Studies on the Derivatives of Biphenylene Oxide. IX. General remarks.

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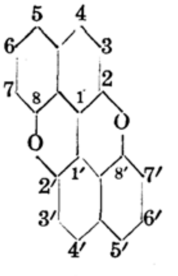
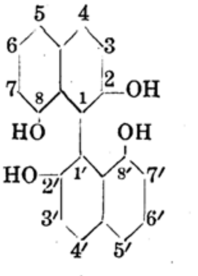
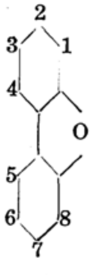
In the previous studies on the derivatives of 1,1′-dinaphthylene-2,8′,-2,8′-dioxide (I), the following facts were recognized by the present author. When the dinaphthylene dioxide was heated only with concentrated nitric acid, it gave rise to a single hexanitro derivative, and when the same dioxide was treated first with nitric acid and then with a mixture of nitric and sulphuric acids, it gave the same hexanitro compound with an isomeric hexanitro derivative. And the former hexanitrodinaphthylene dioxide was rather readily soluble in caustic soda solution, and on hydrolysis yielded a corresponding nitro derivative of 2,2′, 8,8′-tetrahydroxy-1,1′-dinaphthyl (II) quantitatively, while the latter one was much less soluble and gave nothing more than a brown amorphous substance as a hydrolyzed product. A more important fact is that the hydrolyzed product, obtained from the readily soluble dioxide, was reconverted without difficulty into the original dioxide when heated with acetic anhydride, but, on the contrary, that obtained from the less soluble dioxide did not regenerate the original dioxide in the same treatment.



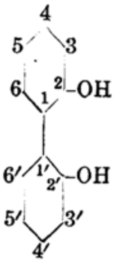
(I)



(II)



(III)



(IV)

Such different behaviours of those isomerides are obviously due to a certain difference in the relative positions of the nitro groups and the pyrone-rings of those compounds. Consequently, in the researches of the stability of such heterocyclic compounds and their hydrolyzed products, it is indispensable to make clear of the effects of substitution, exerted on the opening and closing of such rings.

Although a number of researches have been communicated with regard to the preparations of the nitro derivatives of the dinaphthylene dioxide, the constitutions of almost all the nitro compounds remain undetermined up to the present day. As far as the present author knows, only 5-nitro-(1) and 6,6′-dinitro-(2)dinaphthylene dioxides were presumably established.

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(1) I. S. Travkin, *Org. Chem. Ind.* (U.S.S.R), **2** (1936), 221–226.
(2) I. G. Farbenind. A.-G., Ger. Pat., 545,212, July 29, 1928.

The present author formerly exerted himself in establishing the constitutions of the isomeric hexanitrodinaphthylene dioxides, but he found it very difficult to establish them completely. For example, when the readily soluble hexanitro compound, mentioned above, was oxidized with potassium permanganate in caustic soda solution, a dinitro-hydroxy-phthalic acid was obtained and proved to be 4,6-dinitro-3-hydroxy-phthalic acid (1,2). It was impossible, however, to isolate the other components by which the positions of the other nitro groups could be determined. In addition, the higher nitro derivatives of the dinaphthylene dioxide, unfortunately, have no melting point and decompose explosively when heated. Therefore, it is also unfavourable to identify those compounds which could be obtained by synthesis.

Now, if the same isomeric phenomena be observed also in the derivatives of biphenylene oxide (III), it is desirable to study such effects of substitution exerted on the opening and closing of the furan-ring of this simple compound, because the preparation of the possible isomerides and the orientation of the substituents may be simpler in the derivatives of this compound than in those of the dinaphthylene dioxide.

In the early days of these studies on the derivatives of biphenylene oxide, however, the constitutions of some of the nitro derivatives which had been prepared by the other investigators were not yet rationally established, and besides many of the isomeric nitro compounds had not yet been obtained, so the present author occupied himself first with the establishment of the constitutions of the known nitrobiphenylene oxides and the preparation of the other nitro-derivatives. For these two objects, he employed two methods of preparation,(3) one of which was the direct nitration of biphenylene oxide, and the other, the preparation of nitrobiphenylene oxides from the corresponding nitro derivatives of *o,o'*-biphenol (IV). The nitro compounds thus newly obtained and the amino, acetamino, nitroamino, and nitroacetamino compounds newly derived for the identification of those nitro compounds are as follows:

1-Nitro-biphenylene oxide
4-Nitro- ” ”
1,6-Dinitro-biphenylene oxide
1,8-Dinitro- ” ”
2,7-Dinitro- ” ”
3,6-Dinitro- ” ”
4,6-Dinitro- ” ”
1,3,6-Trinitro-biphenylene oxide
2,3,6-Trinitro- ” ”
2,3.7-Trinitro- ” ”
2,4,6-Trinitro- ” ”
1,3,6,7-Tetranitro-biphenylene oxide
2,3,6,7-Tetranitro- ” ”
2,4,6,7-Tetranitro- ” ”
1-Amino-biphenylene oxide
1-Acetamino- ” ”
1,6-Diamino-biphenylene oxide
1,6-Bisacetamino- ” ”
1,8-Diamino-biphenylene oxide
1,8-Bisacetamino- ” ”
1-Nitro-8-amino-biphenylene oxide
1-Nitro-8-acetamino- ” ”
2-Nitro-3-amino-biphenylene oxide
2-Nitro-3-acetamino- ” ”
7-Nitro-2,6-diamino-biphenylene oxide
7-Nitro-2,6-bisacetamino- ” ”
3-Nitro-2,7-diamino-biphenylene oxide
3-Nitro-2,7-bisacetamino- ” ”
2-Nitro-3,6-diamino-biphenylene oxide
2-Nitro-3,6-bisacetamino- ” ”
3,7-Dinitro-2,6-diamino-biphenylene oxide
3,7-Dinitro-2,6-bisacetamino- ” ”

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(3) S. Yamashiro, *J. Chem. Soc. Japan*, **57** (1936), 714–718 (Part I); **59** (1938), 186∼192 (Part II); **59**, 443∼450 (Part III); **59**, 945∼953 (Part IV); this Bulletin, **16** (1941), 61∼69 (Part VI).

The properties of these compounds, especially the absorption spectra of those new nitro derivatives, were studied in comparison with those of the known nitro compounds. From the experimental results given in Parts I–IV and VI(3) it was found that the nitrosubstitutions in a phenylene residue of biphenylene oxide and in the unsubstituted phenylene residues of nitrobiphenylene oxides take place in the orders of positions 2>3>4>1, and 3>2>1 and 4 (probably 1>4) respectively. Consequently, the o,p-directing powers of the ring-forming oxygen atom, the phenylene residue and the nitrophenylene residue may be represented in the order $-C_6H_4- > -O- > -C_6H_3NO_2-$.

In Parts IV and VII,(4) the nitro and bromonitro derivatives of biphenylene oxide were obtained from the corresponding derivatives of o,o′-biphenol by means of the intramolecular formation of a furan-ring. The present author accomplished this ring-closure successfully by heating o,o′-diacetoxydiphenyls with acid-removers. Many metallic oxides and carbonates were examined as such removers, but the carbonates only were found to be available for the closure of the furan-ring. And the orders of the availability among the carbonates are $Li_2CO_3 > Na_2CO_3 > K_2CO_3$ in alkali metals, and $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$ in alkaline earth metals. It was also found that influences of substituents exerted on the removal of the acetyl groups, and on the formation of the biphenylene oxides, too, are positive in the case of nitro group, though they are negative in the case of bromine, and that the both effects of those substituents come out remarkable in the same order of their relative positions, ortho>para>meta, to the acetoxyl groups.

The reaction mechanisms in the formation of the biphenylene oxides and the reformation of the biphenols from the diacetoxydiphenyls can be reasonably explained as below on the basis of the electronic theory.(5)

When a negative ion such as oxygen ion acts upon an acetoxyl group of a substituted diacetoxydiphenyl, the electromeric effects of the substituents are generally to show certain influences on the removal of the acetoxyl group, though the same effect of the acetyl group in that acetoxyl group induces the removal of the acetyl group itself. And the effects, which are exerted by the negative polar substituents such as nitro and carboxyl groups at certain positions, must be opposite to those exerted by such positive polar substituents like halogens at the same positions. With regard to the relative positions of those polar substituents to the acetoxy group, it can be said from an electromeric point of view that these substituents are considerably effective at the *o*- and *p*-positions, while they are scarcely so at the *m*-position. And the fact that they are most effective at the *o*-position can possibly be explained in no other way than that the acetoxyl group is in this case at the nearest position to the origins of the electromeric effects which affect the elimination of that group.

Now, compare the above-mentioned influence of the acetyl group with the resultant of the influences of the substituents, within each one of the substituted acetoxyphenyl residues of the substituted diacetoxydiphenyl. Then the followinng inference may reasonably be drawn. That is to say,

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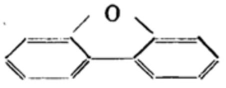
(4) S. Yamashiro, this Bulletin, **17** (1942),

(5) C. K. Ingold, *Chem. Rev.*, **15** (1934), 225.

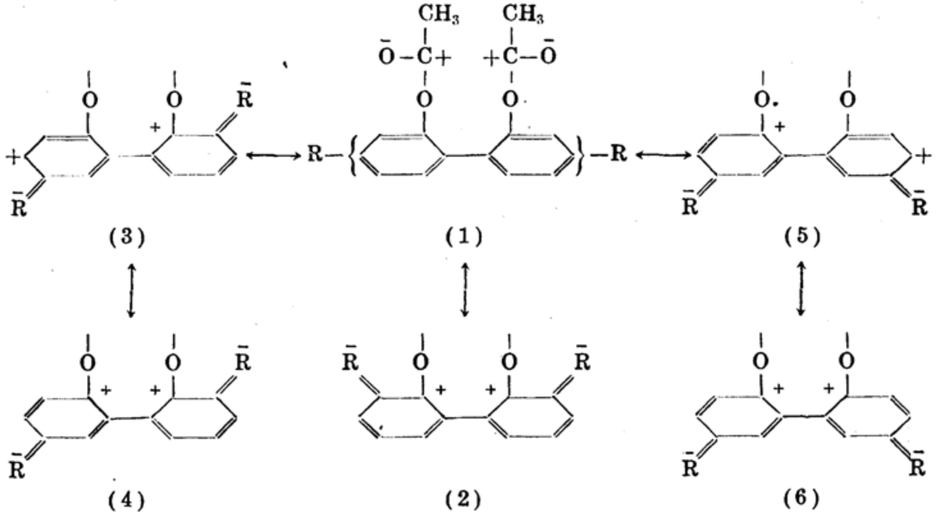
if the former influence positively predominates over the latter, as in the examples I and II, the reaction product may be a biphenol, even if such a predominance occurs in *one* of those residues, as in the example III(i). On the contrary, moreover, if the latter positively predominates over the former in *both* of those residues, as in the example III(ii), a biphenylene oxide may be obtained.

It may also be understood from the example III that when a certain derivative of the diacetoxydiphenyl exists in a special mesomeric state, the corresponding derivatives of both biphenol and biphenylene oxide are to be obtained simultaneously from that derivative.

The most stable structure of biphenylene oxide (formula A) has been previously established by K. Tatematsu and his co-worker⁽⁶⁾ who took into their account the minimum distortion of the natural valency-direction in the closure of the furan-ring according to Mill's hypothesis on the natural valency-angle. If this be the case, the biphenylene oxides are to be readily obtained from the corresponding diacetoxydiphenyls which have such arrangements of double bonds as those in the formulas (1), (2), (3), (4), (5) and (6).



(A)



Three of them, i.e. (1), (3) and (5), however, cannot satisfy the above-mentioned necessary electronic conditions for the formation of the biphenylene oxides. Consequently, in the case of disubstituted compounds, the structural formulas (2), (4) and (6) should be available for the formation of the biphenylene oxides, while all other possible unperturbed structures, for that of biphenols.

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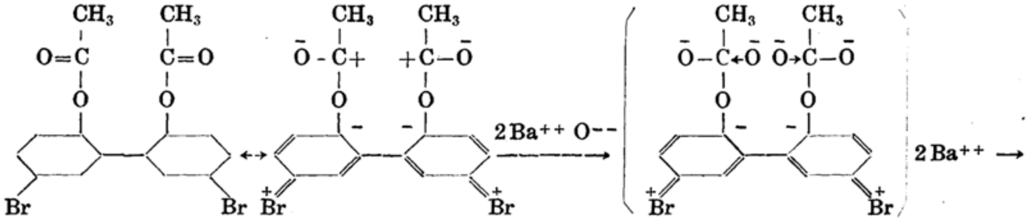
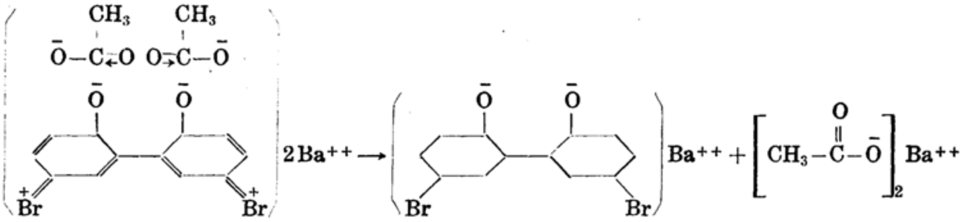
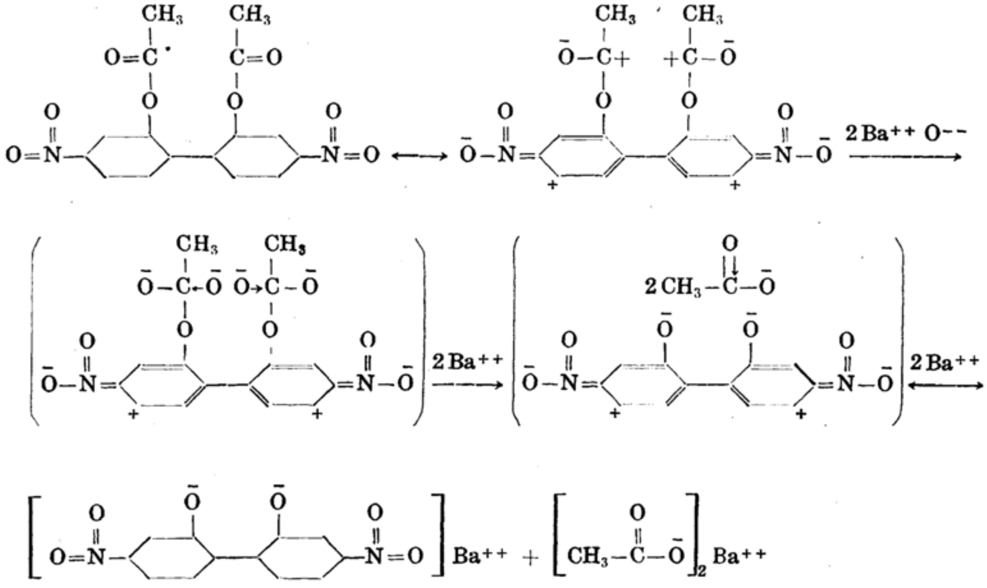
(6) K. Tatematsu and B. Kubota, this Bulletin, **9** (1934), 450.



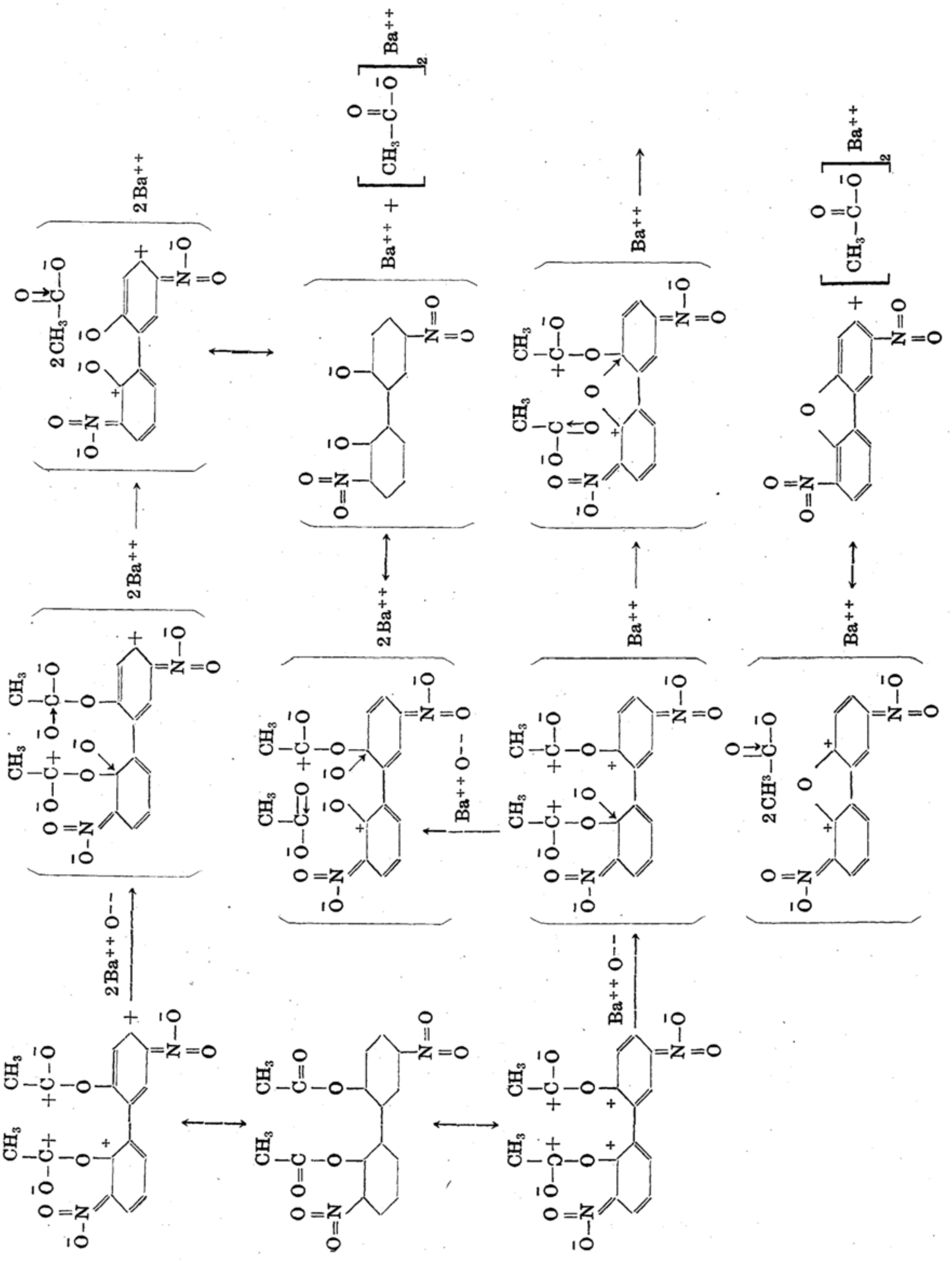
Example I.



Example II.



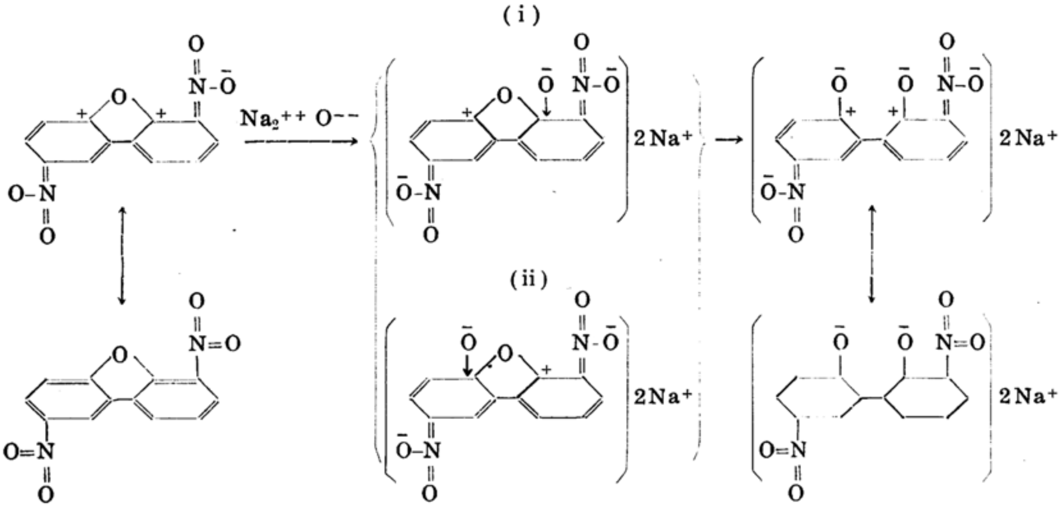
Example III.



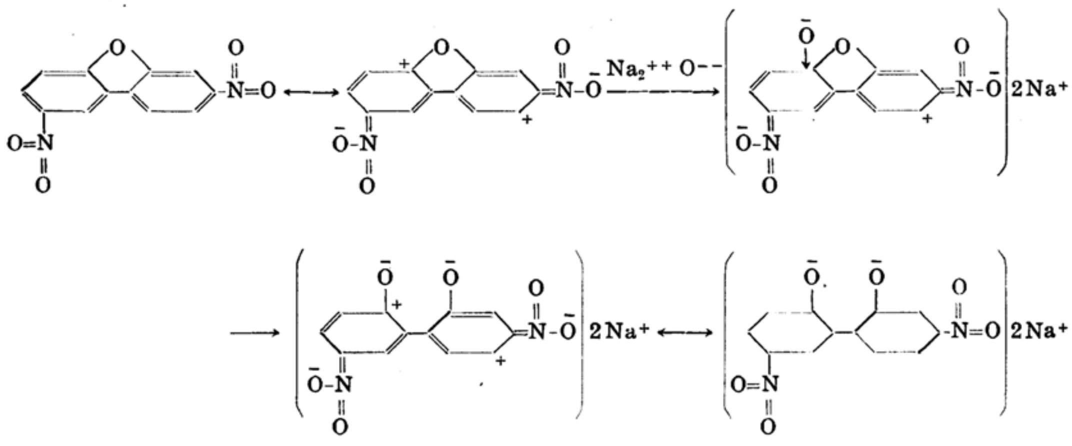
The opening of the furan-rings of the nitrobiphenylene oxides by caustic soda solution was examined in Part VII, and it was found that the tendency of this ring-opening is analogous to that of the ring-formation. That is to say, the increase in the number of the nitro group facilitates that opening, and the influence of the positions of the nitro groups is represented in the order ortho->para->meta-position relative to the ring-forming oxygen atom.

These experimental results can also be reasonably interpreted on the basis of the electronic theory as in the following examples.

Example IV.



Example V.



In the example IV, the main opening-reaction may proceed as in (i), because the positive electromeric effect of the nitrogroup is to be most effective at the *o*-position to this group, as in the case of elimination of the acetoxyl groups from the diacetoxydiphenyls.

In conclusion, the author wishes to express his hearty thanks to Prof. R. Majima of Osaka Imperial University and S. Oba, the principal of Yonezawa Higher Technical School, for their kind advices and encouragements. The cost of these researches has been defrayed from the Japan Society for the Promotion of Scientific Research and from the Scientific Research Expenditure of the Department of Education, to which also the author wishes to record his thanks.

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