# ELECTRONIC CONCEPTION IN ORGANIC CHEMISTRY.
# III. DISSOCIATION AND SEMIHYDROBENZOIN REARRANGEMENT OF αα-DIMETHYL-β-ACETYL GLYCOL.

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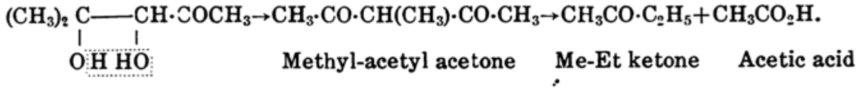
Received September 24, 1929. Published October 28, 1929.

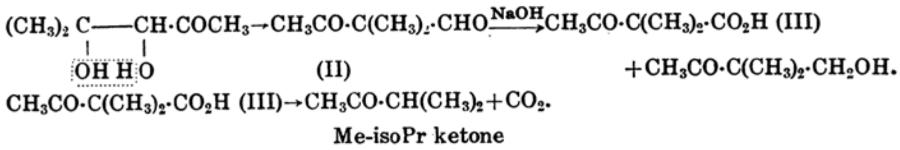
Numerous examples are known on dehydration and molecular rearrangement of pinacones and other hydroxy-compounds, closely related to them, but none has been known which deals with a glycol having substituents other than hydrocarbon-or substituted aromatic hydrocarbon-radicals. In order to see the effect exerted by carbonyl group, the author has studied the action of hot dilute and cold concentrated sulphuric acid on αα-dimethyl-β-acetyl glycol $(CH_3)_2C(OH)\cdot CH(OH)\cdot CO\cdot CH_3$ (I).

It is worthy of note that by the rearrangement of this glycol we cannot usually isolate the reaction products as such, owing to inevitableness of distilling them with acid and base during the analytical procedure, while they are very reactive to both acids and bases. Thus by the semipinacolinic rearrangement, the primary product is methyl-acetyl acetone, but the substances actually isolated will be its hydrolysis products, methyl-ethyl ketone and acetic acid.



$$\underset{\text{OH}}{(CH_3)_2\,C}\text{——}\underset{\text{HO}}{CH\cdot COCH_3}\rightarrow\underset{\text{Methyl-acetyl acetone}}{CH_3\cdot CO\cdot CH(CH_3)\cdot CO\cdot CH_3}\rightarrow\underset{\text{Me-Et ketone}}{CH_3CO\cdot C_2H_5}+\underset{\text{Acetic acid}}{CH_3CO_2H}.$$

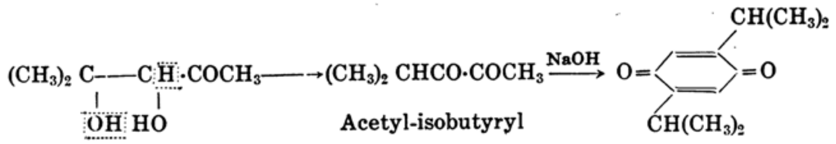
By the semihydrobenzoin rearrangement a tertiary keto-aldehyde (II) is formed, which, as a characteristic of a tertiary aldehyde, will give corresponding acid (III) and alcohol, when boiled with alkali. This β-keto-acid being unstable in free state, will readily lose carbon dioxide and will give methylisopropyl ketone.



$$\underset{\text{OH}}{(CH_3)_2\,C}\text{——}\underset{\text{HO}}{CH\cdot COCH_3}\rightarrow\underset{\text{(II)}}{CH_3CO\cdot C(CH_3)_2\cdot CHO}\xrightarrow{NaOH}CH_3CO\cdot C(CH_3)_2\cdot CO_2H\ \text{(III)}\ +CH_3CO\cdot C(CH_3)_2\cdot CH_2OH.$$

$$CH_3CO\cdot C(CH_3)_2\cdot CO_2H\ \text{(III)}\rightarrow\underset{\text{Me-isoPr ketone}}{CH_3CO\cdot CH(CH_3)_2}+CO_2.$$

By vinyl dehydration acetyl-isobutyryl is formed, which can be distilled from acidic solution, but when warmed with alkali, condensation into quinone, a specific reaction of an α-diketone, will take place.



In addition to these secondary reactions, possibility of a simultaneous reaction, the dissociation of the original glycol into acetone and acetol, is expected from the fact that in acetic acid solution this glycol does not give its own osazone but gives that of acetol.(1) In this way, a mixture of closely related compounds is likely to be obtained by the action of sulphuric acid on dimethyl-acetyl glycol, consequently the choice of analytical procedure must be the matter of the first importance. After careful study, it was ascertained that acetone can be successfully identified by indigo-reaction,(2) methyl-ethyl ketone by vanillin-hydrochloric acid test,(3) methylisopropyl ketone as its *p*-nitrophenyl-hydrazone, and acetol by the formation of 3-oxy-quinaldine,(4) even in case of their mixtures. All these methods are so sensitive that 1 c.c. of 1 % aqueous solution is sufficient for their identification.

**Results.** When dimethyl-acetyl gloycol was boiled with dilute sulphuric acid, acetone, methyl-isopropyl ketone and acetol were formed and isolated from the reaction products. When the glycol was treated with cold concentrated sulphuric acid, these two ketones were again formed, but no trace of acetol was detected. Acetol may be considered to be once formed and undergo subsequent condensation under the influence of concentrated sulphuric acid. Methyl-ethyl ketone and acetyl-isobutyryl were not found in both cases. Taking the secondary reactions into consideration, we can conclude from these results that dimethyl-acetyl glycol undergoes dissociation and semihydrobenzoin rearrangement simultaneously when treated either with hot dilute or cold concentrated sulphuric acid.

## Interpretation of the results.

*Semihydrobenzoin rearrangement of dimethyl-acetyl glycol.* The oxygen of the carbonyl group being the most negative atom in the molecule of this glycol, it may be considered to act as a key atom when the molecule is placed

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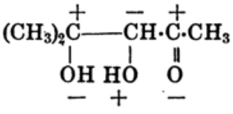
(1) Harries and Pappos, *Ber.*, **34** (1901), 2979.

(2) Baudisch describes on the indigo-reaction of acetol, but under my experimental conditions it gave negative test (see experimental part).

(3) Rosenthaler, *Z. anal. Chem.*, **44** (1904), 292.

(4) Baudisch, *Biochem. Z.*, **89** (1918), 279.

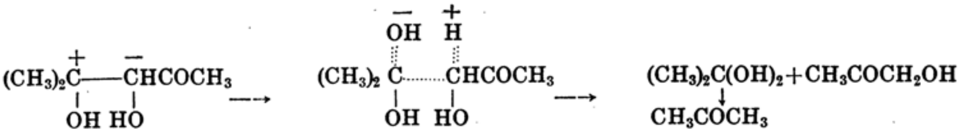
in an activated state.⁽¹⁾ Then the distribution of polarity in this molecule may be shown in the formula (IV), and this polarity being caused by the powerful key atom, it may be well considered to be strong enough to overcome the sterical factor in the substitutional action of cold concentrated sulphuric acid.⁽²⁾ Then it will be easily deduced from the electronic interpretation given in previous paper,⁽³⁾ that this keto-glycol undergoes semihydrobenzoin rearrangement either by hot dilute or by cold concentrated sulphuric acid.



$$(CH_3)_2\underset{\underset{-}{OH}}{\overset{+}{C}}-\underset{\underset{+}{HO}}{\overset{-}{C}H}\cdot\underset{\underset{-}{O}}{\overset{+}{C}}\cdot CH_3$$

(IV)

*Dissociation of the glycol.* As above stated, the secondary carbon of this keto-glycol is induced strongly negative by the influence of carbonyl group. If this induced negativity is supposed to be sufficiently strong, electron pair which binds the secondary and tertiary carbon is drawn to the former so near that it can keep no longer the tertiary carbon in a stable bond. Under these circumstances, only very strongly positive atom, say hydrogen, can form a stable union by this electron pair, for such an atom has, in stable state, its electron at distance from its proton. Therefore, under the influence of an acid, the secondary carbon is to be assumed to form a more stable bond with hydrogen ion than with tertiary carbon, resulting in the dissociation of the glycol.



$$(CH_3)_2\underset{OH}{\overset{+}{C}}-\underset{HO}{\overset{-}{C}}HCOCH_3 \longrightarrow (CH_3)_2\underset{OH}{\overset{\overset{-}{OH}}{C}}\cdots\cdots\underset{HO}{\overset{\overset{+}{H}}{C}}HCOCH_3 \longrightarrow \underset{\underset{CH_3COCH_3}{\downarrow}}{(CH_3)_2C(OH)_2}+CH_3COCH_2OH$$

If the above interpretation is allowable, the dissociation should be started also under the influence of alkali, for in this case a stable bond is considered to be formed first between hydroxyl ion and tertiary carbon atom. This was proved by the fact that dimethyl-acetyl glycol, when treated with *o*-amino-benzaldehyde in alkaline solution, gives 3-oxy-quinaldine, a condensation product of acetol and this reagent.

**Dissociation of the glycol by distillation.** Harries⁽⁴⁾ assumed that the dissociation of dimethyl-acetyl glycol takes place merely by distillation, how-

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(1) An analogy is found in the case of tertiary amino-alcohols. (This Bulletin, **3** (1928), 314.)

(2) It has been assumed that cold concentrated sulphuric acid acts substitutionally and that in substitution sterical factor is predominant over the effect of polarity, so long as the latter is not marked, elimination of the secondary hydroxyl group resulting. (This Bulletin, **4** (1929), 60).

(3) This Bulletin, **4** (1929), 58, 61.

(4) Loc. cit.

ever he could not prove it directly. In fact, when pure dimethyl-acetyl glycol (b.p. 114°/22 mm.) was subjected to two or three successive redistillations under reduced pressure, some measure of a fraction boiling under 100° was always obtained in every time. But the final solution of this question is possible only by finding a sharp method to identify acetone,⁽¹⁾ acetol and the keto-glycol in presence of one another. Formation of oxy-quinaldine, the excellent test for acetol, is inapplicable in this case, for during this procedure, the original glycol gives acetol by the action of alkali, as mentioned above. After various trials, it was found that Denigès' acid mercuric sulphate solution is very satisfactory reagent for this purpose (see experimental part), by virtue of which the presence of both acetol and the keto-glycol in the lower fraction obtained by the redistillation of pure dimethyl-acetyl glycol was proved. Thus the dissociation of the glycol by distillation was directly ascertained. A possible objection against this method that sulphuric acid contained in this reagent may start the dissociation of the glycol, can be overcome by the fact that the solution of pure dimethyl-acetyl glycol gives no crystal of acetol complex. Presumably this is due to the complex formation between the glycol and mercuric sulphate completed speedily enough not to give a chance for the dissociation of the glycol.

## Experimental Part.

**Dimethyl-acetyl glycol.** This glycol was prepared by oxidation of mesityl oxide with potassium permanganate according to Harries.⁽²⁾ But the yield being extremely poor notwithstanding the original description, preparations were carried out under various conditions. The yield, however, could not exceed 37% of the weight of mesityl oxide used, which is only half of that claimed by Harries.

*Exp. 1.* The permanganate solution was dropped in the course of 6 hours at various temperature. The first fractions of the products obtained from 10 gr. mesityl oxide are given in Table 1.

*Exp. 2.* When the permanganate was added in 3 hours at 2—3°, following first fractions were obtained under the pressure of 22 mm.

27—31°, 6.15 gr., 50—65°, 1.25 gr., over 65°, 0.0 gr.

*Exp. 3.* After the reaction (temperature 2—3°, duration 6 hours), the solvent was removed by ordinary distillation, for by vacuum distillation only half of the acetone used was recovered. First fractions distilling under the pressure of 22 mm. was as follows:—

below 50°, 0.75 gr., 50—75° 2.15 gr., over 75°, 0.0 gr.

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(1) Taking the boiling points in consideration, acetone can be excluded.

(2) Harries and Pappos, loc. cit., "Zu einer gut gekühlten und stetig durchgerührten Mischung von 10 gr. Mesityloxyd in 20 c.c. Aceton lässt man langsam eine Lösung von 21. 6 gr. $KMnO_4$, 40 c.c. Wasser und 750 c.c. Aceton tropfen. . . ."

Table 1.

| Fraction. | Reaction temperature. | | | | Remarks. |
|---|---|---|---|---|---|
| | −8° | 2–3° | 7–8° | 20–22° | |
| <50°/22 mm. | 1.85 gr. | 0.6 gr. | 0.3 gr. | 0.0 gr. | Mesityl oxide, (41°/23 mm.). |
| 50–100°/22 mm. | 2.45 gr. | | | 0.15 gr. | Acetol, (54°/18 mm.). |
| >100°/22 mm. | 0.00 gr. | 3.7 gr. | 3.7 gr. | 2.4 gr. | Di-Me-acetyl glycol, (109°/19 mm.). |

As is evident from these experiments, by the oxidation at too low temperature or in too short time, a considerable quantity of mesityl oxide remains unchanged, and by the treatment of the products at a temperature higher than room temperature, dissociation of the glycol into acetol takes place. Separation of the glycol from a fair quantity of mesityl oxide or acetol was proved to be a laborious and fruitless matter. The best conditions for the preparation were the reaction temperature 7—8°, and the duration 6 hours.

### Methods of identification of the products.

*Indigo-reaction.* In dilute aqueous solution of acetone small quantity of *o*-nitro-benzaldehyde was dissolved at temperature not exceeding 50°. After cooling, add 15 % aqueous caustic soda solution, and the well-known precipitate of indigo will appear(1). Under these conditions, other ketones, acetol, and the keto-glycol did not interfere. In the case of acetol (1 and 10 % aqueous solutions were tested), long white needles crystallized from the solution in which *o*-nitro-benzaldehyde had been dissolved. On addition of caustic soda these crystals were dissolved again, and the solution turned reddish brown. On the other hand, Baudisch(2) has described that aqueous acetol solution, prepared from monochloro-acetone and freshly precipitated barium hydroxide, gives indigo-reaction by *o*-nitro-benzaldehyde and alkali even in the cold. However, it is worthy of notice what he had prepared was aqueous acetol solution, but not pure acetol, and what the present author dealt with was the aqueous solution of *pure acetol*, prepared, according to Nef,(3) from monochloro-acetone and fused potassium formate in dried methyl alcohol.

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(1) Rosenthaler, "Der Nachweiss der organishcer Verbindungen" p. 162.

(2) Baudisch, loc. cit.

(3) *Ann.*, **335** (1904), 259.

*Vanillin-hydrochloric acid test.*(1) 1 % vanillin solution in concentrated hydrochloric acid was mixed, before use, with equal volume of concentrated sulphuric acid, to which 1 c.c. of dilute (1 %) aqueous solution to be examined was added. The colours produced in the instant when they were mixed, and these after heated in the boiling water bath were observed (Table 2).

Table 2.

| Colour change | Acetone. | Me-Et ketone. | Me-isoPr ketone. | Acetol. | Di-Me-acetyl glycol. |
|---|---|---|---|---|---|
| Before heating. | No change. | Green. | No change. | No change. | Pink. |
| After heating. | Violet. | Blue. | Violet.* | Black brown. | Brown. |

*Flourescence of green and purple is seen in the beginning.

The blue colour produced by methyl-ethyl ketone being extremely deep, this ketone can be detected by this method in presence of others. The typical colours given by acetone and methyl-isopropyl ketone are distinguished only when methyl-ethyl ketone is absent.

*p-Nitrophenyl-hydrazones.* Stress was placed upon properties of crystals, for the melting points of phenyl-hydrazones, as is known, are not often decisive for the purpose of identification. Some properties of crystals of *p*-nitrophenyl-hydrazones of the three ketones are given in Table 3.

Table 3.

| | *p*-Nitrophenyl-hydrazone of | | |
|---|---|---|---|
| | Acetone. | Me-Et ketone. | Me-isoPr ketone. |
| Crystal-form freshly prepared. | Prismatic needles. | Mossy. | Fibrous |
| Crystal-form recrystallized from aq. alcohol. | | Long parallelogram. | Prismatic needles. |
| Dichroism. | Marked.<br>Pale yellow(x′),*<br>Brownish yellow(z′). | The same. | Weak.<br>Pale yellow(x′),<br>Yellow(z′). |
| Extinction. | Oblique. | The same. | The same. |
| Extinction-angle | Variable. | The same. | The same. |
| Mean values $\theta x'$** | 34.0° | 35.5° | 40.0° |
| Mean values $\theta z'$ | 54.0° | 51.1° | 47.3° |

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(1) Rosenthaler, *Z. anal. Chem.*, **44** (1904), 292.

*The crystal is pale yellow when observed by the ray which propagates with larger velocity through it, and brownish yellow by the slower ray.

**$\theta_x'$ and $\theta_z'$ represent angles between the prominent edge and the direction of the faster and slower rays respectively.

*Solubilities.* When 0.01 gr. *p*-nitrophenyl-hydrazones of three ketones are dissolved in 6 c.c. of hot 50 % alcohol, the hydrazone of methyl-ethyl ketone crystallizes out on cooling, but that of acetone separates out only very slowly, whereas the derivative of methyl. isopropyl ketone remains dissolved, this being soluble even in 3.6 c.c. of 30% aqueous alcohol-

As is evident from the above table, acetone can be identified by freshly prepared crystals of its *p*-nitrophenyl-hydrazone, and methyl- isopropyl ketone by those recrystallized from aqueous alcohol.

*A new test for Acetol.* Insoluble complex of mercuric sulphate and a carbonyl compound is precipitated by heating dilute aqueous solution to be tested with equal volume of Denigès' reagent in boiling water bath.⑴ Each carbonyl compound has its own complex and own velocity of complex formation. The results obtained from experiments on 1% aqueous solutions of several acetyl compounds are given in Table 4.

Table 4.

| | Precipitates. | Precipitation takes place |
|---|---|---|
| Acetone. | White dense crystals. | After 1 min. all at once. |
| Me-Et ketone. | The same.* | After 2 min. gradually. |
| Me-isoPr ketone. | Faintly yellow dense crystals. | After 10 min. gradually. |
| Acetol. | White scaly crystals with pearly lustre.** | After 2 min. gradually. |
| Di-Me-acetyl glycol. | Yellowish brown dense crystals. | Within 1 min. all at once. |

*This precipitate has been described as being yellow,⑵ but the fresh precipitate formed from dilute aqueous solution of pure methyl-ethyl ketone was almost as white as the acetone complex.

**Mercury deposits by prolonged heating.

By this way, acetol can be detected in presence of the keto-glycol, but not in presence of acetone, for in this case only white heavy precipitates are formed.

**Action of hot dilute sulphuric acid.** 10 gr. of the glycol was boiled with 150 c.c. of dilute sulphuric acid (1:5) for 3 hours. The solution which had been opaque and yellow, gradually turned reddish brown and black oil

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(1) Denigès, *Ann. chim. phys.*, [7] **18** (1899), 381 & 399; Thorpe and Whitely, "Organic Chemical Analysis", p. 109.

(2) Thorpe and Whitely, "Organic Chemical Analysis", p. 110.

separated on the surface. Yellow liquid dropped from condenser and light greenish yellow vapour was observed in the neck of the flask.

Volatile Part. The raw product was subjected to rapid distillation. The first 10 c.c. of the distillate consisted of almost homogeneous yellow liquid lighter than water. The colour of the succeeding distillate turned lighter as distillation went on, and finally faded away. Distillation was stopped when the acidity of the distillate sank below 0.01 normal. However, even this last distillate reduced greedily cold Fehling's solution. This volatile part contained acidic substances equivalent to 4.3 c.c. of decinormal alkali, and was colored markedly yellow when rendered alkaline. By redistillation of this alkaline solution, it was separated into neutral and acidic fractions.

*Neutral constituents.* Neutral fraction was saturated with anhydrous potassium carbonate and separated oil was extracted with ether. After drying, the ethereal solution was subjected to fractional distillation, and following fractions were obtained: (a) 40–60°, 0.15 gr., (b) 60–80°, 0.0 gr., (c) 80–100°, 0.2 gr., (d) 140–155°, 0.2 gr.

As the fraction (a) contained considerable quantity of ether, it was shaken with equal volume of water, and this aqueous solution was tested for acetone and methyl-ethyl ketone. Acetone was identified by indigo reaction and by its *p*-nitrophenyl-hydrazone. The absence of methyl-ethyl ketone (b. p. 71°) was ascertained by vanillin-hydrochloric acid test. Fraction (c) was similarly tested for methyl-ethyl-and methyl-isopropyl ketones. The latter was isolated as its *p*-nitrophenyl-hydrazone, the former being proved to be absent also in this fraction. Fraction (d) was acidic for litmus, reduced cold Fehling's solution, and gave iodoform reaction by tincture of iodine and ammonia. It was identified to be acetol (b. p. 145–6°) by converting it into 3-oxy-quinaldine. It is not clear why this strongly acidic substance distilled out from alkaline solution and was found in this fraction.

The yellow vapour and condensed liquid observed during the reaction seem to indicate the presence of acetyl-isobutyryl (b. p. 115°), but no fraction distilling 100–140° was obtained, nor it was detected by the formation of quinones.

*Acidic fraction.* Acetol was easily identified. In order to detect other volatile acids, acetol was oxidized into little volatile lactic acid by Fehling's solution and the content was acidified and distilled. But the distillate was too slightly acidic to be fully analysed. Only the presence of minute quantity of lactic acid which escaped partly with water could be assumed by iodoform reaction.

Non-volatile Part. Though the residue of the first distillation was extracted with ether and treated as usual, nothing but black rosinous matter was obtained.

### Action of cold concentrated sulphuric acid.

Under mechanical agitation, 100 c.c. of well cooled concentrated sulphuric acid was slowly dropped into 10 gr. of dimethyl-acetyl glycol, kept at the temperature below 0°. As sulphuric acid was added, the solution was colored crimson and turned reddish brown in the course of time. Cooling and stirring were kept for two hours after all the acid had been added, and the content, which smelled strongly of an essential oil, was poured into 1 litre of ice water. Black particles were observed suspended in the solution but the quantity being too small, the solution was distilled without being filtered. Subsequent separation and identification of the products were carried out exactly in the same way as in the previous case.

Volatile Part. *Neutral constituents.* Ethereal solution of neutral consistuents was fractionated into three fractions: (a) 40–50°, 1 c.c., (b) 90–110°, 0.1 gr. (c) over 110°, 0.1 gr. Acetone and methyl-isopropyl ketone were detected in (a) and (b) fractions respectively. Fraction (c) was tested for acetyl-isobutyryl by means of *o*-phenylene-diamine, but no precipitate was formed.

*Acidic fraction.* Though this fraction smelled strongly of the same smell as emitted by the raw product, it contained but a trace of acidic constituents, for only 0.1 c.c. of decinormal alkali was sufficient for neutralization of 50 c.c. of the distillate.

It must be mentioned that both neutral and acidic fractions were quite indifferent to Fehling's solution, thus no trace of acetol was detected. Under the assumption that acetol was once formed and underwent subsequent condensation, it was attempted, in vain, to find some relation between its consensation product and the smell emitted by the raw products and the acidic fraction.

Non-volatile Part. Non-volatile part consisted of a brown rosinous matter, soluble in ether and water, which reduced Fehling's solution very slowly when heated in boiling water bath, but not Schiff's reagent. Attempts to get a definite compound from this part ended in failure.

## Summary.

In order to see the effect of the carbonyl group, action of hot dilute and cold concentrated sulphuric acid on $\alpha\alpha$-dimethyl-$\beta$-acetyl glycol was studied.

This keto-glycol was found to undergo semihydrobenzoin rearrangement and dissociation into acetone and acetol simultaneously. The primary product of the semihydrobenzoin rearrangement of this glycol being decomposed during the subsequent treatments, only the secondary products, methyl-isopropyl ketone, could be isolated. The dissociation of dimethyl-acetyl-glycol was started not only by acid, but also by alkali. These results can be easily deduced from the electronic interpretation given in previous papers.

That the dissociation of dimethyl-acetyl glycol takes place merely by distillation was directly proved by identifying acetol by a new method.

Methods to identify acetone, methyl-ethyl ketone, methyl-isopropyl ketone, acetol and dimethyl-acetyl glycol with limited quantity of the sample in presence of one another, were carefully studied and established.

I beg to tender my sincere thanks to Prof. K. Matsubara for his kind inspection of this paper.

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