C₆H₅
|
C
‖
C
R₂Al⟨ ⟩AlR₂
C
‖
C
|
C₆H₅

4

Examination of Figure 1,[20] however, shows that the bridging aluminum and carbon atoms form a rectangular array where the aluminum atoms are bonded only to the α acetylenic carbon atoms. The AlC≡C–moiety is nearly linear and the C≡C bond length is equal to the usual acetylenic bond length of 1.207 ± 0.02 Å. The aluminum-bridging carbon distances of 2.184 and 1.992 Å and the Al–C–Al angle of 91.73° suggest bonding *via* one Al–C σ bond and overlap between one carbon 2p π orbital with the aluminum 3p_z orbital. The acetylenic group can thus be considered to be a three-electron donor. This bonding scheme is probably responsible for the unusual stability previously noted for unsaturated organogallium and -indium dimers.[21] The structure can be viewed as a model for the π complex suggested in **2** with the aluminum atom interacting with the acetylenic carbon atom having the greater electron density.

The autoreactivity of **3** substantiates the view that **5**

5 → **6** ↓ **7** ← **8**
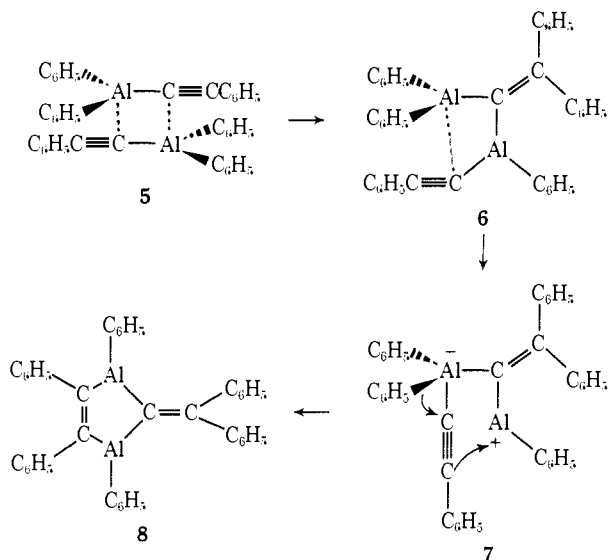
is a good model for the intermediate in the carbalumination of alkynes; **3** heated above its melting point of 144° forms a red melt which, upon hydrolysis, yields 1,1-diphenylethylene. Hydrolysis with D₂O gives 1,1-diphenyl-2,2-dideuterioethylene and deuteriophenylacetylene. The absence of *trans*-stilbene is significant, for this additional product arises when triphenylaluminum attacks phenylacetylene.[17] Further heating of the red melt of **3** (>150°) and hydrolysis now reveals the presence of 1,1-diphenylethylene, *cis*-stilbene, and a

less volatile hydrocarbon.[22] The former two hydrocarbons can be readily envisaged as stemming from **6** and **8**, respectively, in which **6** could arise from the autocarbalumination of **5** with the regiospecificity controlled by the π-complexation and in which **8** could arise from a π-complexed intermediate (**6**) which facilitates migration of a phenyl group from aluminum to the more electronegative sp-hybridized α-carbon atom. This rearrangement would also be favorable because the negative charge buildup on the α sp carbon can be delocalized over at least two carbon atoms by rearranging to the *cis*-stilbene moiety in (**8**).[23]

In summation, the foregoing structural and chemical study delineates an instance where the starting material clearly displays dual π-complexation between aluminum and the acetylenic linkage and where its regiospecificity in carbalumination is most readily explained by minimal distortions from its ground-state configuration.

(22) S. G. Rhee, unpublished studies, State University of New York at Binghamton.
(23) The ease with which unsymmetrical organoaluminum compounds undergo disproportionation makes unlikely the isolation of structures 6 and 8 from the reaction melt. But the absence of the expected *trans*-stilbene from a precedented cis carbalumination necessitates that the novel and exclusive trans carbalumination be determined by intermediates similar to 6 and 7.

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Electroreductive Synthesis of Symmetrical Organomercurials from 1,ω-Dibromides[1]

Sir:

Isolation of organomercurials from electroreduction of organic compounds at a mercury cathode is well known.[2] Low to moderate yields of symmetrical dialkylmercury compounds from the electroreduction of ketones were first reported more than half a century ago,[3] and such reports are numerous.[4] On the other hand, moderate yields of organomercurials from organic bromides have been achieved only for substituted

(1) Part III. For Part II, see J. Casanova and H. R. Rogers, *J. Org. Chem.*, in press.
(2) (a) H. Lehmkuhl, "Organic Electrochemistry," M. Baizer, Ed., Marcel Dekker, New York, N. Y., 1973, p 623; (b) A. P. Tomilov and I. N. Brago, "Progress in Electrochemistry of Organic Compounds," Vol. 1, A. N. Frumkin and A. B. Ershler, Ed., Plenum Press, London, 1971, p 242.
(3) J. Tafel, *Ber.*, 39, 3626 (1906).
(4) (a) J. Haggerty, *Trans. Electrochem. Soc.*, 56, 421 (1929); (b) T. Arai, *Bull. Soc. Chem. Jap.*, 32, 184 (1959); (c) C. Schall and W. Kirst, *Z. Elektrochem.*, 29, 537 (1923); (d) J. Tafel, *Ber.*, 42, 3146 (1909).

(20) The weighted *R* factor obtained from the full-matrix least-squares refinement of 1281 reflections measured on a Picker diffractometer is currently 0.026. Relevant crystallographic data are ·D₂ₕ¹⁵-Pbca; Z = 4, ρ_calcd = 1.19 g/cm³ for Al₂(C₆H₅)₄(C≡CC₆H₅)₂;[4] a = 19.07 (s), b = 23.23 (2), c = 7.211 (6) Å.
(21) E. A. Jeffery and T. Mole, *J. Organometal. Chem.*, 11, 393 (1968).

benzyl bromides[5] and for 1-iodo-1-methyl-2,2-diphenyl-cyclopropane.[6] Alkyl halides, unadorned by structural features which might stabilize an intermediate radical or anion, however, have been reported[7] to give little or no organomercurials. Conventional chemical preparations of organomercurials, while general in scope, are usually poor in yield.[8] The best of these preparations involve organometallic metal halide interchange[8b,c,9] or reductive symmetrization.[9b]

We wish to report that controlled potential electro-reduction of 1,ω-dibromides in which ω is 4 or greater, using a stirred mercury cathode, produces excellent yields of symmetrical organomercurials in an overall three-electron reduction (see Table I). The electro-

Table I. Preparation of Organomercurials by Controlled Potential Electroreduction of 1,ω-Dibromides at −2.5 V[a]

Dibromide	Solvent	Yield (%) of R₂Hg
Br(CH₂)₄Br	DMF[b,c]	93
Br(CH₂)₄Br	CH₃CN[d]	58
Br(CH₂)₄Br	Dioxane-H₂O[d]	50
Br(CH₂)₃C(CH₃)HBr	DMF[b,d]	94[e]
Br(CH₂)₅Br	DMF[b,d]	96[f]
Br(CH₂)₆Br	DMF[b,d]	52[g]
Br(CH₂)₇Br	DMF[b,d]	56
Br(CH₂)₁₂Br	DMF[b,d]	49

[a] Mercury cathode vs. saturated calomel electrode. [b] Dimethylformamide. [c] Supporting electrolyte, tetrabutylammonium fluoroborate. [d] Supporting electrolyte, tetraethylammonium fluoroborate. [e] The product was composed of the two possible (C₅H₁₁)₂Hg isomers, di-2-pentylmercury and di-n-pentylmercury, in the ratio of 9:1, respectively. [f] The product was a mixture of di-n-pentylmercury and pentamethylenemercury in the ratio of 4:1, respectively. [g] In addition, 34% of (n-C₆H₁₃Hg)₂ was obtained.

reduction of 1,4-dibromobutane and 1,5-dibromopentane in dimethylformamide at 40–50 V applied potential was previously reported[10] to give a mixture of cyclobutane and butane and n-pentane, respectively. In our hands, controlled current electroreduction at high applied potential failed to produce organomercurials, and the principal products were hydrocarbons in very poor yield (see Table II). Such dependence of the yield of organomercurials on potential has been reported previously.[5,6] Most of the dialkyl mercury compounds described here have been prepared previously.[11] They have been characterized by us by conversion to the

(5) J. Grimshaw and J. J. Ramsey, J. Chem. Soc. B, 60 (1968).
(6) J. L. Webb, C. K. Mann, and H. M. Walborsky, J. Amer. Chem. Soc., 92, 2042 (1970).
(7) (a) A. J. Fry, "Synthetic Organic Electrochemistry," Harper and Row, New York, N. Y., 1972, p 172: ref 2a; (b) J. W. Sease and R. C. Reed, Extended Abstracts, Electrochemical Society Meeting, New York, N. Y., May 4–9, 1969, p 328.
(8) (a) F. C. Whitmore, "Organic Compounds of Mercury," Reinhold, New York, N. Y., 1921; (b) G. E. Coates and K. Wade, "Organometallic Compounds," Vol. 1, Methuen and Co., London, 1967, pp 157–166; (c) F. Wagenknect and R. Juza, "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd ed, G. Brauer, Ed., Academic Press, New York, N. Y., 1965, p 1118.
(9) (a) C. S. Marvel and V. L. Gould, J. Amer. Chem. Soc., 44, 153 (1922); (b) N. N. Mel'nikov, Zh. Obshch. Khim., 16, 2065 (1946).
(10) M. R. Rifi, J. Amer. Chem. Soc., 89, 4442 (1967).
(11) (a) W. Jones, D. Evans, T. Gulwell, and D. Griffiths, J. Chem. Soc., 45 (1935); (b) F. Hager and C. Marvel, J. Amer. Chem. Soc. 45,, 822 (1923); (c) G. Beinert and J. Parrod, C. R. Acad. Sci., 255, 1930 (1962); (d) G. Bahr and G. Meier, Z. Anorg. Allg. Chem., 294, 22 (1958); (e) N. Hagihara, M. Kumada, and R. Okawara, Ed., "Handbook of Organometallic Compounds," W. A. Benjamin, New York, N. Y., 1968.

Table II. Controlled Current Electroreduction of 1,ω-Dibromides in Dimethylformamide

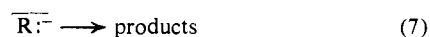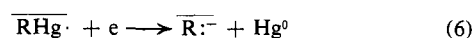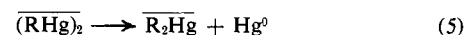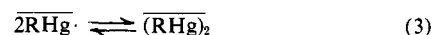| Dibromide	Current (mA)	Potential[a]	Products (%)
Br(CH₂)₄Br[b]	200	13	c-C₄H₈ (0.3), n-C₄H₁₁ (7.1), 1-butene (0.7)[c]
Br(CH₂)₄Br[d]	200	14	c-C₄H₈ (0.3), n-C₄H₁₀ (4.2), 1-butene (0.7)
Br(CH₂)₄Br[e]	700	29	c-C₄H₈ (1.3), n-C₄H₁₀ (45), ethene (66)[f]
Br(CH₂)₅Br[e]	700	26.5	n-C₅H₁₂ (28)

[a] Applied potential in volts. [b] Supporting electrolyte, tetrabutylammonium fluoroborate. [c] 1-Butene has been reported to result from the Hofmann elimination of tetrabutylammonium salts (A. J. Fry and R. G. Reed, J. Amer. Chem. Soc., 94, 8475 (1972), and ref 10). [d] Supporting electrolyte, lithium perchlorate. [e] Supporting electrolyte, tetraethylammonium fluoroborate. Ethene is an artifact, the product of Hofmann elimination of tetraethylammonium salts (vide supra). Triethylamine was the only product recovered from the catholyte.

respective alkyl bromides with bromine,[12] by high resolution mass spectra,[13] which revealed unmistakable RHg⁺ and Hg⁺ isotope patterns, and by ¹H and ¹³C magnetic resonance chemical shifts and coupling constants.[14] Di-2-pentylmercury, previously unreported, gave 2-bromopentane upon cleavage with bromine. Di-n-hexyldimercury, obtained in 34% yield from 1,6-dibromohexane, represents what we believe to be the first isolation of a mercury(I) compound in electro-reduction. Such compounds have been previously suggested by Dessy[15] for implication as possible intermediates in electroreduction at mercury. Di-n-hexyldimercury has been characterized by reaction with bromine to produce n-C₆H₁₃Br, mass spectrum C₆H₁₃-Hg⁺, Hg₂²⁺, Hg₂⁺, and (C₆H₁₃Hg)₂⁺ all with characteristic mercury isotope distributions, and by elemental analysis.

The formation of organomercurials in high yields from 1,ω-dibromides, but not from the equivalent monobromides, the isolation of a mercury(I) species, and the characteristic ECE[16] chronoamperometric (potentiostatic) curves which are observed, lead us to conclude that a mechanism similar to that proposed by Webb, Mann, and Walborsky[6] may be central to the behavior observed in the present case. The salient features of such a mechanism are expressed in Scheme I

Scheme I

$$RBr \longrightarrow \overline{RBr} \cdot \quad (1)$$

$$\overline{RBr} \cdot + e + Hg^0 \longrightarrow \overline{RHg} \cdot + Br^- \quad (2)$$

$$2\overline{RHg} \cdot \rightleftharpoons \overline{(RHg)_2} \quad (3)$$

$$\overline{(RHg)_2} + RBr \rightleftharpoons (RHg)_2 + \overline{RBr} \cdot \quad (4)$$

$$\overline{(RHg)_2} \longrightarrow \overline{R_2Hg} + Hg^0 \quad (5)$$

$$\overline{RHg} \cdot + e \longrightarrow \overline{R:}^- + Hg^0 \quad (6)$$

$$\overline{R:}^- \longrightarrow products \quad (7)$$

(12) (a) Reference 8a, p 1230; (b) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, p 75.
(13) (a) M. I. Bruce, Advan. Organometal. Chem., 6, 313 (1968); (b) W. F. Bryant and T. H. Kinstle, J. Organometal. Chem., 24, 573 (1970).
(14) F. J. Weigert and J. D. Roberts, Inorg. Chem., 12, 313 (1973).
(15) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, J. Amer. Chem. Soc., 88, 460 (1966).
(16) G. Cauquis, "Organic Electrochemistry," M. Baizer, Ed., Marcel Dekker, New York, N. Y., 1973, p 56.

Figure 1.
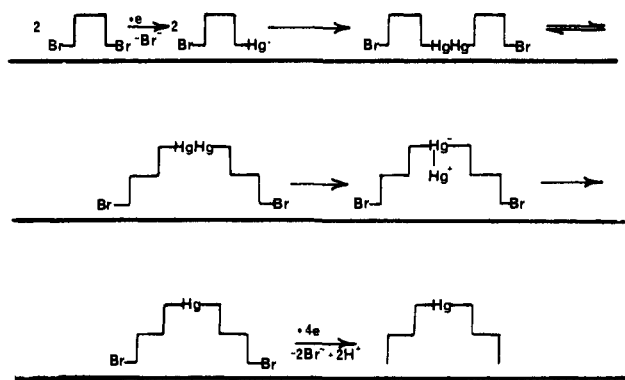
(illustrated for a monobromide).[17] The most cogent aspects of the present proposal are the assumptions that, for step 4, $K_{eq} \gg 1$ and that disproportionation of $(RHg)_2$ occurs faster in the high field gradient near the electrode surface than it does in the bulk of the solution. If these assumptions are correct, the presence of a second C–Br bond in the dibromides will restrain the mercury(I) dimer to a region proximal to the electrode surface, where disproportionation can occur readily. Evidence for the radical (RHg·) in electroreductions is abundant.[6,18] Disposition of (RHg·) depend upon concentration, potential, and acid conditions.[18c,d] Electrolytic symmetrization of alkylmercuric halides is well documented.[19] The Jensen mechanism for disproportionation[20] (step 4, Scheme I), would be expected to lead to a marked increase in the rate of disproportionation near the electrode surface, where the field gradient may be as high as 10^6 V/cm and the chemistry of highly polarized species might well be affected.[21] Since we find that the first electron is consumed at a rate close to the rate of disappearance of starting material, there is little reason to invoke autocatalytic production of $RHgBr^{6,22}$ as an important intermediate, at least at these potentials.

Our present understanding of this unusual reaction is summarized in Figure 1, illustrated for the C_4 case. These results suggest a central role of adsorption in the fate of electroorganic processes. Work continues on the mechanism and scope of this process.

(17) The bar over a formula denotes adsorption on the electrode surface.
(18) (a) C. A. Kraus, *J. Amer. Chem. Soc.*, 35, 1732 (1913); (b) H. M. Billinge and B. G. Gowenlock, *J. Chem. Soc.*, 1201 (1962); (c) R. Benesch and R. E. Benesch, *J. Amer. Chem. Soc.*, 73, 3391 (1951); (d) *J. Phys. Chem.*, 56, 648 (1952).
(19) L. G. Marakova, "Organometallic Reactions," Vol. 2, E. I. Becker and M. Tsutsui, Ed., Wiley-Interscience, New York, N. Y., 1971, pp 374, 375.
(20) Reference 12b, p 142.
(21) Reference 7a, p 57.
(22) A. Kirrman and E. Kleine-Peter, *Bull. Soc. Chim. Fr.*, 894 (1957).
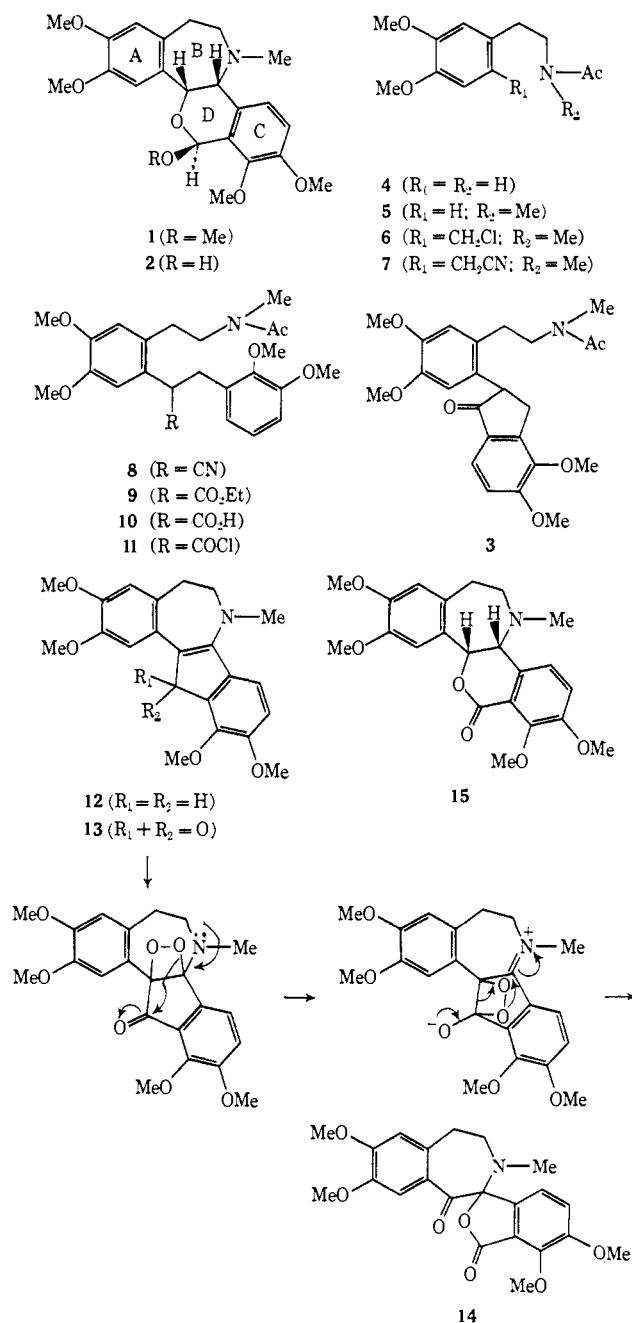
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Received January 2, 1974

Photosensitized Oxidation of an Enaminoketone. The Total Synthesis of a Rhoeadine Alkaloid

Sir:

The oxidation of enamines by singlet oxygen has been reported[1] to proceed *via* a dioxetan intermediate which undergoes facile decomposition to carbonyl compounds in a process promoted by the pair of electrons on the nitrogen atom. We now report that in extending this reaction to an enaminoketone system, the decomposition of the corresponding dioxetan is accompanied by a novel and useful rearrangement. Specifically, the enaminoketone 13 has been oxidatively rearranged to the ketolactone 14 by this method thus

1 (R = Me)
2 (R = H)

4 ($R_1 = R_2 = H$)
5 ($R_1 = H; R_2 = Me$)
6 ($R_1 = CH_2Cl; R_2 = Me$)
7 ($R_1 = CH_2CN; R_2 = Me$)

8 (R = CN)
9 (R = CO₂Et)
10 (R = CO₂H)
11 (R = COCl)

3

12 ($R_1 = R_2 = H$)
13 ($R_1 + R_2 = O$)

15

14

providing a convenient solution to the problem of achieving the desired substitution pattern in ring C of

(1) J. E. Huber, *Tetrahedron Lett.*, 3271 (1968); T. Matsuura and I. Saito, *ibid.*, 3273 (1968).