenic ketones in the series of alkyl- and arylacetylenes and diacetylenes.

EXPERIMENTAL

The PMR spectra were recorded with a Varian DA-60-IL spectrometer (60 MHz), the chemical shifts were given in a δ scale, the standard was HMDS, and the solvent was $CdCl_3$. The IR spectra were recorded with a UR-10 instrument, and the UV spectra were recorded with a Specord UV-VIS instrument. The products were analyzed by thin-layer chromatography on Silufol and by GLC (glass column 2.5 m ×8 mm with 2.5% OV-1 on Chromosorb G).

Synthesis of α-Acetylenic Ketones Using Acid Bromides

1-Phenyl-1-butyn-3-one (IIa). Ketone (IIa) was similarly synthesized, 70% yield; bp 79-80°C (0.3 mm); n_D^{20} 1.5780. 2,4-DNPH, mp 193-194° [6].

3-Octyn-2-one (IIb). A solution of 1.23 g (0.01 mole) of $AcBr_3$ in 5 ml of benzene was added to a solution of 1.8 g (0.005 mole) of bis(1-hexynyl)mercury (Ib) in 30 ml of heptane at 70°C. In 5 min, precipitation was observed. The mixture was stirred for 30 min at 80-90°C. Isolated was (SiO_2, ether—hexane, 1:1) 0.9 g (70%) of (IIb), bp 67-68°C (8 mm); n_D^{20} 1.4490. 2,4-DNPH, mp 87-88° [6].

3,5-Decadiyn-2-one (IIc). Ketone (IIc) was similarly prepared, 40% yield, dark red, a liquid which was homogeneous according to thin-layer chromatography and GLC with a strong fruity odor; bp 74-75°C (0.7 mm); n_D^{20} 1.5125. Found: C 80.91; H 7.95%. $C_{10}H_{12}O$. Calculated: C 81.04; H 8.16%. IR spectrum (ν, cm^{-1}): 2235, 2150 (C =C), 1675 (CO). PMR spectrum (δ, ppm): 1.36 (3H, CH_3), 1.65 (3H, CH_3CO), 1.96 (4H, CH_2CH_2), 2.8 (2H, $CH_2C \equiv C$). 2,4-DNPH, mp 65°C. Found: C 58.57; H 4.97; N 16.98%. $C_{16}H_{16}N_4O_4$. Calculated: C 58.53; H 4.91; N 17.07%.

1,3-Diphenyl-1-propyn-3-one (IIIa). Bis(2-phenylacetylenyl)mercury (2 g) (0.005 mole) (Ia) and 1.85 g (0.01 mole) of benzoyl bromide in 50 ml of toluene were stirred for 12 h at 90°C. The mixture was cooled, and the precipitate was filtered. From the solution was isolated (SiO_2, ether—hexane, 1:1) 0.8 g (80%) of (IIIa), bp 128-130°C (0.25 mm). 2,4-DNPH, mp 212°C [6]. The precipitate was purified by sublimation at 100-120°C (0.2 mm). Obtained was 1.5 g of (IVa), mp 197-198°C. Found: C 24.70; H 1.51; Br 30.10%. C_8H_5BrHg. Calculated: C 25.18; H 1.31; Br 29.37%. IR spectrum (ν, cm^{-1}): 2130 ($C \equiv C$), 1650 (Ph), 1670 (CO).

1-Phenyl-2,4-nonadiyn-1-one (IIIc). Ketone (IIIc) was similarly prepared, 75% yield, bp 141-142°C (0.5 mm); n_D^{20} 1.5850. Found: C 85.30; H 6.82%. $C_{15}H_{14}O$. Calculated: C 85.68; H 6.71%. IR spectrum (ν, cm^{-1}): 2230, 2150 ($C \equiv C$), 1780, 1730 (CO), 1690, 1650 (Ph). UV spectrum [λ_{max}, nm (ε)]: 216 (11,700), 223 (9500), 256 (7860), 267 (12,800), 280 (15,700), 306 (11,400). 2,4-DNPH, mp 130°C. Found: C 64.45; H 4.64; N 14.6%. $C_{21}H_{18}N_4O_4$. Calculated: C 64.60; H 4.65; N 14.35%. In addition, 1.2 g of a crystalline product was isolated which was insoluble in most solvents and could not be purified.

Synthesis of α-Acetylenic Ketones Using Acid Anhydrides (General Procedure)

A solution of 0.01 mole of mercury acetylenide and 0.02 mole of the anhydride in 30 ml of CH_2Cl_2 was added to 5.32 g (0.02 mole) of $AlBr_3$ in 100 ml of CH_2Cl_2 under argon. Slight warming and precipitation were observed. In 15 min, the precipitate was filtered, the solution was decomposed with water, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with a 5% solution of $NaHCO_3$, a 60% solution of Na_2SO_4, and water. The Na_2SO_4 was dried. The product was purified (SiO_2, ether—hexane, 1:1) and distilled in vacuo.

Yields: (IIa) 70%, (IIc) 51%, (IIIa) 60%, (IIIc) 60%, (Va) 60%, bp 110-111°C (0.5 mm), n_D^{20} 1.5920. 2,4-DNPH, mp 195°C [7]. UV spectrum [λ_{max}, nm (ε)]: 230 (16,300), 298 (13,500). PMR spectrum (δ, ppm): 2.24 (3H, CH_3), 6.42 (H, J =16 Hz, CH), 7.58 (Ph, HC =). Yield of (Vc) 40%, bp 104-105°C (0.35 mm), n_D^{20} 1.5320. Found: C 82.41; H 8.36%. $C_{12}H_{14}O$. Calculated: C 82.72; H 8.10%. IR spectrum (ν, cm^{-1}): 2240, 2150 (C =C), 1650 (CO), 1625 (C =C). UV spectrum [λ_{max}, nm, (ε)]: 212 (14,600), 247 (12,400), 260 (9400), 279 (9800), 295 (8130). PMR spectrum (δ, ppm): 1.36 (3H, CH_3), 1.96 (4H, CH_2CH_2), 2.42 (3H, CH_3CH =), 3.8 (2H, CH_2C = C), 6.5 (H, J =16 Hz, =CH), 7.52 (H, Ch =). 2,4-DNPH, mp 103-104°C. Found: C 61.29; H 4.96; N 15.91%. $C_{18}H_{18}N_4O_4$. Calculated: C 61.01; H 5.12; N 15.81%.

CONCLUSIONS

1. A new reaction in the acetylene series was observed, namely, acylation of mercury acetylenides, opening up a new way to synthesize α-acetylenic ketones, and the limits of its applicability were studied.

2. A series of previously unknown mercury acetylenides were synthesized.

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