Letters to the Editor

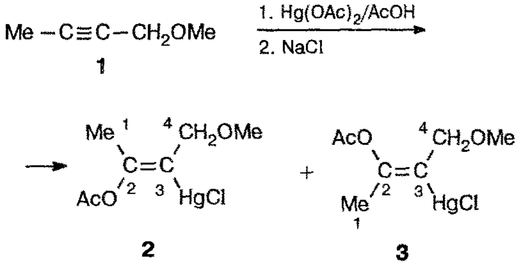
Stereochemistry of acetoxymercuration of 1-methoxy-2-butyne

V. R. Kartashov,[a]* *T. N. Sokolova,*[a] *O. A. Frolovskaya,*[a] *N. V. Malisova,*[a] *Yu. K. Grishin,*[b] *and N. S. Zefirov*[b]

[a]*Nizhnii Novgorod Technical State University,*
24 ul. Minina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 36 9475
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 0126

It was found previously[1] that the reaction of methylphenylacetylene with $Hg(OAc)_2$ in AcOH gives a *cis*-isomer in a low yield (8 to 15 %, depending on the reagent ratio). The yield of the *cis*-isomer increases to 45 % in a similar reaction with methyl(*m*-chlorophenyl)acetylene.[2] In view of this, a problem arises concerning the stereochemistry of acetoxymercuration of acetylenic compounds containing substituents of structural types other than aryl groups.

We studied the stereochemistry of the reaction of $Hg(OAc)_2$ with alkyne **1** in AcOH:



It was found that stereoisomers **2** and **3** are the products of the reaction, formed in a 66 : 34 ratio. The reaction studied is the first example of predominant formation of a *cis*-isomer in the acetoxymercuration of alkynes.

The structures of compounds **2** and **3** were established by ^1H and ^{13}C NMR spectroscopy. The criteria used for structural assignment of compounds such as **2** and **3** have been reported previously.[1,3]

The reaction was carried out by the known procedure.[1] The reaction of alkyne **1** (0.58 g, 6.9 mmol) and $Hg(OAc)_2$ (2.20 g, 6.9 mmol) in AcOH (30 mL) for 20 h gave 1.64 g of a mixture of crystalline products (yield 63 %). The reaction products were isolated after work-up of the reaction mixture with 1 % aqueous NaCl. The mixture was dissolved in boiling MeOH, and the insoluble decomposition products were filtered off. The solvent was removed to give 1.15 g of crystals, which were analyzed by NMR spectroscopy. Compounds **2** and **3** were isolated by fractional crystallization from MeOH. ***Z*-4-Methoxy-2-methoxycarbonylbuten-2-yl-3 mercury chloride (2)**: m.p. 114—115 °C. ^1H NMR ($CDCl_3$), δ: 1.947 (s, 3 H, CH_3, $^4J_{Hg,H}$ = 11.0 Hz); 4.036 (s, 2 H, $C\underline{H}_2{-}OCH_3$, $^3J_{Hg,H}$ = 164.5 Hz); 3.297 (s, 3 H, $CH_2{-}OC\underline{H}_3$); 2.080 (s, 3 H, $OCOC\underline{H}_3$). ^{13}C NMR ($CDCl_3$), δ: 138.96 (C(3), $^1J_{Hg,H}$ = 2307 Hz); 149.17 (C(2), $^2J_{Hg,H}$ = 83 Hz); 17.37 (CH_3, $^3J_{Hg,H}$ = 142 Hz); 71.22 (CH_2, $\underline{C}H_2OCH_3$, $^2J_{Hg,H} \le$ 5 Hz); 169.49 (CO, $O\underline{C}OCH_3$, $^4J_{Hg,H}$ = 20 Hz); 58.03 (CH_3, $CH_2O\underline{C}H_3$). ***E*-4-Methoxy-2-methoxycarbonylbuten-2-yl-3 mercury chloride (3):** m.p. 84—86 °C. ^1H NMR ($CDCl_3$), δ: 2.001 (s, 3 H, CH_3, $^4J_{Hg,H}$ = 20 Hz); 3.091 (s, 2 H, $C\underline{H}_2OCH_3$, $^3J_{Hg,H}$ = 142.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 140.36 (C(3), $^1J_{Hg,H}$ = 2352 Hz); 147.65 (C(2), $^2J_{Hg,H}$ = 305 Hz); 22.82 (CH_3, $^3J_{Hg,H}$ = 94 Hz); 70.54 (CH_2, $\underline{C}H_2OCH_3$, $^2J_{Hg,H} \le$ 5 Hz); 168.24 (CO, $O\underline{C}OCH_3$, $^4J_{Hg,H}$ = 16 Hz); 58.07 (CH_3, $CH_2O\underline{C}H_3$); 20.75 (CH_3, $OCOCH_3$).

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Chemiluminescence during the decomposition of dispiro(adamantane-1,2-dioxetane) cocrystallized with Eu(fod)$_3$ induced by mechanical destruction of crystals

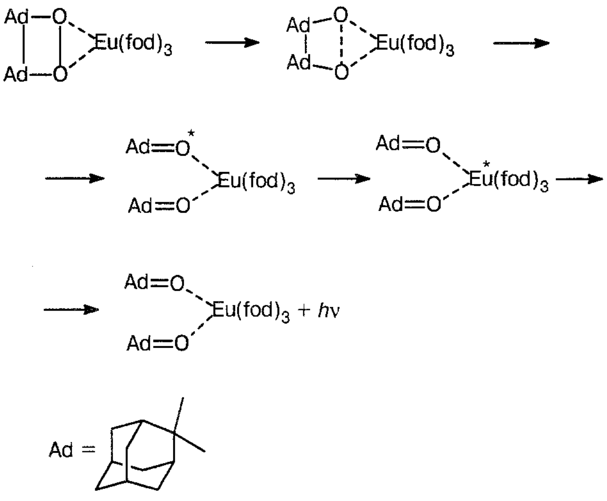
V. P. Kazakov,* V. A. Antipin, A. I. Voloshin, and I. A. Khusainova

Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066

It is known that decomposition of 1,2-dioxetanes into two carbonyl fragments results in formation of electron-excited states and is accompanied by chemiluminescence (CL).[1] The strained and twisted peroxide dioxetane cycle is sensitive to effects originating, *e.g.*, from coordination with lanthanide ions or adsorption on the surface,[2] which accelerate the decomposition of the peroxide. It has previously been shown[3] that coordination of the O—O bond in dispiro(adamantane-1,2-dioxetane) (**1**) with Eu(fod)$_3$ (where "fod" is 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) considerably increases the rate of its decomposition into adamantanone. We found that mechanical impact (time of dynamic contact: 1.5—2.5 ms; time of static contact: 0.3±0.05 s; impulse: $5 \cdot 10^2$ g cm s^{-1}) on cocrystallized dioxetane **1** and Eu(fod)$_3$ (molar ratio 1 : 1) is accompanied by light emission (Fig. 1) in the form of damping, randomly distributed pulses, analogous to those observed during crystalloluminescence.[4] The emission is predominantly observed in the red spectral region (recording through an OS-14 light filter, $\lambda > 550$ nm). This implies that Eu^{III} serves as the emitter.

The above phenomenon probably has the following origin: crystals of the [Eu$^{III} \cdot$ **1**] complex undergo destruction under impact, and hence the conditions of coordination of the dioxetane with the chelate change. This may favor the formation of a structure of the complex similar to the transition state, which precedes the cleavage of peroxide bonds, and cause irreversible decomposition of **1** with excitation of adamantanone in the complex with Eu(fod)$_3$. Subsequently, Eu*(fod)$_3$ is formed due to intramolecular transfer of energy (Scheme 1).

Scheme 1



When a mechanical mixture of dioxetane **1** with Eu(fod)$_3$ is affected by impact, light emission also occurs. Its intensity is lower than that of cocrystallized reagents, although the type and structure of pulses remain the same (see Fig. 1). Model systems (crystals of Eu(fod)$_3$, chelate mechanically mixed or cocrystallized with adamantanone, and 1,2-dioxetane) affected similarly did not display light pulses.

Thus, the luminescence observed in the dioxetane—Eu(fod)$_3$ system originates from impact-initiated chemiluminescent decomposition of dioxetane **1** in a complex with Eu(fod)$_3$.

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