THE STABLE ALKYLATION PRODUCTS OF ORGANONITROSOHYDROXYLAMINES¹

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ABSTRACT

The stable alkylation products of alkyl and aryl nitrosohydroxylamines seem to exist in a hitherto unknown structure, the diimide dioxide linkage. The alternative possibility is the alkyl diazotate monoxide structure, but the latter cannot account for the pure methane evolved when the substances are treated with methyl halide Grignard reagent. The principal products of this reaction with Grignard reagents are diimide monoxides formed subsequently by addition of an equivalent of reagent with elimination of the original alkoxy group as its magnesium salt. Nitration of N-methyl-N'-phenyldimide dioxide shows that in salt-forming media (nitric-sulphuric) the N $_2O_2R$ group is electrically negative, but dipole moment studies show that it is highly degenerate. This resonance stabilization is not unexpected in view of the high stability of the diimide dioxides in acidic nedia.

The first nitrosohydroxylamines were prepared (1) by reaction of nitric oxide with substances containing an active methylene group in presence of ethanolic sodium hydroxide. Typical is the reaction with acetone which may be postulated as follows:



The second, more orthodox, method of preparation involved the nitrosation of an arylhydroxylamine (2), and led to the preparation of salts such as ammonium phenylnitrosohydroxylaminate (cupferron). The free acids are rather unstable.

When the silver salts of these nitrosohydroxylamines (II, M = Ag) are treated with alkyl iodides two products, designated α and β , are formed. The β isomers may be desig-

nated as the nitroso derivatives of hydroxylamine O-ethers, since they give a positive Liebermann test and some may be synthesized by nitrosation of the O-alkylhydroxyl-amines (3, 4).

The structure of the α derivative was not proved. Hantzsch (5) suggested structures III or IV while Bamberger and Ekecrantz (6) suggested either IV or V. To this list may be added VI, although it is in conflict with one structure proposed for nitroso dimers (7, 8, 9, 10, 11).

There are two claims that nitroso dimers are best represented by structure VI or charge-distorted modification of it. An X-ray diffraction study (8) of tribromonitroso-

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CANADIAN JOURNAL OF CHEMISTRY. VOL. 37, 1959

benzene has been interpreted in terms of a central plane containing two nitrogen and two oxygen atoms, but it is doubtful whether this definition is justified when six bromine atoms are present. A more specific claim (10) that the *cis* and *trans* isomers of VI (R = Me) have been isolated may be interpreted in terms of polymorphism. Moreover, there is no convincing reason to expect that substances having structure VI would show the instability characteristic of nitroso, carboxylic, or peroxidic dimers. For these reasons we prefer to exclude VI for consideration as a nitroso dimer, and to include it among the possible structures of the α -alkylated nitrosohydroxylamines.



In view of present knowledge structure III is inadmissable because it may clearly be assigned to isonitramines (12). The postulation of structures IV or V is justified by the observation (13) that basic hydrolysis of the methyl derivative of phenylnitrosohydroxylamine regenerates the salt (II, M = Na or K). We have extended this observation by hydrolysis of the dimethyl α derivative of the salt I using hydrazine as the basic reagent. Subsequent precipitation by use of sodium or barium hydroxide yields the appropriate salt of I rather than of methylene dinitramine (14).

Thus hydrolytic evidence favors IV or V rather than III, but it should be noted that VI is not excluded by this criterion since the alkylazoxy linkage is known to react with alkalis (15). The principal evidence favoring IV and V in contrast to VI has been presented by Bamberger (6, 13), who reduced methyl phenylnitrosohydroxylaminate and its p-bromo analogue. Reduction with zinc and acetic acid was said to give diazonium salts, while neutral reduction with aluminum amalgam gave the methyl ester of benzene-diazotic acid. However, identification seems to have been accomplished only by odor and color tests. Only when the reduction was alkaline (4% sodium amalgam) was phenyl-hydrazine or its p-bromo analogue characterized in favor of structures IV and V rather than VI. But alkaline conditions also would yield sodium phenylnitrosohydroxylaminate by hydrolysis. Since this salt is easily reduced to phenylhydrazine, Bamberger's argument is not entirely convincing.

In order to evaluate further the criterion of reduction for a choice between structures IV, V, and VI we have applied alternative reducing agents to the methyl derivative of phenylnitrosohydroxylamine. We have found, like Bamberger, that the substance is fairly resistant. It is practically unchanged by reagents like titanous chloride in acetic anhydride, aqueous sodium bisulphite, aqueous sodium arsenite, and aqueous (47%) hydriodic acid, although a 4% yield of aniline was obtained from the latter reaction. A 24% yield of aniline was obtained, together with unchanged reagent and unidentifiable material, by catalytic reduction with platinum. But also, the alkaline reagent, sodium hydrosulphite, gave a 4% yield of phenylhydrazine together with a 65% recovery of the original substance. In fact the only reduction which might support Bamberger's contention for IV and V is that with lithium aluminum hydride which gives a 40% yield of phenylhydrazine. However, the latter reductant must be considered together with Grignard reagents which it resembles in its behavior.

Treatment of the methyl α derivative from phenylnitrosohydroxylamine with methyl halide Grignard reagent by the Kohler modification of the Zerewitinoff analysis (16)

680

shows that one equivalent of pure methane is liberated easily. Enough may be collected at room temperature for demonstration of an uncontaminated infrared spectrum. The analysis shows also that 1.5 equivalents of Grignard reagent are added during the process. Since it has been shown that the isolable reaction product is fixed as its magnesium salt (and therefore cannot easily undergo further reaction), the evidence for active hydrogen would seem to exclude IV or V as possible structures, but not VI with its methylene group adjacent to an azoxy linkage. Accordingly VI ($R = C_6H_5$, R' = Me) is now designated for the α derivative of phenylnitrosohydroxylamine, and it is named N-phenyl-N'methyldiimide dioxide.*

When methylphenyldiimide dioxide (VII, R = H) is treated with an excess of bromotoluene Grignard reagent in ethyl ether the significant product is N-4-tolyl-N'-phenyldiimide N'-oxide (17) (XII, R' is *p*-tolyl). When an excess of VII is used to ensure complete consumption of the Grignard reagent both methanol and toluene (IX, R' = tolyl) can be isolated. On the basis of this information the reaction may be formulated as follows:



Although either of the oxide linkages might be expected to co-ordinate with the Grignard reagent only the co-ordination shown in VIII would seem to be propitious for elimination of R'H, IX. The remaining dipolar fragment, X, should then co-ordinate and add Grignard reagent to give XI, from which XIII (R = H) (finally leading to methanol) and XII would be produced. It is noteworthy that none of the isomeric N'-4-tolyl-N-phenyldiimide N'-oxide (the structure of which was proved (17) by facile bromination in the phenyl substituent) was found among the reaction products.

*It has become evident that the nomenclature of azo and azoxy compounds is inadequate for communication among chemists. A revision has been suggested (15), but this in turn cannot be used to describe structures such as VI. Consequently we suggest that azo compounds be designated by the Chemical Abstracts classification, N,N'-diimide (R—N=N—R'), that azoxy compounds be called diimide oxides (or monoxides), and that substances with structures corresponding to VI be called diimide dioxides. For example the α - and β -4-chlorophenylazoxybenzenes would be renamed N-phenyl-N'-[4-chlorophenyl]diimide N-oxide and N'-oxide respectively. From this adaptation of amine oxide nomenclature it becomes simple to describe the unsymmetrical azo and azoxy compounds as well as our diimide dioxides.

CANADIAN JOURNAL OF CHEMISTRY, VOL. 37, 1959

When an otherwise comparable experiment is carried out by use of methyl chloride Grignard reagent the isolable product, besides unchanged VII, would then be designated as N-methyl-N'-phenyldiimide N'-oxide. This oily product (XII, R' = Me) has been characterized by analysis and by reaction with lithium aluminum hydride which converts it to the previously known N-methyl-N'-phenyldiimide. The structure of XII (R' = Me) is assigned principally by analogy with XII (R' = tolyl), but also it might be expected that the structure isomeric with XII (in which the amine oxide group is vicinal to the methylene group) would liberate methane from methyl halide Grignard reagent. Actually the product (XII, R' = Me) was very sluggish in this respect and only 0.3 equivalent could be discovered under the forced conditions of pyridine solvent at 100° C.

The yield of XII is always low (when R' = Me, 14%) and this circumstance is not unexpected in view of the known reactivity of N-oxides toward Grignard reagents. For example the free N-oxide group in VIII would be expected to oxidize Grignard reagent, leading to reduction products. Presumably such reactions would be slower than the series shown as VII \rightarrow XIII. In order, then, to rationalize the low yields of diimide monoxides from the dioxides in terms of side reactions with the Grignard reagent we have chosen an especially difficult example. The addition of N-methyl-N'-phenyldiimide dioxide to an equivalent of benzyl chloride Grignard reagent in diethyl ether gives a yield not exceeding 7% of the monoxide. About 40% of the diimide dioxide is recovered indicating that much of VIII or X does not react further, and that some of the Grignard reagent is consumed in reactions not included in the formulation VII \rightarrow XIII. The recovery of at least 7% of a derivative of benzaldehyde from the remaining complex mixture indicates that reduction of the monoxide has occurred subsequent to its formation.

$$C_{6}H_{5}N_{2}OCH_{2}C_{6}H_{5} \xrightarrow{RMgX} ROMgX + H_{5}C_{6}-C_{=}N-N-C_{6}H_{5} \xleftarrow{rearr.} H_{5}C_{6}-N_{2}-CH_{2}-C_{6}H_{5}$$

This latter reaction seems to be a significant one because reversal of addition (Grignard reagent into diimide dioxide) only raises the monoxide yield to 10%. However, threefold dilution under the latter conditions raises this yield to 14%. Moreover, equivalent addition into a tube containing a downward-pitched screw which conveys its contents into a dry-ice bath within 1 minute, Fig. 1, raises the final yield of diimide monoxide to 20%. It would appear from these experiments that low yield of diimide monoxide is partly due to reaction of XI (or some XII formed in the system before hydrolysis) with Grignard reagent. This conclusion is not vitiated by the 25% yield to be obtained when benzyl chloride Grignard reagent in diethyl ether is added slowly to the whole of N-methyl-N'-phenyldiimide in dioxane. It may be expected that the dibenzylmagnesium which remains in solution after precipitation of magnesium halides is less reactive toward XI or XII than is the whole Grignard reagent.

There are contradictions in the literature with respect to the structure that we have assigned to XII ($\mathbf{R'} = \text{benzyl}$). The diimide monoxide produced by this reaction has also been obtained by the peracid oxidation of benzaldehyde phenylhydrazone, XIV (18). Of the three possible structures which may be written, Bergmann *et al.* favored the epoxy arrangement XVII; but later two independent groups of workers favored the



structure N-benzyl-N'-phenyldiimide N-oxide, XVI. One group (19) based its contention on bromination to N-benzyl-N'-p-bromophenyldiimide N-oxide, but a repetition (20) of this bromination was unsuccessful. The other group (21) approved XVI because a reaction of XIV with ethyl chloride Grignard reagent yielded diphenylamidine, XIX, but their argument is unconvincing. Indeed the formation of XIX may be explained at least as well on the basis of XV.



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Fig. 1.

683

CANADIAN JOURNAL OF CHEMISTRY. VOL. 37, 1959



As may be seen by this formulation the reduction of $XV \rightarrow XIX$ is accomplished by the oxidation of Grignard reagent. By contrast the mechanism of Witkop and Kissman does not include the necessary oxidation step. On the other hand their mechanism does include reactions involving active hydrogen, although Witkop and Kissman searched for and could not find ethane. Lack of evidence for active hydrogen under normal conditions of Grignard treatment is confirmed by our results, although we did observe the formation of gas indicative of active hydrogen under forcing conditions (i.e. with prolonged reaction at 100° C when N-methylmorpholine was used as the reaction medium). This behavior is not unexpected when substances like XVIII, XIV, and XIX are present. For example acetone anil can be made to show the presence of active hydrogen (22). In summary it may be said that neither Pausacker nor Witkop and their co-workers have any real evidence for designation of XVI as the structure for the peroxidation product of benzaldehyde phenylhydrazone.

Actually this conclusion was drawn some years ago (19) by Lythgoe and his co-workers after preparation of both 4-chlorobenzylphenyldiimide monoxides by peroxidation of 4-chlorobenzylphenyldiimide. The product corresponding to XV was geoisomerized to the peroxidation product of 4-chlorobenzaldehyde. Also this chloro analogue of XV was brominated to give the 3-bromo-4-chlorobenzyl analogue, whereas the peroxidation product corresponding with XVI was brominated to give N-4-chlorobenzyl-N'-4-bromo-phenyldiimide N'-oxide.

Thus by the standard proof (17) Lythgoe and his co-workers have demonstrated the structure (XV) as the product that we obtain from phenylmethyldiimide dioxide and benzyl chloride Grignard reagent. This demonstration is not vitiated by the possibility that a modernized version of structure XVII may also explain part of the experiments of Lythgoe and his co-workers.

The behavior of Grignard reagents with N-methyl-N'-phenyldiimide dioxides provides an explanation for the action of lithium aluminum hydride in terms of the reaction sequence VII \rightarrow XII inclusive, where the metal hydride replaces Grignard reagent. Moreover the heterogeneous reductants mentioned by Bamberger should behave as metal hydrides and also give N-phenyldiimide N-oxide (XII, R' = H) initially, which ultimately would be reduced to the phenylhydrazine that eventually is obtained.

It should be noted that the nomenclature devised for diimide dioxides does not imply that characteristic properties may be specified for this group alone. In all instances at least one alkyl group must be attached to a nitrogen and no diimide dioxide has been prepared in which both organic groups attached to nitrogen are aromatic. For example an attempt to oxidize 4,4'-dichlorodiphenyldiimide to the dioxide with boiling 40%nitric acid leads only to 4,4-dichloronitrodiphenyldiimide oxide (23). On the other hand both organic groups attached to nitrogens may be aliphatic. Traube (1) prepared N,N'methylene-bis-[N-methyldiimide]tetroxide and the ethyl homologue by treatment of the silver salt of methylene-bis-nitrosohydroxylamine (I) with the alkyl iodides. We have

684

prepared the 2-chloroethyl analogue (XX) by the same method taking advantage of the unusual stability of these substances toward prolonged boiling with 70% nitric acid in order to destroy the unstable isomer, di-2-chloroethyl methylene-bis-nitrosohydroxyl-aminate (XXI). We have also prepared methylene-bis-[methyldiimide]tetroxide and its



ethyl analogue by treatment of the sodium or ammonium salt of I with dialkyl sulphate but in this event the nitroso isomers corresponding with XXI evidently are destroyed *in situ*, since the tetroxides corresponding with XX are isolated in a pure state.

The chemical reactions of these aliphatic diimides have been examined by use of methylene-bis-[methyldiimide]tetroxide but they are not very informative. Pyrolysis gives methanol, nitrous oxide, and carbon, while alkaline hydrolysis gives formic acid, methanol, and nitrous acid. Treatment with bromobenzene Grignard reagent gives a small yield of benzophenone phenylhydrazone. On the other hand treatment with methyl iodide Grignard reagent under analytical conditions (Soltys machine) shows that reaction in isoamyl ether is limited to evolution of gas indicative of two equivalents of active hydrogen. A precipitate is formed immediately, which accounts for the fact that only 0.1 equivalent of Grignard reagent is found additionally to be consumed in the system.

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The infrared spectra through the $1600-600 \text{ cm}^{-1}$ range have been determined for a series of diimide dioxides, the monoxides derived from them, some oxime methyl ethers, and some methyl isonitramines (III). These spectra are shown in Table I. Among this limited number of examples two bands may be assigned tentatively to the motion of the diimide dioxide linkage. The first of these is a weak to medium absorption at 1194–1210 cm⁻¹, while the other is a consistently strong band at 995–1018 cm⁻¹. These bands are not observed among the other candidates of Table I. On the other hand the spectra of diimide dioxides are noticeably transparent in the 1000–700 cm⁻¹ range whereas the O-ethers and the isonitramines show considerable absorption in this region. Although such spectral evidence that structure VI, and not III, IV, or V, is correct for α methylation derivatives of nitrosohydroxylamines.

The behavior of the alkyldiimide dioxide linkage as an aromatic substituent is of interest. Despite the inertness of this diimide dioxide linkage it may be displaced by forced bromination, and 4-bromonitrobenzene is obtained when N-methyl-N'-4-nitro-phenyldiimide dioxide is treated in this manner. The oxidizing action of the alkyldiimide dioxide linkage may be involved, since N-methyl-N'-4-nitrophenyldiimide dioxide may be converted in part to nitrobenzene by prolonged reflux in ethanol. This reduction finds its counterpart in the oxidation of the ethanol to acetaldehyde.

Infrared spectra in the 1600-600 cm⁻¹ region as liquids (L), solutions in carbon disulphide and carbon tetrachloride (S), in Nujol mulls (M), or in potassium bromide pellets (P)

Substance	Method		_						_									_			
N-Methyl-N'-phenyldiimide dioxide	L	1590 W		1475 S	1430 S	1312 M	1294 M	1197 M		1100 M		1042 S	1014 S								
N-Methyl-N'-4-chlorophenyl- diimide dioxide	S			1486 S	1464 S	1308 M		1200 M		1095 S		1050 S	1015 S								
N-Benzyl-N'-phenyldiimide dioxide	s	1595 W		1472 S	1430 S	1305 W	1290 W	1210 W		1095 W		1036 S	1008 S								
N-N'-Dibenzyldlimide dioxide	s	1600 W		1486 S	1438 S	1325 M	1285 S	1210 W				1034 S	1018 S								
N-Methylene-bis-(N'-methyl- dlimlde) dioxide	М		1515 M	1482 S	1428 S	1315 M	1292 S	1205 M		1086 S		1040 S	995 S				795 S				
N-Methylene-bls-(N'-ethyl dilmlde) dioxlde	м		1515 M	1482 S	1428 S	1315 M	1286 S	1194 M		1086 S		1040 S	1008 S				784 M				
N-Methylene-bis-(β-chloro- ethyldiimide) dioxide	М		1520 M	1488 S	1430 S	1320 W	1280 S	1194 M		1085 S		1032 S	1018 S				783 M				
N-Methyl-N'-phenyldiimide N'-monoxide	L	1605 M	1495 S	1452 M	1425 M	1320 S	1308 S		1160 W	1108 W	1070 M	1025 S		926 M			775 S		688 S		
N,N'-Diphenyidiimide monoxide	L	1595 W	1478 S	1455 M	1440 S	1330 S	1300 S		1164 M	1095 W	1072 M	1025 M		925 M			762 S		682 S		
N-Phenyl-N'-tolyldiimide N-monoxide	L	1605 M	1495 S	1458 M	1440 S	1325 M	1294 S		1165 M	1096 W	1070 M	1022 M		925 W			771 S		685 S		
N-Phenyl-N'-tolyldilmide N'-monoxlde	L	1600 M	1500 S	1460 S	1447 S	1330 M	1295 M		1165 M	1098 W	1075 W	1027 W		922 W			763 S		684 S		
N-Benzyl-N'-tolyldiimide N'-monoxide	Р	1602 M	1470 S	1440 M	1430 S	1310 S	1298 S		1170 W		1064 M	1022 M		918 M			775 S		680 S		
Benzophenone oxime O-methyl ethera	L	1595 W	1570 W	1498 M	1450 S	1428 W		1307 M		1168 M		1054 S	1032 S	1001 W		918 W		845 W	772 S	738 W	693 S
syn-Benzaldoxime O-methyl ether ^b	L	1600 M	1589 W	1493 W	1450 M	1427 W		1312 M		1169 M		1055 S	1030 M	1002 W		919 S		845 M	7 57 S	747 S	692 S
Benzophenone oxime N-methyl ether ^a	s			1490 M	1440 S					1169 M			1033 W	1001 W							704 M
Dlisopropyl isonitramine	L		1550 S		1470 M		1388 M	1330 M	1239 S	1177 W	1142 M				963 M	920 S	906 S				702 M
Di-n-propyl isonitramine	L		1558 S		1472 M	1432 M	1382 W	1338 M	1239 S		1145 VW			1005 W	947 S		890 W				699 M
Di-n-butyl isonitramine	L		1555 S		1465 M	1432 M	1379 W	1344 M	1240 S	1162 VW	11 45 W			1005 W	959 M	942 M	887 M				695 M

^aPrepared according to Semper, L. and Lechertadt, L. Ber. 51, 928 (1918). ^bPrepared according to Aurvens, K. V. and Otters, B. Ber. B, 57, 446 (1924).

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686

CANADIAN JOURNAL OF CHEMISTRY, VOL. 37, 1959

The dissimilarity of the diimide dioxide linkage with that of the monoxides may be observed by nitration of N-methyl-N'-phenyldiimide dioxide. It is well known (24) that aromatic diimide monoxides are slowly nitrated, and almost not at all in the aromatic ring adjacent to the $N \rightarrow O$ linkage. However when substitution in this NO-adjacent ring does occur the group enters in the meta position (25). By contrast N-methyl-N'-phenyldiimide dioxide is nitrated rapidly in nitric – sulphuric acid mixture. As would be expected from this rapidity the 58% yield of this rapid nitration is predominantly (81%) the para isomer. Only 7% is found as the meta isomer and 12% as the ortho isomer.

The meta isomer could not be hydrogenolized satisfactorily to metanitroaniline but its positional isomerism seems to be proved by the tin – hydrochloric acid reductions of the ortho and para isomers to ortho- and para-nitroaniline respectively. Moreover the para isomer may be reduced to the amine which can be diazotized and then converted to N-methyl-N'-4-chlorophenyldiimide dioxide. This compound has been synthesized (2) from 4-chlorophenylnitrosohydroxylamine.

The crystallography of this 4-chloro analogue has been examined carefully in connection with a single crystal study now in progress. Incidental to this study it has been found that this typical diimide dioxide is monomeric. It has also been found that, unlike nitramines (26), the "atom polarization" of N-methyl-N'-4-chlorophenyldiimide dioxide is normal in the sense that it amounts to only a few per cent of the total (P_{E+A}) distortion polarization in a weak electric field. However the orientation polarization seems to present an anomaly.

From the formal structural representation of the diimide dioxide linkage one may draw an analogy with the nitro group. The dipole moment studies (Table II) might at

Electrical polarizations of some diimide dioxides in benzene at $20\pm0.05^{\circ}$ C

	Polari	zation va	lues		Soli				
Diimide dioxide		β (neg.)	Р _т , сс	$R_{\rm D},$ cc	$d_4^{2_0}$	e	$P_{E+A}, \\ cc$	μ, Debyes	
N-Methyl-N'-phenyl	8.03	.307	267	42.8ª				3.26	
N-Methyl-N'-(4-nitrophenyl)	7.23	.437	309	50.1ª	1.465℃	2.815	50.7	3.50	
N-Methyl-N'-(2-nitrophenyl)	15.47	.424	614	47.9ª	-	-		5.19	
N-Methyl-N'-(3-nitrophenyl)	8.11	.424	342	48.1^{a}				3.74	
N-Methyl-N'-(4-chlorophenyl)	4.55	.397	200	$\frac{46.3^{b}}{48.6^{a}}$	1.470° 1.470°	3.020	50.9	2.69	
N-Benzyl-N'-phenyl	5.72	.317	299		1.3920	2.780	61.0	3.36	
N-Benzyl-N'-benzyl	4.60	.315	267		1.292°	2.834	71.1	3.05	
N',N'-Methylene-bis-N-methyl"	11.36	.228	342	37.9^{b}				3.80	

TABLE II

^aExtrapolated n_0^{20} of solutions. ^bCalc. for $n_{\alpha}+n_{\beta}+n_{\gamma}/3$ of solid. ^cAir displacement. ^dFlotation in zinc chloride. ^eDioxane used instead of benzene as solvent.

first inspection seem to confirm this analogy. This N₂O₂CH₃ group might then be assigned the group moment 3.26 D, negative with respect to hydrogen, just as the nitro group moment is 4.0 D, negative according to the orientation polarization of nitrobenzene. Actually the observed moment (3.74 D) of N-methyl-N'-3-nitrophenyldiimide dioxide is approximate to the value calculated from $\mu_{\text{resultant}} = (m_1^2 + m_2^2 + 2m_1m_2 \cos \theta)^{\frac{1}{2}} = 3.69$ D, where m_1 and m_2 are the group moments of N₂O₂CH₃ and NO₂, and θ is 120° C. However the calculated value for N-methyl-N'-4-nitrophenyl diimide dioxide (0.74 D) is widely divergent from the observed moment of 3.50 D. Likewise, a calculation

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of moment for N-methyl-N'-2-nitrophenyldiimide dioxide ($\theta = 60^{\circ}$ C) gives $\mu = 6.29$ D which is considerably higher than the observed value (5.19 D). A comparable discrepancy is found for N-methyl-N'-4-chlorophenyldiimide dioxide which shows a moment of 2.64 D, about one Debye greater than that expected by calculation.

If one reconsiders the $N_2O_2CH_3$ group in respect of these discrepancies it is apparent that a simple analogy with the nitro group is not valid, and this distinction may be seen in the geometry of the group. One may depict *cis* and *trans* forms and would expect distinct physical and chemical differences. However, the variation in structure probably is more subtle than can be expressed by this simple geometry.



It would appear from the results of Table II that the group moment of the diimide dioxide group is subject to wide variation depending on the substituents that may be attached to it. This variation is best explained in terms of N–N bond rotation, in which the anharmonicity is a function of the group substituent to the diimide dioxide linkage. Of course this concept conflicts with the orthodox doubly bonded diimide structure, but it is doubtful that the diimide dioxides should assume such a structure. Indeed, it would appear that the adjacent positive charge of a diimide dioxide structure such as XXII is somewhat anomalous and is better explained as a resonance hybrid of XXIIIa and b.



The resonance formulation is not intended to depict *trans* planarity; indeed the rotameric conformation of XXIII is thought to account for the apparent anomalies among the nitro and chloro derivatives described above. Certainly the conformation is not *trans* as shown in XXIII because in this event the electric moment of N,N'-dibenzyldiimide dioxide would be zero instead of 3.05 D (Table II).

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EXPERIMENTAL*

N-Methyl-N'-phenyldiimide Dioxide

To a mixture of cupferron (160 g, 0.6 mole) and sodium bicarbonate (140 g, 1 mole) in 1160 ml of water was added 210 g (1 mole) of dimethyl sulphate during 7 hours with stirring. Cooling with a water bath was necessary. After 15 subsequent hours of stirring

*Melting points have been corrected against appropriate standards (Can. J. Technol. 34, 89 (1956)). X-Ray diffraction patterns are recorded, using CuK_{α} (Ni filtered) radiation, in Ångstroms at relative intensities $[I/I_1]$.

688

at 20° C the deep-red system was extracted with a total of 1500 ml of diethyl ether. This extract, dried with calcium chloride, was distilled finally at 0.5 mm to yield 119 g of oil, b.p. 98–100° C, which partially solidified. This product was diluted by addition with $\frac{1}{2}$ volume of petroleum ether, b.p. 40–60° C, then cooled, and finally filtered. The solid was crystallized from 3.5 l. of petroleum ether (b.p. 40–60° C) and cooled to give 94 g, m.p. 37.5–39° C (60%). A similar recrystallization raised the melting point to 39.5–40.5° C. Absorption in the ultraviolet region showed λ_{max} at 262 m μ ; E_{max} 10,690. The X-ray diffraction pattern was [10] 3.48; [9] 4.78; [7] 4.14; [6] 7.16; [5] 4.17; [4] 6.58; [3] 3.13; [2] 2.89, 3.38; [1] 5.19, 3.17, 3.09, 2.85, 2.61.

When this substance was heated to 100° C with 85% sulphuric acid or chlorosulphonic acid it was recovered unchanged. Likewise it was unaffected by 6 hours' treatment with acetic anhydride at 200° C.

Hydrazine Phenylnitrosohydroxylaminate

A mixture of 4.56 g (0.03 mole) of N-methyl-N'-phenyldiimide dioxide and 3.0 g (0.06 mole) of 100% hydrazine hydrate was refluxed for 17 hours, then cooled, and diluted with 15 ml of absolute ethanol. Several crystal crops totalling 3.40 g (66%, m.p. 127–128° C) were combined and crystallized from 90 ml of absolute ethanol, 2.61 g (51%) of the salt, m.p. 127–128° C (decomp.); recrystallized, m.p. 128.5–129° C. Calc. for $C_6H_{10}O_2N_4$: C, 42.3; H, 5.92; N, 32.9. Found: C, 42.3; H, 6.02; N, 33.8. Acidification of 0.25 g in 3 ml of water by 3 ml of 12% hydrochloric acid gave 1.6 g (77%), m.p. 56.5–58° C, of phenylnitrosohydroxylamine. After crystallization from 5 ml of petroleum ether (b.p. 40–60° C) the product, m.p. 58–59° C, was characterized by mixture melting point. The presence of hydrazine was demonstrated by treatment of the salt with aqueous picric acid. The hydrazine picrate melted at 182–183° C.

Reduction of N-Methyl-N'-phenyldiimide Dioxide

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(a) Catalytic reduction.—A solution of 3.8 g (0.025 mole) in 50 ml of absolute ethanol with Adams catalyst absorbed 2 moles of hydrogen and then yielded aniline, b.p. 180–184° C (756 mm), which was characterized as acetanilide, 0.43 g, 24%, m.p. 112–114° C. Also 12% of the original dioxide was recovered unchanged.

(b) By hydriodic acid.—After 2 days' reflux of 1.0 g (0.0066 mole) in 3 ml of 47% hydriodic acid, 0.76 g (76%) of the original dioxide was recovered unchanged. An ether extract of the remainder was treated with oxalic acid in ether to give 4.6 mg (0.25%) of aniline oxalate, m.p. and m.m.p. 153.5–155.5° C.

(c) By sodium hydrosulphite.—A mixture of 0.99 g (0.0065 mole) in 8 ml of ethanol and 6.8 g (0.039 mole) of sodium hydrosulphite in 20 ml of water was heated with stirring at 80° C for 45 minutes. Extraction with diethyl ether yielded 65% of the unchanged starting material. The aqueous-alcoholic solution was concentrated under reduced pressure and the residue was extracted by ether to give 90 mg of oil. Treatment with picric acid yielded 104 mg (4.7%) of crude phenylhydrazine picrate, m.p. 135–137° C, which was crystallized from benzene, m.p. and m.m.p. 145.5° C.

(d) By lithium aluminum hydride.—A solution of 0.99 g (0.0065 mole) in 25 ml of dry ether was added to a solution of 0.813 g (0.0215 mole) of lithium aluminum hydride in 25 ml of the same diethyl ether with stirring during 20 minutes at 20° C. After a subsequent 30-minute stirring time the system was treated with 5 ml of 10% aqueous sodium hydroxide and then extracted with ether to yield 0.4 g of an oil. Distillation at 125–130° C (18 mm) gave 0.23 g (40%) of phenylhydrazine, characterized by conversion to *p*-chlorobenzaldehyde phenylhydrazone, m.p. and m.m.p. 125–126° C.

CANADIAN JOURNAL OF CHEMISTRY, VOL. 37, 1959

Bromination of N-Methyl-N'-phenyldiimide Dioxide

A mixture of N-methyl-N'-phenyldiimide dioxide (3.04 g, 0.02 mole) with 8 g (0.05 mole) of bromine in 10 ml of carbon disulphide was refluxed with 150 mg of iron filings for 15 hours. Subsequent steam distillation (4 l.) yielded 1.06 g, m.p. $68.5-71.5^{\circ}$ C, which was crystallized from 7 ml of ethanol, and 0.48 g (6.1%, m.p. 89.8–90.8° C) of crude 1,2,3,5-tetrabromobenzene, crystallized further from ethyl acetate, m.p. 99–99.7° C. Calc. for C₆H₂Br₄: C, 18.3; H, 0.51. Found: C, 18.3; H, 0.73. Chloroform extraction of the steam distillation residue gave 0.51 g, m.p. 219–220° C, crystallized from dioxane, m.p. 221.6–221.9° C. This substance was not identified. Calc. for C₇H₃Br₄: C, 21.7; H, 0.75.

N-Methyl-N'-4-nitrophenyldiimide Dioxide

To a chilled solution of 10.6 ml (0.26 mole) of 99% nitric acid and 45.3 ml (0.846 mole) of 100% sulphuric acid was added 19.8 g (0.13 mole) of N-methyl-N'-phenyldiimide dioxide during 15 minutes with constant stirring at 0° C. After a short time of warming to room temperature the system was poured into 400 g of crushed ice. Filtration removed 25.5 g which was twice crystallized from carbon tetrachloride to yield 12 g (47%) of the para-nitro derivative, m.p. 152–153° C. Calc. for $C_7H_7N_3O_4$: C, 42.6; H, 3.58; N, 21.3. Found: C, 42.7; H, 3.33; N, 20.8. The X-ray diffraction pattern was [10] 3.18; [8] 7.76, 7.49; [6] 4.69; [5] 5.04; [3] 3.68, 3.52; [2] 11.1; [1] 2.31; [0.5] 2.16. The ultraviolet absorption in ethanol gave λ_{max} at 243 m μ , 330 m μ with E_{max} 10,970 and 567 respectively. The substance was recovered unchanged after 12 hours at 200° C with acetic anhydride.

An unsuccessful attempt was made to prepare this compound by peroxidation of methyl 4-nitrobenzenediazotate (27). This ester was prepared via the silver salt from 4-nitrobenzenediazonium sulphate by Bamberger's method but the 2 g obtained from 6.9 g of p-nitroaniline was used without characterization because of its tendency toward decomposition. The orange-yellow solid (0.011 mole) was mixed with 15 ml of acetic acid and 9 ml of 30% hydrogen peroxide and kept at 0° C for 12 hours, then at 25° C for 2 days. Upon treatment with 150 ml of water and extraction with ether 1.11 g of red-brown solid was obtained upon evaporation. This solid was developed on a chromatoplate (28) (prepared from 80% silica gel and 20% plaster of Paris at 120° C) together with p-nitrophenol and also N-methyl-N'-4-nitrophenyldiimide dioxide. The developer was 18:1 benzene-acetone. By means of a sulphuric – nitric acid spray (95:5) only p-nitrophenol and not the diimide dioxide could be detected.

A mixture of 2.51 g (0.013 mole) of N-methyl-N'-4-nitrophenyldiimide dioxide and 9.2 g (0.078 atom) of granulated tin was treated with 18.8 ml (0.188 mole) of concentrated hydrochloric acid during 25 minutes. After 40 minutes of reflux the system was cooled and treated with 20 g of sodium hydroxide in 40 ml of water and then steam-distilled. From the distillate was obtained 0.89 g, m.p. 135–140° C, of *p*-phenylenediamine which was crystallized from benzene, m.p. and m.m.p. 139–140° C, 0.3 g (22%).

N-Methyl-N'-4-aminophenyldiimide Dioxide

A mixture of the para-nitro derivative (0.97 g, 0.0049 mole) and 15 ml of hydroiodic acid (sp. gr. 1.5) was heated under reflux for 15 minutes. After 12 hours at 20° C the system was diluted with 20 ml of water to precipitate 0.25 g (26%) of unchanged starting material, m.p. 152–153° C, after crystallization from carbon tetrachloride.

The amine (0.19 g, m.p. 171–172.5° C, 23%) was precipitated by addition of alkali to pH 8. It was crystallized from ethanol (95%), m.p. 176.5–176.8° C. The X-ray diffraction

pattern was [10] 4.81; [9] 3.51; [7] 4.25; [5] 3.47; [4] 7.56, 3.03; [2] 6.58, 5.86, 5.26, 2.05; [1] 2.93, 2.61. Calc. for $C_7H_9N_3O_2$: C, 50.3; H, 5.43; N, 25.1. Found: C, 50.7; H, 5.35; N, 25.5.

4-Chlorophenylhydroxylamine (2)

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To a refluxing system comprised of 180 g (1.14 mole) of 4-chloronitrobenzene in 1200 ml of ethanol and 24 g (0.45 mole) of ammonium chloride in 300 ml of water was added 300 g (4.6 atom) of zinc dust in 10-g lots. One-minute periods of addition and stirring were alternated with 1-minute periods of reflux until the color of the reaction mixture passed its lightest stage of brown and began once more to darken. The residual zinc dust was quickly filtered hot. Steam distillation of the filtrate gave 50 g (30.5%), m.p. 83- 83.5° C.

N-Methyl-N'-4-chlorophenyldiimide Dioxide

(a) From N-Methyl-N'-4-aminophenyldiimide dioxide.—To a suspension of N-methyl-N'-4-aminophenyldiimide dioxide (100 mg, 0.006 mole) in 0.8 ml of concentrated hydrochloric acid plus 0.5 ml of water at 0° C was slowly added a solution of 50 mg of sodium nitrite in 0.3 ml of water. To the orange-yellow reaction mixture at 0° C was then added 90 mg of cupric chloride in 0.75 ml of concentrated hydrochloric acid during 20 minutes. The system was then slowly warmed to 20° C and subsequently heated at 60° C for 10 minutes. When the mixture was cooled 60 mg (54%) of N-methyl-N'-4-chlorophenyldiimide dioxide separated, m.p. 70–71° C. After crystallization from petroleum ether (b.p. 40–60° C) a mixture melting point (71–72° C) with an authentic specimen (2) was not depressed. The X-ray diffraction pattern was [10] 5.34; [9] 3.52; [8] 3.36; [6] 3.71; [5] 4.36; [4] 4.92; [3] 6.28; [2] 2.19, 1.91; [1] 6.51, 2.94, 2.59, 2.51, 2.44, 2.22.

(b) From 4-chlorophenylhydroxylamine.—A solution of 50 g (0.348 mole) of 4-chlorophenylhydroxylamine in 335 ml of ethanol was acidified (2) with 135 ml of 2 N hydrochloric acid and the stirred system was held at 5° C. Then 24.6 g (0.356 mole) of sodium nitrite in saturated aqueous solution was added during 30 minutes. The precipitate was filtered off, washed with water, and, partially dried, was suspended in a solution of 80.5 g (0.761 mole) of sodium bicarbonate in 935 ml of water. The stirred suspension was treated with 45 ml (0.475 mole) of methyl sulphate. After 40 minutes the system was chilled and filtered. The crude product (54 g) was dissolved in a minimum of boiling ethanol. The hot filtrate was chilled to remove 4-chlorophenyl-bis-diimide (9.4 g, 23.9%). The filtrate was steam-distilled and 17.5 g (m.p. 69–70° C, 27%) of N-methyl-N'-4-chlorophenyldimide dioxide was obtained from the ether extract of the distillate. After crystallization from petroleum ether (b.p. 40–60° C) it melted at 73.1–74.6° C. Rod-shaped crystals suitable for X-ray diffraction studies were obtained from p-cymene; they cleaved well along (100), (001), and (102).

The refractive indices were measured by the crushed crystal immersion method (29) as α , 1.49, about 10° C from (010), while β is 1.67 along (001), and γ is 1.78 about 20° C from (100). The density by flotation in aqueous zinc chloride at 29° C is 1.476, while by the air-displacement method (30) it is 1.470. Calculations of the polarization (from $\alpha + \beta + \gamma$ divided by 3) gave 46.2 cc in contrast to 50.9 cc obtained from $\epsilon = 3.020$ by dielectric constant measurement of the pelleted solid (31).

Zero level Weissenberg photographs of crystals mounted on the *b*-axis (in capsules because of sublimation) were carried out with CuK_{α} radiation giving constants: $a = 17.20 \pm 0.04$ Å, $b = 3.91 \pm 0.01$ Å, and $c = 13.11 \pm 0.04$ Å of a monoclinic cell with $\beta = 108.0 \pm 0.2^{\circ}$ C. Since this corresponds with a cell volume of (838 Å)³ and the molecular volume

CANADIAN JOURNAL OF CHEMISTRY, VOL. 37, 1959

is calculated as $(210 \text{ \AA})^3$ there are four molecules per unit cell. Molecular weight by the Rast method was determined at 190 (calc., 186.6).

Examination of Weissenberg photographs showed no extinctions on (hkl), but (oko) reflections were found only when k = 2n and (hol) reflections only when l = 2n. The space group is therefore assigned at $P2_{l/c}$. Structure factors have been determined (32).

p-Chloroaniline

692

Although N-methyl-N'-4-chlorophenyldiimide dioxide was unaffected by hydriodic acid at 100° C for 30 minutes, reduction was effected in a mixture of 0.56 g (0.003 mole) of the substance with 2.14 g (0.018 atom) of granulated tin to which 3.7 ml (0.095 mole) of concentrated hydrochloric acid was added during 3 minutes. Subsequently the system was maintained at 90–100° C for 30 minutes and at 20° C for 12 hours. After treatment with 6 g of sodium hydroxide in 6 ml of water the system was ether-extracted. Evaporation of the extract left 105 mg, m.p. 60–68° C, which was crystallized from petroleum ether (b.p. 40–60° C), 50 mg (13%) of p-chloroaniline characterized by m.p. and m.m.p. of 68.5–70° C.

4-Nitrobromobenzene

A system comprised of 0.98 g (0.005 mole) of N-methyl-N'-4-nitrophenyldiimide dioxide, 1.6 g (0.01 mole) of bromine, 100 mg of iron filings, and 5 ml of carbon disulphide was refluxed for 3 hours and then steam-distilled. The cooled distillate (220 ml) yielded 0.14 g, m.p. $67.6-69.5^{\circ}$ C, of crude 4-nitrobromobenzene which was crystallized from ethanol, m.p. $113-115^{\circ}$ C, 90 mg (9%), and then from commercial hexane, m.p. and m.m.p. $122.7-123.3^{\circ}$ C.

Nitrobenzene

When a solution of N-methyl-N'-4-nitrophenyldiimide dioxide (2.56 g, 0.013 mole) in 50 ml of 95% ethanol was refluxed for 41 hours the cooled system precipitated 1.31 g (51%) of starting material, m.p. 152–153.5° C. Distillation of the filtrate gave 0.26 g of an oil, b.p. 78° C (10 mm), which on redistillation was shown to be nitrobenzene (0.23 g, 14%, b.p. 208–212° C at 756 mm, n_{p}^{20} 1.55256, m.p. and m.m.p. 6–7° C).

In an experiment, identical except for the addition of 0.1 g of concentrated sulphuric acid and for a 120-hour reflux, only 13% of starting material was recovered and 48% of nitrobenzene was obtained. Additionally a precipitate was formed in a trap containing acid – alcoholic 2,4-dinitrophenylhydrazine solution which surmounted the reflux condenser. This was proved by mixture melting point to be acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 162–164° C.

N-Methyl-N'-3-nitrophenyldiimide Dioxide

The mother liquor (1100 ml) from which the N-methyl-N'-4-nitrophenyldiimide dioxide was removed (see above) was concentrated to a volume of 250 ml and then cooled to give 5.2 g, m.p. 103–111° C. A second crop (1.18 g, m.p. 108–113° C) was obtained by concentrating the filtrate and then eluting it on a Doucil column (1 in. \times 14 in.) by means of 450 ml of 1:1 Commercial hexane – carbon tetrachloride. The combined eluates gave 6.38 g which was crystallized from 400 ml of benzene, 1.04 g (4%) of N-methyl-N'-3-nitrophenyldiimide dioxide, m.p. 128–132° C. Recrystallization from methanol raised this melting point to 133–134° C. Calc. for C₇H₇N₃O₄: C, 42.6; H, 3.58; N, 21.3. Found: C, 42.3; H, 3.50; N, 21.4. The X-ray diffraction pattern was [10] 3.23; [3] 7.86; [2] 4.65; [1] 4.25, 3.94, 3.70; [0.5] 6.10, 5.27. The ultraviolet absorption in ethanol at 23° C showed λ_{max} at 254 Å with E_{max} 15,350.

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GEORGE ET AL.: ORGANONITROSOHYDROXYLAMINES

N-Methyl-N'-2-nitrophenyldiimide Dioxide

The eluted Doucil column (see above) was further eluted, now with carbon tetrachloride (450 ml) and then with chloroform (400 ml). These eluates gave 2.22 g, m.p. 52–60° C, and 0.55 g, m.p. 62–66° C, respectively. The combination was crystallized from a 1:1 mixture of benzene and petroleum ether (b.p. 40–60° C), 1.9 g 7.4%, m.p. 60–64° C. A similar recrystallization raised this melting point to 66.5–67.3° C. Calc. for $C_7H_7N_3O_4$: C, 42.6; H, 3.58; N, 21.3. Found: C, 42.3; H, 3.67; N, 20.9. The X-ray diffraction pattern was [10] 4.13, 3.52; [9] 7.79; [8] 5.81, 4.87, 3.87, 3.39; [6] 5.21, 2.54; [5] 4.64; [4] 3.05; [1] 7.08, 6.44. The ultraviolet absorption in ethanol at 23° C was λ_{max} 258, 289 Å with E_{max} 10,830 and 9,415 respectively.

A system comprised of 100 mg (0.0005 mole) of this isomer with 0.37 g (0.0031 atom) of granulated tin and 0.75 ml of concentrated hydrochloric acid was refluxed for 40 minutes. The cooled system, treated with 1.2 g of sodium hydroxide in 8 ml of water was ether extracted. The extract contained 35 mg, m.p. 93–97° C. This was crystallized from benzene, m.p. 100–101° C (14 mg, 26%), and then was characterized by m.p. and m.m.p. (100–102° C) as orthophenylenediamine.

N, N'-Dibenzyldiimide Dioxide

This substance was prepared in 38% yield, m.p. $58-59^{\circ}$ C, from N-benzylhydroxylamine (33) by the previously reported procedure (3). The X-ray diffraction pattern was [10] 4.53; [8] 4.10; [7] 3.16; [6] 5.38, 4.71; [5] 3.96, 3.10; [4] 2.36; [3] 2.60; [2] 7.0; [1] 2.24, 2.91, 3.29, 3.58.

A 4% solution in benzene showed bands with the following per cent transmission (% T) at the recorded frequency in cm⁻ⁱ: (89) 494, (90) 555, (86) 601, (51) 710, (66) 741, (91) 835.

N-Benzyl-N'-phenyldiimide Dioxide

To a solution of sodium ethoxide (1.38 g Na in 50 ml of absolute ethanol, 0.06 mole) was slowly added 9.3 g (0.06 mole) of cupferron. After further addition of 7.59 g (0.06 mole) of freshly distilled benzyl chloride the system was refluxed for 210 minutes. Removal of the solvent under reduced pressure left a brown residue which was extracted by diethyl ether. The evaporated extract was crystallized from a hexane–ether mixture, 2.28 g (16.7%), m.p. 80–81° C. Calc. for $C_{13}H_{12}N_2O_2$: C, 68.4; H, 5.31; N, 12.3. Found: C, 68.6; H, 5.42; N, 12.2. The X-ray diffraction pattern was [10] 4.25; [9] 5.75; [8] 3.90; [7] 4.60, 4.73; [6] 4.10; [5] 3.55, 3.17; [4] 5.06; [3] 3.26, 2.36; [2] 3.38, 3.44, 3.03; [1] 2.93.

Action of Grignard Reagents on Diimide Dioxides

(a) In the Soltys apparatus.—N-Methyl-N'-phenyldiimide dioxide was studied by the reported procedure (34) in isoamyl ether with methyl iodide Grignard reagent in the same solvent which was distilled from sodium and then from methyl iodide Grignard reagent under nitrogen. The system evolved gas at 25° C but in order to complete the reaction it was heated by boiling water bath for 10 minutes prior to and 10 minutes after the addition of aniline. The active hydrogen was found to be 0.88 and 1.01 equivalent for two determinations in which "addition" of reagent was 1.66 and 1.59 equivalent. In a separate determination the gas was collected before the addition of aniline and was shown to be methane, free from ethane, by infrared absorption in a gas cell with potassium bromide windows: 3205 (W), 2916 (M), 2814 (S), 2786 (S), 1341 (M), 1328 (M), 1290 (S), 1258 (M), 1023 (M) cm⁻¹. Under comparable conditions the gas from N-methyl-N'-phenyldiimide N'-monoxide did not appear to be evolved at 25° C, and at 100° C it did not exceed 0.3 equivalent, although pyridine was the solvent. N,N'-Dibenzyldiimide

693

CANADIAN JOURNAL OF CHEMISTRY. VOL. 37, 1959

dioxide (9) in isoamyl ether medium showed 0.7 active hydrogen and 0.3 equivalent of Grignard addition. In the better solubilizing medium, N-methylmorpholine, the active hydrogen was 1.5 and the equivalent of Grignard addition was 1.9. The gas evolved was proved by infrared absorption to be only methane. A simple Zerewitinoff determination in pyridine (finally at 100° C) gave 0.4 active hydrogen. N-Benzyl-N'-phenyldiimide dioxide in isoamyl ether medium showed 0.5 active hydrogen and 0.7 equivalent of Grignard addition, whereas the determination in N-methylmorpholine showed 1.9 equivalent each of hydrogen and Grignard addition. The gas evolved was entirely methane (infrared). A Zerewitinoff determination in pyridine at 100° C showed 0.2 equivalent of active hydrogen.

(b) N,N'-Diphenyldiimide monoxide.—An ether solution (265 ml, 0.1 N, 0.027 mole) of bromobenzene Grignard reagent was added slowly to a solution of N-methyl-N'-phenyldiimide dioxide (2.6 g, 0.0172 mole) in 50 ml of diethyl ether during 150 minutes with constant stirring. Subsequently the system was treated with 100 ml of saturated ammonium sulphate. The ether phase was steam-distilled (0.93 g of unidentified oil in the distillate) and the residue was extracted by diethyl ether. Distillation of this red extract gave a 0.69-g fraction, b.p. 80–120° C (0.6 mm), and a 1.18-g fraction, b.p. 115–130° C (0.6 mm). The latter fraction, crystallized from 4 ml of petroleum ether (b.p. 40–60° C) gave 0.58 g, m.p. 34.5–35.5° C (17%), of diphenyldiimide monoxide identified by mixture melting point (35–36° C) after recrystallization from 4 ml of methanol.

(c) N-Methyl-N'-phenyldiimide N'-oxide.—Methyl chloride Grignard reagent (185 ml, 0.21 N, 0.0389 mole) was added slowly to a stirred solution of 4.2 g (0.0276 mole) of N-methyl-N'-phenyldiimide dioxide in 50 ml of diethyl ether during 3 hours at 20° C. After subsequent decomposition by means of 100 ml of saturated ammonium sulphate a deep-red solid (37 mg, m.p. 126–127° C decomp.) separated from the ether layer. This unidentified solid melted at 140.5° C after crystallization from benzene (60.8% C, 3.70% H). The ether layer was steam-distilled. Ether extraction of the steam distillate removed 2 g of a yellow oil, the higher boiling fraction of which (b.p. 106° C at 1 mm) was 14% of unchanged starting material, m.p. 37–39° C, while the lower boiling fraction gave 0.90 g (b.p. 90–106° C at 16 mm). Crystallization from petroleum ether, b.p. 40–60° C, gave 0.54 g (14%) of N-methyl-N'-phenyldiimide N'-monoxide, m.p. -3 to 0° C. Two similar crystallizations raised this melting point to $6.5-8.5^{\circ}$ C, $n_{\rm D}^{20}$ 1.556. Calc. for C₇H₈N₂O: C, 61.7; H, 5.85; N, 20.6. Found: C, 61.9; H, 6.18; N, 20.7. The brown viscous residue from steam distillation (1.27 g) was not identified.

(d) N-Methyl-N'-phenyldiimide.—To a stirred solution of 180 mg (0.0047 mole) of lithium aluminum hydride in 10 ml of absolute diethyl ether was added 180 mg (0.0013 mole) of N-methyl-N'-phenyldiimide N'-monoxide during 10 minutes. After 35 minutes of subsequent stirring 1 ml of water was added and the system was filtered. The ether extract of the filtrate, dried over magnesium sulphate, was mixed with 3 ml of ether containing 180 mg of anhydrous oxalic acid to give 95 mg, m.p. 138–139° C, of crude methylphenyldiimide oxalate. Two crystallizations from absolute ethanol gave 36 mg (13%), m.p. 145–146° C, which did not depress the melting point of an authentic specimen (35, 36).

(e) N-4-Tolyl-N'-phenyldiimide N'-monoxide.—To a solution of 3.8 g (0.025 mole) of N-methyl-N'-phenyldiimide dioxide in 50 ml of dry diethyl ether was slowly added during 4 hours at 25° C 200 ml of 0.185 N p-bromotoluene Grignard reagent (0.037 mole). Then 100 ml of saturated aqueous ammonium chloride solution was added. Evaporation of the separated non-aqueous layer left a red liquid which was steam-distilled. Ether

694

extraction of the distillate (250 ml) gave 60 mg of $p_{,p'}$ -bitolyl. Ether extraction of the steam distillation residue gave 4.75 g of oil which was distilled, the first fraction (b.p. $100-120^{\circ}$ C, 0.5 mm) of which was more bitolyl (total 0.21 g, 6%) identified after methanol crystallization by m.p. and m.m.p., 118-119°C. The higher boiling fraction (2.85 g, b.p. 120-150° C at 0.5 mm) was crystallized from methanol, 2.23 g, m.p. 42-48° C. Two further crystallizations raised the melting point to $50-51^{\circ}$ C (1.67 g, 31.5%), and a mixture melting point with an authentic specimen (17) was not depressed. The X-ray powder diagram was [10] 4.35; [9] 3.72; [8] 4.62; [7] 7.49; [6] 3.05; [5] 6.52; [4] 3.15; [3] 5.27; entirely identical with that of the authentic sample but appreciably different from that of N-4-tolyl-N'-phenyldiimide N-monoxide, also prepared by Bigiavi and Sabatelli, [10] 4.67; [9] 3.95; [8] 3.34; [7] 9.34; [6] 3.65; [5] 4.17; [4] 5.34; [3] 5.65; [2] 4.98; [1] 3.49. In a separate experiment the mixture of 0.048 mole of p-bromotoluene Grignard reagent and 0.032 mole of the diimide dioxide reacted for 2 hours at 20° C. A Gilman test 1 (37) for excess Grignard reagent was then negative. The red oil obtained after hydrolysis was dried and distilled through a 10-plate column to give 2.04 g, b.p. 40-70° C (756 mm), and 1.65 g, b.p. 70-115° C (756 mm), as well as 5.34 g, b.p. 100-140° C at 10 mm. The first fraction was redistilled, 0.44 g (43%), b.p. 50-60° C, and identified as methanol by its p-nitrobenzoate, m.p. and m.m.p. 95-96° C. The second fraction was redistilled, b.p. 100-110° C (756 mm), 0.43 g (12% as toluene) which was converted to 2,4,6-trinitrotoluene, m.p. and m.m.p. 80-81° C for characterization.

(f) N-Benzyl-N'-phenyldiimide N'-oxide.—The best preparation involved the addition of 100 ml of 0.2 N benzyl chloride Grignard reagent in diethyl ether (0.02 mole) to a dioxane solution of N-methyl-N'-phenyldiimide dioxide (1.53 g, 0.01 mole in 50 ml) during 90 minutes. Then 25 ml of saturated aqueous ammonium chloride was added. The white solid which separated was filtered off and its quantity was augmented by chilling the non-aqueous layer at 0° C for 12 hours, 0.54 g (25%) as N-benzyl-N'-phenyldiimide N'-monoxide, m.p. 198–199° C decomp. This melting point was not depressed by admixture with a sample prepared according to Lynch and Pausacker (19). Moreover the X-ray diffraction patterns were identical: [10] 3.90; [9] 5.60; [8] 4.40; [7] 8.98; [6] 4.20; [5] 4.82; [4] 5.40; [3] 3.44; [2] 10.3; [1] 3.66. Calc. for C₁₃H₁₂N₂O: C, 73.6; H, 5.70; N, 13.2. Found: C, 73.8; H, 5.34; N, 13.2.

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Preparations in diethyl ether alone were less successful. The yield by adding Grignard reagent to an equimolar amount of the diimide dioxide in 65 ml of ether was 10%, which was lowered to 7% by reversing the order of addition, while threefold dilution with consequent longer addition time gave 14% yield. The best yield in diethyl ether (20%) was obtained by adding equivalent amounts at equivalent concentrations of the reagents from two burettes into a tube in which a downward pitched screw conveyed the mixture to a dry-ice-cooled trap within 1 minute of the time of introduction.

The other products of these reactions are of interest. The red oil remaining after evaporation of the filtered non-aqueous part of the hydrolyzate showed at least 6 constituents when examined on a chromatoplate (28). Column chromatography of the red oil on alumina (100–150 mesh activated at 150° C for 10 hours) eluted by benzene gave 3.18 g which was rechromatographed similarly to give 2.74 g that yielded 0.51 g (19%) of bibenzyl (m.p. and m.m.p. $51-52^{\circ}$ C) by crystallization from methanol. The methanolic filtrate on treatment with 2,4-dinitrophenylhydrazine reagent gave 0.58 g (m.p. $227-228^{\circ}$ C, 7%) of crude benzaldehyde 2,4-dinitrophenylhydrazone, identified by m.p. and m.m.p. (234–236° C) after crystallization from benzene.

Elution of the alumina columns by chloroform gave a liquid (1.99 g) which was crystal-

695

CANADIAN JOURNAL OF CHEMISTRY, VOL. 37, 1959

lized from petroleum ether (b.p. 40-60° C) to give unchanged starting material, m.p. 38-39° C, 1.85 g, 40%, characterized by mixture melting point.

A modification of the preparation of N-benzyl-N'-phenyldiimide N'-oxide was made by filtration of the reaction system. To a stirred solution of 6.1 g (0.04 mole) of N-methyl-N'-phenyldiimide dioxide in 50 ml of absolute diethyl ether was added 0.06 mole of benzyl chloride Grignard reagent (300 ml, 0.2 N) during 2 hours. The system was filtered under nitrogen to remove the white precipitate from the ultimately red solution. Hydrolysis of this filtrate by addition of 50 ml of saturated aqueous ammonium chloride gave 3.6 g of viscous oil after drying and evaporation of the ether. Treatment of this oil with 15 ml of hexane precipitated 0.1 g (1.2%) of N-benzyl-N'-phenyldiimide N'-oxide, m.p. 198–199° C after crystallization from toluene, authenticated like the main bulk of this product by mixture melting point and infrared spectra.

The hexane-soluble portion of the oil was chromatographed on alumina to yield by hexane elution 0.6 g (10%) of unchanged methylphenyldiimide dioxide (m.p. $38-39^{\circ}$ C) and then by carbon tetrachloride elution 0.1 g (1.3%, m.p. $154-155^{\circ}$ C after crystallization from cyclohexane) of benzaldehyde phenylhydrazone, authenticated by mixture melting point and infrared spectra.

The white precipitate from the reaction system was hydrolyzed by treatment with 75 ml of saturated aqueous ammonium chloride. The ether extract of the hydrolyzate, evaporated and then dissolved in hot toluene, yielded 1.2 g (14%) of N-benzyl-N'-phenyldiimide N'-oxide, m.p. 198–199° C. Evaporation of the mother liquors left 4.5 g of unidentified red oil.

Solvolysis of N-Benzyl-N'-phenyldiimide N'-Monoxide

A mixture of 0.5 g (0.00236 mole) of the monoxide and 5 ml of glacial acetic acid (13) was gently refluxed for 15 minutes and then poured into 25 g of crushed ice. The system, neutralized by addition of sodium bicarbonate, was ether-extracted. Evaporation left an oil (0.76 g) from which 0.28 g (42%) of benzaldehyde 2,4-dinitrophenylhydrazone (m.p. and m.m.p. 235–236° C) was isolated by treatment with 2,4-dinitrophenylhydrazine reagent.

Analysis of N-Benzyl-N'-phenyldiimide N'-Monoxide in the Soltys Machine

By the technique used for analysis of methylphenyldiimide dioxide the N-benzyl-N'phenyldiimide N'-monoxide did not react at all at room temperature; at 100° C it yielded only 0.5 active hydrogen and 0.7 equivalent of addition. Consequently the isoamyl ether was replaced by N-methylmorpholine (dried over solid potassium hydroxide, then barium oxide, and distilled under nitrogen, b.p. 136–136.5° C). In this reaction medium 1.9 equivalent of active hydrogen and 1.9 equivalent of addition were observed, after 20 minutes at 100° C. No gas was evolved at 25° C. A Zerewitinoff determination at 100° C in pyridine showed 0.3 equivalent of active hydrogen.

N', N'-Methylene-bis-[N-ethyldiimide]tetroxide

A solution of 45 g (0.294 mole) of monoammonium methylene-bis-nitrosohydroxylaminate (1) in 140 ml of 8% aqua ammonia was stirred during 24 hours while 88.5 ml (0.675 mole) of diethyl sulphate was added gradually, the pH being maintained at 8 by addition of more ammonia. The precipitate which was filtered off weighed 8.2 g, m.p. 145° C, after it was dried and washed with chloroform. This 15% molar yield of ammonium N-ethyl-N'-diimidomethylnitrosohydroxylaminate dioxide could be purified by rapid solution in 40 ml of water at 70° C, followed by quick cooling to avoid decom-

696

position with evolution of colorless gas. The recovery was 41% of that added, m.p. 150.1–150.6° C decomp., but a second crop, m.p. 149° C, could be obtained by dilution of the liquors with ethanol. Calc. for C₃H₁₁N₅O₄: C, 19.8; H, 6.13; N, 38.6. Found: C, 19.9; H, 6.40; N, 38.1.

The reaction liquor from which the ammonium salt precipitated was treated during 7 hours with 50 ml of diethyl sulphate and sufficient ammonia to maintain the pH at 8. The clear solution was then extracted three times with chloroform and these extracts were vacuum evaporated to leave 10 g of gummy solid which was treated with 10 ml of 68% nitric acid. After the strenuous evolution of nitrogen oxides had ceased the hot solution was cooled and neutralized by strong alkali. The crystals (4.4 g, m.p. 75.8–76.3° C) were N',N'-methylene-bis-[N-ethyldiimide]tetroxide.

This compound also was obtained when 2.96 g (0.014 mole) of the ammonium salt described above was dissolved in 10 ml of water with 12 ml of 10% aqueous sodium hydroxide (0.03 mole) and was treated during 24 hours with 3.9 ml (0.03 mole) of diethyl sulphate. The product (1.3 g) was crystallized from 95% ethanol (1.5 ml per g) 0.68 g, m.p. 78.9° C. More of the same compound was obtained (0.4 g) by concentration of the mother liquors followed by fume-off with hot nitric acid. Calc. for $C_5H_{12}N_4O_4$: N, 29.2. Found: N, 29.6.

The methyl analogue was prepared in the same manner but with less complication because the ammonium salt did not precipitate. Consequently a 33% yield, m.p. 136° C, could be obtained within one day. The X-ray diffraction diagram was [10] 5.88; [9] 3.87; [8] 3.80; [7] 3.12; [6] 3.58; [5] 5.21; [4] 2.60; [3] 3.23; [2] 3.96, 3.35; [1] 2.40, 2.32, 2.36.

N,N'-Methylene-bis-methyldiimide tetroxide, m.p. 136° C, may be crystallized from 70% nitric acid in which it is quite stable, even during several hours at the boiling point of this medium. The density at 20° C of the solid substance is 1.368 (flotation) in comparison with 1.378 calculated from the following X-ray data. The crystal is orthorhombic pyramidal with $a = 14.38 \pm 0.04$ Å, $b = 15.16 \pm 0.04$ Å, $c = 7.16 \pm 0.02$ Å when crystallized from benzene. Reflections (Weissenberg) are found in (*hkl*) only when h+k, k+l, and l+h are even; in (*hol*) only when h = 2n, l = 2n, and h+l = 4n; in (*okl*) only when k = 2n, l = 2n, and k+l = 4n. Hence the space group is $C_{2\gamma}^{19}(F_{ddm})$. There will be eight molecules per unit cell with a twofold molecular symmetry axis. Since the volume of the unit cell is 1561 Å³, the total number of electrons is 688. The absorption coefficient for CuK_a radiation is thus 12.6 cm⁻¹.

The crystals are twinned parallel to the *b*-axis and are strongly piezoelectric, indicating lack of centrosymmetry. The refractive indices measured by the crushed crystal technique are $\alpha = 1.38$, $\beta = 1.445$, $\gamma = 1.48$, so $\alpha + \beta + \gamma/3 = 1.44$. A tentative orientation was chosen and structure factors were determined (38).

N, N'-Methylene-bis-[N- β -chloroethyldiimide]tetroxide

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A suspension of 2.23 g (0.0146 mole) of monoammonium methylene-bis-nitrosohydroxylaminate in 50 ml of water was treated with water until solution was complete. To this solution was added 4.96 g (0.0202 mole) of silver nitrate in 25 ml of water. The silver salt was filtered off, washed twice with water, and thrice with absolute ethanol. It was then suspended in 30 ml of absolute ethanol and 5.55 g (0.029 mole) of 1-chloro-2-iodoethane was added. After 5 days the silver iodide was filtered off and washed with absolute ethanol. Evaporation of the filtrate left 2.16 g which was treated with 2 ml of 68% nitric acid to destroy the nitroso compounds. After the strenuous reaction had subsided the system was diluted with water and the crystals were filtered off, 1.20 g

CANADIAN JOURNAL OF CHEMISTRY. VOL. 37, 1959

(37%), m.p. 87.8–89.5° C, not raised by crystallization from ethanol (5 ml per g). Calc. for C₅H₁₀N₄O₄Cl₂: N, 21.4. Found: N, 21.8.

Bromobenzene Grignard Reagent with Methylene-bis-[methyldiimide]tetroxide

Into 75 ml (0.1375 mole) of bromobenzene Grignard reagent under nitrogen at 0° C was added 3.28 g (0.02 mole) of the powdered tetroxide during 30 minutes with strong gas evolution. The brownish-red system was filtered to remove a gummy mass from which, after hydrolysis, 0.50 g (15%) of the tetroxide was recovered by decomposition of the remainder with 70% nitric acid, m.m.p. 134° C. The filtered reaction mixture was hydrolyzed by 12% hydrochloric acid and the dried non-aqueous layer was distilled, finally at 130° C (20 mm) to remove 2.02 g of biphenyl. Continuation gave a distillate, b.p. 140–240° C (9 mm), which was dissolved in 4 ml of ethanol, 0.71 g, m.p. 126–130° C. This 13% yield of benzophenone phenylhydrazone was twice crystallized from ethanol, m.p. 133–133.5° C, not depressed by admixture with the authentic compound.

Pyrolysis of Methylene-bis-[methyldiimide]tetroxide

The substance decomposed smoothly when 4.92 g (0.03 mole) was heated during 2 hours at 210-220° C. After 15 minutes at 245° C the distillate was converted by means of *p*-nitrobenzoyl chloride to 1.68 g (89%) of the methyl ester. The pyrolysis residue (0.32 g, 93%) was carbon. Analysis of the evolved gas showed that 86% was nitrous oxide.

Qualitative and Quantitative Tests with Methylene-bis-[methyldiimide]tetroxide

A Barger-Rast molecular weight determination in camphor was 163, calc. 164. The substance was unaltered by treatment with acid hydrogen peroxide during 7 hours, and it did not react after 12 hours in methanol with sodium borohydride, but a vigorous reaction occurred with lithium aluminum hydride. However, no products could be isolated from the latter reaction. No reaction occurred with benzaldehyde, p-nitrobenzaldehyde, cyclohexanone, urea, but a vigorous reaction occurred with hot phenyl-hydrazine. No recognizable product was obtained. The alkaline hydrolysis of the tetroxide yielded methanol, formic acid, nitrous acid, and perhaps some hydrogen cyanide either with 30% aqueous sodium hydroxide or with sodium ethoxide.

The active hydrogen determination was carried out in the Soltys machine by the prescribed procedure (34) in isoamyl ether for 20 minutes at 100° C, but it was observed that a precipitate formed immediately upon addition of the reagent and a red solution was formed which faded upon heating. The active hydrogen was found to be 1.9 equivalent. The amount of Grignard reagent which underwent an addition reaction was only 0.1 equivalent, undoubtedly due to the insolubility of the original precipitate from which methane was evolved.

Electrical Polarization Studies

Dielectric constants and specific volumes of either benzene or (in one instance) dioxane solution were carried out as described previously (39, 40) and calculations were made by the method of Halverstadt and Kumler (41). The distortion polarization was determined either from refractive index, additive refractions, or by direct determination with the solid substance (31). Densities were determined by an air-displacement method (30) or by flotation. The results are shown in Table II.

Infrared Spectra

The spectra have been obtained with a Perkin-Elmer 21 spectrometer by Messrs. Bedard and Myers of Canadian Armament Research and Development Establishment,

698

Quebec, Que., to whom we are indebted. The samples were studied as Nujol mull (M), as solutions in carbon tetrachloride and carbon disulphide (S), or, whenever possible, as liquids (L) and these notations are made in Table I, where the principal wave numbers in the significant range are recorded.

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