Acid Catalysis of the Claisen Rearrangement. 1. Formation of 4,4'-Bis(2*H*-chromenyl)mercury Derivatives from Aryl 2-Propynyl Ethers

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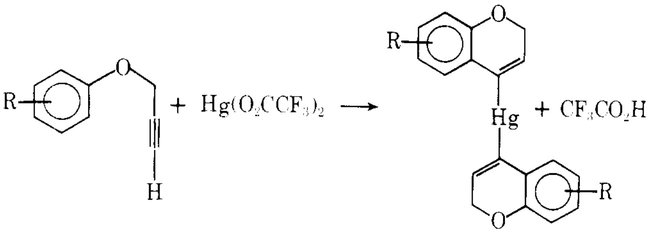
Schmid[1] has reported that phenyl propynyl ether when refluxed with silver tetrafluoroborate in chloroform gives 2*H*-chromene via a charge-induced Claisen rearrangement. Extending this reaction to 1,4-bis(aryloxy)-2-butynes we found[2] that the product may be a 4-substituted-2*H*-chromene or a 6*H*-benzofuro[3,2-*c*]-1,6a-dihydro-11a-methylbenzopyran depending on the aryl group and the reaction time. We felt that soft Lewis acids[3] other than Ag^+ ion might also induce such rearrangements and therefore undertook a survey of the interaction of various soft Lewis acids with aryl 2-propynyl ethers (1). The initial phase of this study revealed a very novel reaction of mercury(II) trifluoroacetate[4] with 1, which we now report.

Treatment of a series of 1 in dichloromethane solution with an equimolar amount of $Hg(O_2CCF_3)_2$ at room temperature followed by quenching with alkaline sodium borohydride[5] produced good to excellent yields of crystalline products. Elemental analysis of these products, listed in Table I, indicated the incorporation of a mercury atom. The fact that these compounds survived $NaBH_4$ treatment indicates the mercury atom is covalently bound. The NMR spectra are very similar to that reported[6] for 2*H*-chromene except the coupling due to H-4 is absent. Based on these data the 4,4'-bis(2*H*-chromenyl)mercury structure (2) is assigned to these compounds.



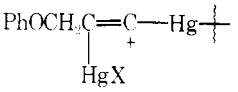
1 2

Organomercurials of this type have not been previously reported.[7]

Additional support for this assignment comes from the mass spectral fragmentation[8] of 2, e.g., for **2a:** *m/e* 464 (14%, M^+, $C_{18}H_{14}Hg^{202}O_2$), 262 (10%, M − Hg), and 131 (100%, $C_9H_7O^+$).

Since terminal alkynes are known[9] to yield mercury bis(acetylides) on treatment with certain mercuric salts, it is reasonable to postulate the intermediacy of 3 in the formation of **2.** Indeed compound **3a,** prepared via standard procedures, produces **2a** smoothly under the rearrangement conditions. The mechanism of conversion of 3 into 2 could involve two quite different mechanisms depending upon whether the mercuric ion triggers rearrangement via a σ or a π complex with the triple bond. After formation of 3 a π complex between 3 and remaining mercuric ion could effect a charge-induced Claisen rearrangement analogous to the process proposed[1] for rearrangement of 1 in the presence of silver(I) ion. Unlike silver ion, however, mercuric ion may form strong σ complexes as well as π complexes. Conversion of the initial π complex into a σ complex capable of cyclization via intramolecular electrophilic aromatic substitution, a process which may be viewed as a metal ion promoted Friedel–Crafts alkenylation of an aromatic ring by an alkyne,[11,12] is therefore an additional possibility.

Two different σ complexes 4 and 5, differing by the site of charge localization, may form. The preferred site of charge localization was determined by hydration (mercuric acetate, methanol, trace of sulfuric acid or methanol, sulfuric acid) of **3a.** Under these conditions the only product isolated was phenoxypropanone. That this product arises directly from **3a** and not from prior decomposition of **3a** to **1a** is evidenced by the fact that **1a** does not produce the ketone nearly as quickly as **3a** under identical conditions. Phenoxypropanone would be expected to readily form from compounds such as 6, as the facile protonolysis of vinylic C–Hg bonds is well known.[13] Intermediate 6 in turn would arise from nucleophilic attack on 5. Thus hydration of **3a** implicates 5 as the more favorable σ complex. Since 5 can form only a five-membered ring on cyclization with the adjacent aromatic ring (under aprotic conditions), we favor an electrocyclic mechanism initiated by a π complex for 2*H*-chromene formation as shown in Scheme I.[14]



$\mathrm{PhOCH_2}\underset{\mathrm{HgX}}{\underset{|}{\mathrm{C}}}{=}\underset{+}{\mathrm{C}}\text{—Hg—}$

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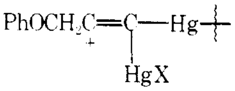
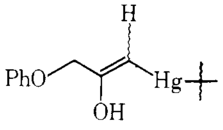


$\mathrm{PhOCH_2}\underset{+}{\mathrm{C}}{=}\underset{\mathrm{HgX}}{\underset{|}{\mathrm{C}}}\text{—Hg—}$

5



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Results of the interaction of 1 with other soft Lewis acids

Table I. Physical and Spectral Data for 4,4'-Bis(2*H*-chromenyl)mercury Derivatives

	R (1)	registry no.	Yield,[c] %	mp, °C (corr)	NMR[b] ($CDCl_3$), δ
a	H[a]	66901-46-0	75	141–142	6.03 (2 H, t, *J* = 3.4 Hz), 4.90 (4 H, d, *J* = 3.4 Hz)
b	4-CH_3[a]	66901-45-9	83	177–178.5	6.07 (2 H, t, *J* = 3.6 Hz), 4.88 (4 H, d, *J* = 3.6 Hz)
c	4-OCH_3	66901-44-8	97	172–173	6.17 (2 H, t, *J* = 3.6 Hz), 4.88 (4 H, d, *J* = 3.6 Hz)
d	4-Cl		83[d]		
e	2-Cl	66901-43-7	54	196.5–197	6.13 (2 H, t, *J* = 3.8 Hz), 5.08 (4 H, d, *J* = 3.8 Hz)
f	2,4-Cl_2		72[e]		

[a] IR (KBr) **2a:** 1470 (s), 1220 (s), 1080 (s), 750 (s) cm^{-1}. IR (KBr) **2b:** 1480 (s), 1220 (s), 820 (s) cm^{-1}. [b] Compare 2*H*-chromene (ref 6): (CCl_4) δ 6.30 (1 H, d with t-like fine structure, H-4), 5.60 (1 H, d × t, $J_{3,4}$ = 10 Hz, H-3), 4.72 (2 H, d × d, $J_{2,3}$ = 3.5 Hz, $J_{2,4}$ = 1.7 Hz, H-2). The resemblance of the spectrum of **2b** to that of 4,4'-bis(6-methyl-2*H*-chromene) is even more striking: mp 115–116 °C; NMR δ 6.8 (3 H, m), 5.8 (1 H, t, *J* = 4 Hz), 4.7 (2 H, d, *J* = 4 Hz), 2.3 (3 H, s). [c] Isolated product. Correct elemental analysis (±0.4%) was obtained for all new compounds. Purification consisted of filtration through alumina followed by recrystallization from hexane–chloroform. [d] The product isolated was 1-(4-chlorophenoxy)-2-propanone characterized by NMR and by conversion to the semicarbazone; mp 189.5–190.5 °C (lit.[10] mp 181–182 °C). An authentic sample gave a semicarbazone, mp 189.5–190.5 °C. [e] The product isolated was 1-(2,4-dichlorophenoxy)-2-propanone characterized by comparison with an authentic sample.

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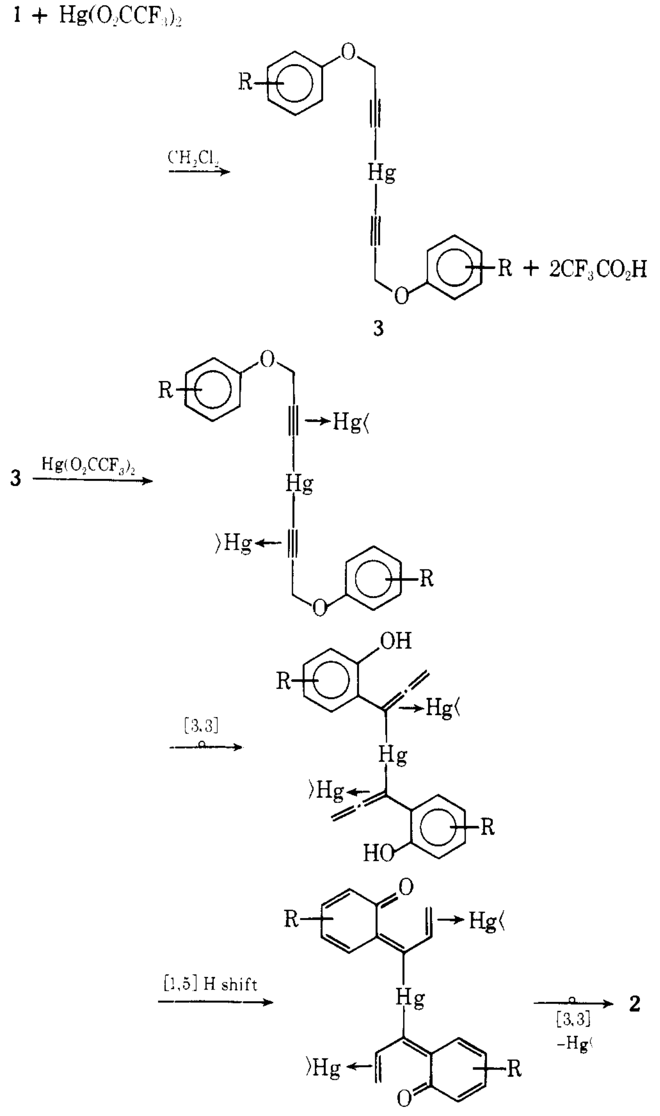
Scheme I



will be reported in due course as will the utility of 2 in organic synthesis.

Experimental Section

Melting points were determined on a Fischer–Johns melting point apparatus and are corrected. Spectral data was collected as follows: IR, Perkin-Elmer 435B (KBr); NMR, $CDCl_3$; Me_4Si reference (δ 0.00), Varian T-60; mass spectra, Hitachi Perkin-Elmer RMU-6E. The mass spectra were kindly provided by Dr. J. D. Willett of the University of Idaho, Moscow, Idaho. Microanalyses were performed under the supervision of Mr. Mike Gilles in the Michigan Technological University microanalytical laboratory.

General Procedure for the Preparation of 2. Equimolar amounts of 1a and mercuric trifluoroacetate were mixed, under N_2, in dichloromethane (5 mL/mmol) and stirred at room temperature for 2 h. The reaction was then quenched slowly (frothing) with excess alkaline (2 M NaOH) 2 M $NaBH_4$ solution. The mixture was filtered and the organic phase was washed with water. The dried ($MgSO_4$) organic layer was rotary evaporated to yield the products listed in Table I as colorless crystalline solids.

Acknowledgment. We wish to thank Dr. K. K. Balasubramanian for supplying spectral data for 4,4′-bis(6-methyl-2*H*-chromene). This research was supported by the Research Corp.

Registry No.—Phenyl 2-propynyl ether, 13610-02-1; *p*-tolyl 2-propynyl ether, 5651-90-1; *p*-anisyl 2-propynyl ether, 17061-86-8; *p*-chlorophenyl 2-propynyl ether, 19130-39-3; *o*-chlorophenyl 2-propynyl ether, 17061-92-6; 2,4-dichlorophenyl 2-propynyl ether, 17061-90-4; mercuric trifluoroacetate, 13257-51-7; 1-(4-chlorophenoxy)-2-propanone, 18859-35-3; 1-(2,4-dichlorophenoxy)-2-propanone, 17199-30-3.

References and Notes

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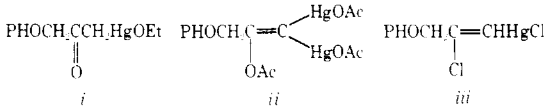
(2) Part 2. *J. Org. Chem*, submitted for publication.
(3) R. Pearson, Ed., "Hard and Soft Acids and Bases", Dowden, Hutchinson, and Ross Publishing Co., Stroudsburg, Pa., 1973.
(4) H. C. Brown and M. H. Rei, *J. Am. Chem. Soc.*, **91**, 5646 (1969).
(5) H. C. Brown and H. J. Hammar, *J. Am. Chem. Soc.*, **89**, 1522 (1967).
(6) R. Hug, Gy. Fráter, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **54**, 306 (1971).
(7) The reaction of 1 with other mercuric salts has been described. Compounds such as 3 have been observed only under alkaline conditions with HgI_2 and $Hg(CN)_2$ (see also ref 9). Under neutral conditions 1 reacts with mercuric oxide (in aqueous ethanol) to give i and with mercuric acetate to give ii. Under acidic conditions mercuric chloride and 1 yield iii: A. Filippova, et al., *Dokl. Vses. Konf. Khim. Atsetilena, 4th*, **2**, 206 (1972).


$\mathrm{PHOCH_2CCH_2HgOEt}$ (C=O) *i*; $\mathrm{PHOCH_2C(OAc){=}C(HgOAc)_2}$ *ii*; $\mathrm{PHOCH_2C(Cl){=}CHHgCl}$ *iii*

(8) The mass spectra of alkyl and aryl bis(ethynyl)mercury compounds are dominated by C–Hg bond fission and Hg extrusion, cf. N. A. Bell and S. W. Brewer, *J. Chem. Soc., Perkin Trans. 2*, 717 (1974).
(9) J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926); the reported melting point of bis(3-phenoxyprop-1-ynyl)mercury is 120.5–121 °C.
(10) K. S. Bokarev and N. N. Melnikov, *Chem. Abstr.*, **49**, 14678 (1955).
(11) R. M. Roberts and M. B. Abdel-Baset, *J. Org. Chem.*, **41**, 1698 (1976).
(12) Mercuric ion catalysis of a [3,3] sigmatropic rearrangement via a σ complex has been reported: L. E. Overman and C. B. Campbell, *J. Org. Chem.*, **41**, 3338 (1976).
(13) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw-Hill, New York, N.Y., 1968.
(14) This paper is dedicated to the memory of Professor H. Schmid.

Photocyclodimerization of Bicyclo[6.3.0]undec-1(8)-en-9-one. Synthesis of Highly Congested Pentacyclopropellanones

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There has been considerable interest recently in pentacyclopropellanes wherein two propellane units share a common cyclobutane ring from theoretical and synthetic viewpoints.[1] Within this class of highly strained compounds, those constituted of large carbocyclic rings fused to the cyclobutane ring are expected to show unusual chemical and physical properties as a consequence of significantly repulsive nonbonded interaction of hydrogens between two kinds of carbocyclic rings facing each other. In this connection, we present here the synthesis of highly congested pentacyclopropellanes as a part of studies on the synthesis of sterically crowded polycyclic propellanes.[2]

For the purpose of building up such pentacyclic skeleton, photocyclodimerization of bicyclic cyclopentenones 1–4 was