The products obtained by the methods (i) and (ii) were identical with the sample prepared by the procedure (iii).

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Summary

The Reimer–Tiemann reaction of \( m \)-iodophenol yielded three products in contrast with literature reported by Hodgson and Jenkinson and the products were confirmed unambiguously to be 2-iodo-4-hydroxy-, 2-hydroxy-6-iodo-, and 2-hydroxy-4-iodo-benzaldehydes, respectively.

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Shingo Matsumura and Shuichi Seto: Studies on the Cyclopentadienide Anion.

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Hafner and Vöpel\(^1\) have already found that the condensations of one molar equivalent of 6-dimethylamino-3,4-fulvenediacarbonylaldehyde (I) with two molar equivalents of various active methylene compounds formed 6-dimethylamino-3,4-divinylfulvene derivatives represented as the formula II. In analogy with the reaction mechanism of azulene synthetic process elaborated by Nozoe and the present authors,\(^3\) there is also a possibility of the formation of 6-aminoazulene derivatives by the reaction of I with malononitrile or cyanoacetic ester. This paper describes some results obtained on examination of this point.

The reaction of one molar equivalent of I with three molar equivalents of malononitrile, in the presence of one drop of diethylamine, afforded red crystals III in a good yield. The condensation of one molar equivalent of 6-hydroxy-3,4-fulvenediacarbonylaldehyde\(^4\) (IV) with three molar equivalents of malononitrile, in the presence of over one molar equivalent of diethylamine, produced red crystals V in a fairly good yield. The analytical values of III and V respectively correspond to molecular formulae of \( \text{C}_{18} \text{H}_{13} \text{N}_7 \) and \( \text{C}_{21} \text{H}_{17} \text{N}_7 \).

The reaction of one molar equivalent of I or IV with three molar equivalents of malononitrile, by the use of over one molar equivalent of potassium hydroxide in place of diethylamine, formed red crystals VI, whose analytical values correspond to the molecular formula of \( \text{C}_{17} \text{H}_5 \text{N}_8 \text{K} \cdot \frac{1}{2} \text{H}_2 \text{O} \).

The ultraviolet absorption spectra (Table I) of these condensation products are very similar to each other and these compounds are assumed to have a common skeletal

\(^*\) Katahira-cho, Sendai (松村篤午, 柴戸秀一).
structure. These absorption spectra, however, indicate that these products are not 6-
aminoazulene derivatives. There are absorption bands due to ammonium salt at 3140~
2500 cm\(^{-1}\) region in the infrared spectra of III and V. It is interesting to note that the
infrared spectra of these condensates show a sharp band for unsaturated cyano group
at 2223 cm\(^{-1}\).

These observations supported the view that all of these condensation products are
1,2,4-tris(2,2-dicyanovinyl)cyclopentadienyl salts. The reaction of VI with tropylium
cation in water solution easily formed red crystals VII, whose analytical values agree with C\(^{24}\)H\(^{15}\)N\(^{6}\). The use of various organic solvents such as ethanol, dioxane, and ben-
zene in place of water could not isolate any pure product. From the molecular formula of VII, heptafulvalene derivative is taken into consideration for the structure of the compound VII. However, its ultraviolet and infrared spectra are very similar to those of the starting material VI, so that the compound VII is not heptafulvalene derivative
but tropylium 1,2,4-tris(2,2-dicyanovinyl)cyclopentadienide.

Treatment of VI with phosgene produced very unstable crystals VII of m.p. 186°
decomp.), whose analytical values correspond to the molecular formula of C\(^{24}\)H\(^{15}\)O\(^{2}\)N\(^{2}\)Cl\(^{2}\).
The infrared spectrum of VII exhibits a sharp band at 2245 cm\(^{-1}\) for cyano group.
There is also the strongest band due to the C–Cl stretching vibration at 818 cm\(^{-1}\). The compound VII was so unstable that further examination on the structure* of VII was not made.

Experimental*4

**Reaction of 6-Dimethylamo-3,4-fulvenedicarboxaldehyde (I) with Malononitrile**—a) One drop
of Et\(_2\)NH was added to a suspension of 100 mg. of I and 110 mg. of malononitrile in 2 cc. of EtOH,
by which the mixture became immediately deep red solution and red crystals began to separate out.

3) T. Nozoe et al.: to be published.
After allowing the mixture to stand for 3 hr. at room temperature, the crystals that precipitated out were collected by filtration and recrystallized from Me₂CO-EtOH mixture to 160 mg. of III as red scales, m.p. 288~270°.

b) To a suspension of 200 mg. of I and 240 mg. of malononitrile in 3 cc. of EtOH, a solution of 100 mg. of KOH dissolved in 2 cc. of EtOH-H₂O (2:1) mixture was added and the reaction mixture was treated as in the foregoing case to afford 360 mg. of red crystals IV, m.p. above 300°.

**Reaction of 6-Hydroxy-3,4-fulvenedicarboxaldehyde (IV) with Malononitrile**—a) To a suspension of 250 mg. of IV and 330 mg. of malononitrile in 5 cc. of EtOH, 100 mg. of Et₂NH was added. The red precipitate thereby formed was recrystallized from Me₂CO-EtOH mixture to 200 mg. of red scales V, m.p. 237~240°.

b) To a suspension of 250 mg. of IV and 330 mg. of malononitrile in 3 cc. of EtOH, a solution of 100 mg. of KOH dissolved in 2 cc. of EtOH-H₂O (2:1) mixture was added and the reaction mixture was treated as in the foregoing cases, by which 220 mg. of red crystals IV were obtained.

**Action of Tropylium hydroxytriflororoborate on (VI)**—To a solution of 50 mg. of VI dissolved in 100 cc. of H₂O, 50 mg. of tropylium hydroxytriflororoborate was added and the solution was warmed on a water bath for 30 min., by which red crystals began to separate out. The crystals were recrystallized from Me₂CO-EtOH mixture to 40 mg. of red microscals VII, m.p. above 300°.

**Action of Phosgene on (VI)**—To a solution of COCl₂ dissolved in 20 cc. of CHCl₃, 30 mg. of VI was added and the mixture was warmed on a water bath. Evaporation of CHCl₃ formed orange-yellow crystals. The crystals were recrystallized from AcOEt-petr. ether to ca. 10 mg. of yellow needles VIII, m.p. 185~186°(decomp.). *Anal. Calcd. for C₂₁H₂₅O₂N₂Cl₂: C, 54.54; H, 0.95; N, 20.09. Found: C, 53.97, H, 0.73; N, 20.65.*

The measurements of the infrared and ultraviolet spectra were carried out by Messers. Y. Nishiyama and H. Sato, and microanalyses were made by Miss Yoko Endo and Miss Yukiko Endo of this Institute. The authors wish to express their sincere gratitude to the above-mentioned peoples.

**Summary**

The reaction of 1:3 mole ratio of 6-dimethylamino-3,4-fulvene dicarboxaldehyde or 6-hydroxy-3,4-fulvenedicarboxaldehyde and malononitrile, in the presence of base, easily formed stable cyclopentadienyl salt derivatives.

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*2 The Structure like VIIIb or VIIIc for VIII may be assumed from the above-mentioned data and the following mechanism.

*3 Sometimes the crude product obtained by the reaction of VI with phosgene exhibits an absorption band for the carbonyl group of acid chloride at 1770 cm⁻¹.

*4 All melting points are uncorrected.