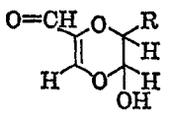
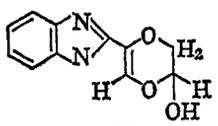
of adenosine 5′-aldehyde differs from the trialdehyde II only in that one of the methylene hydrogens is replaced by an adenosyl moiety. In this case the intermediate XII would form.



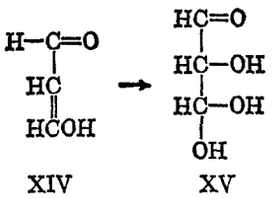
XII, R = adenosyl

Similar intermediates would form in the overoxidation of hexofuranosides[41] in which R would be an oxygen–aglycone group. The overoxidation of anhydropentose benzimidazole derivatives[42] could also occur *via* a similar intermediate (XIII) in which the imidazole ring plays the role of the aldehydic group in IV.



XIII

The overoxidation of 2-deoxy-D-*erythro*-pentose (2-deoxyribose) is also accompanied by an increase in absorbance. In this case malondialdehyde is formed and the absorbance is probably due to the enol form of the compound (XIV) which can be hydroxylated to give the hydrated hydroxymalonaldehyde (XV).



XIV XV

(41) T. G. Halsall, E. L. Hirst, and J. K. N. Jones, *J. Chem. Soc.*, 1427 (1947).

(42) C. F. Huebner, R. Lohmar, R. L. Dimler, S. Moore, and K. P. Link, *J. Biol. Chem.*, **150**, 503 (1945).

Summary

It has been shown that 2,3-dihydro-6-formyl-3-hydroxy-1,4-dioxine (IV) is an intermediate in the overoxidation of 1,4-anhydroallitol. The effect of pH on the rate of overoxidation has been explained in terms of its effect on the rate of formation and rate of oxidation of IV. It appears probable that the oxidation involves the monoanions of the oxidant and the substrate.

The overoxidation of maltose, 2-deoxy-D-*erythro*-pentose, adenosine 5′-aldehyde, anhydropentose benzimidazole derivatives, and hexofuranosides can proceed *via* analogous intermediates.

Registry No.—I, 10334-28-8; IV, 10334-29-9; sodium metaperiodate, 7790-28-5.

Photochemistry of Nitroso Compounds in Solutions. VII.[1] Photoaddition of Nitrosamines to Various Olefins

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Received December 27, 1966

The photoaddition of N-nitrosodimethylamine and N-nitrosopiperidine to various model olefins was shown to take place smoothly in the presence of an acid. The primary photoadduct was shown to be an α-*t*-aminonitrosoalkane which underwent various secondary reactions. For the nitrosoalkane derived from monosubstituted and symmetrically disubstituted olefins the secondary process was dimerization to a *trans*-nitroso dimer or tautomerization to an α-*t*-amino oxime. The nitrosoalkane derived from unsymmetrically di- or more substituted olefins readily underwent a cleavage reaction to give a ketoxime and an iminium salt. The orientation of the addition was exclusively in one direction wherein the amino moiety attached itself to the least-substituted carbon atom. Steric hindrance was shown to retard the photoaddition.

In the previous report one of us demonstrated that, in the presence of a dilute acidic medium, N-nitrosodialkylamines readily undergo a light-catalyzed addition across the carbon–carbon double bond of cyclohexene to yield α-*t*-aminocyclohexanone oximes.[2] This photoaddition to cyclohexene has been shown to be a general reaction when both alkyl groups are secondary but not tertiary.

In the meantime, two addition reactions of N-chloramine to olefins under different conditions have been reported. The first one is the addition of a chloramine through dialkylamino radical generated by a redox metal ion couple, such as Cu^{+}–Cu^{2+} or Fe^{2+}–Fe^{3+} systems.[3] The second is the addition through a dialkylaminium radical, a Hofmann–Löffler rearrangement intermediate, generated in a strongly acidic medium, *e.g.*, 4 *M* H_2SO_4–AcOH.[4] Although there exists good evidence that the intermediates involved are quite different, the limited results available now do not permit a conclusion to be drawn with regard to the nature of these two addition reactions. For the interest of practical applications, it was desirable to explore the scope and limitation of the photoaddition of the N-nitrosodialkylamines. It was hoped that such a study would furnish a clue to the probable reaction mechanism and further provide a comparison of these three addition reactions.

In order to shed some light on the nature of this photoaddition, work was undertaken to clarify the question of orientation reactivity and stereochemistry of the reaction. In this report the photoaddition of

(1) For paper VI, see Y. L. Chow and A. C. H. Lee, *Can. J. Chem.*, **45**, 311 (1967).

(2) Y. L. Chow, *Can. J. Chem.*, **43**, 2711 (1965).

(3) (a) F. Minisci and R. Galli, *Tetrahedron Letters*, 167 (1964); 3197 (1964). (b) F. Minisci and R. Galli, *Chim. Ind.* (Milan), **45**, 1400 (1963); **46**, 546 (1964).

(4) R. S. Neale, *J. Am. Chem. Soc.*, **86**, 5440 (1964); R. S. Neale, *Tetrahedron Letters*, 483 (1966).

TABLE I
ANALYSIS

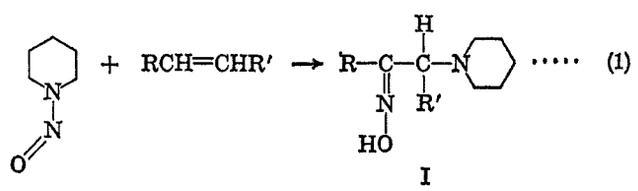
Compd	Mp, °C	Formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
syn Ia	152–154	$C_{10}H_{18}N_2O$	65.86	65.88	9.82	9.96	15.34	15.37
anti Ib	163–165	$C_{13}H_{24}N_2O$	69.66	69.60	10.43	10.78	12.36	12.49
Ib HCl[a]	218–222	$C_{13}H_{25}N_2OCl$	59.95	60.10	9.72	9.70	10.61	10.78
Ic	*b*	$C_{10}H_{20}N_2O$	65.17	65.17	10.84	10.94	15.18	15.20
syn Id	117–117.5	$C_{13}H_{18}N_2O$	71.52	71.52	7.91	8.31	12.55	12.83
syn Ie	*c*	$C_{13}H_{26}N_2O$	69.89	69.00	11.74	11.55	12.24	12.38
syn If	101–103	$C_{14}H_{18}N_2O$	72.99	73.01	7.95	7.88	12.40	12.17
anti If	171–174	$C_{14}H_{18}N_2O$	73.32		8.03		12.22	
V	101–102	$C_{20}H_{40}N_4O_2$	65.41	65.17	10.95	10.94	15.33	15.20
IIb	*d*	$C_{10}H_{20}N_2O$	65.33	65.17	10.79	10.94	15.26	15.20
IIb HCl[a]	204–205	$C_{10}H_{21}N_2OCl$	54.13	54.42	9.71	9.52	12.81	12.69

[a] *anti* configuration. [b] A liquid mixture with a *syn/anti*, 1:7. [c] Liquid. [d] A liquid mixture with *syn/anti*, 1:1.

N-nitrosopiperidine and N-nitrosodimethylamine to olefins with various degrees of substitution are described. The choice of these two nitrosamines stems from the fact that the former has been shown to undergo the photoaddition efficiently,[2] while the latter carrying primary methyl groups is expected to react with even greater efficiency.

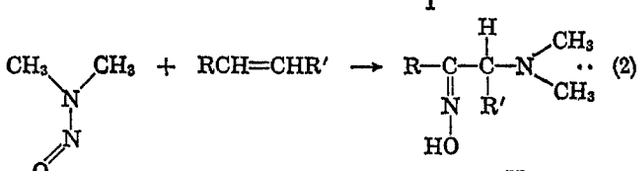
Results

The photoaddition was run with the same apparatus and followed the same procedure as described earlier.[2] The addition of either N-nitrosopiperidine or N-nitrosomethylamine to cyclopentene, cyclohexene, and *cis*-cyclooctene in 0.1–0.3 *N* methanolic hydrochloric acid solution proceeded smoothly following typical zero-order kinetics. These reactions were conveniently followed by the decrease of the nitrosamino absorption at 345 mμ which remained unchanged unless the solutions were irradiated. The products having the general formulas I and II (eq 1 and 2) were isolated as either the free bases or as the corresponding hydrochlorides, depending upon the work-up procedure. Only one



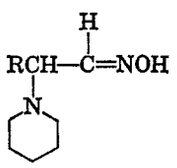
(1)

I

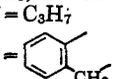


(2)

II



III

a, R=R′=$(CH_2)_3$
b, R=R′=$(CH_2)_6$
c, R=C_3H_7; R′=H
d, R=C_6H_5; R′=H
e, R=R′=C_3H_7
f, R=R′= 
g, R=R′=$(CH_2)_4$

geometric isomer of 2-piperidinocyclopentanone oxime (Ia) and 2-dimethylaminocyclohexanone oxime (IIg) were obtained for which the *syn* configuration was assigned based on the same argument advanced previously.[2] For 2-piperidinocyclooctanone oxime (Ib) and 2-dimethylaminocyclopentanone oxime (IIb), both *syn* and *anti* isomers were present in the photoadducts in which the *anti* isomers were shown to be the predominant products by the nmr spectra. While *anti* IIb and *syn* IIb could be obtained by a silicic acid chromatography, only *anti* Ib was isolated in pure state since *syn* Ib was formed in minor amounts. The structures, as well as *syn–anti* configurations,[5] were based on the elemental analysis and infrared and nmr data. The isomer which had the methylene or methine proton resonate at lower field was assigned to the *syn* configuration and *vise versa*.[6–8] The pertinent parameters of these are listed in Tables I and II.

The limited solubility of *trans*-4-octene in the reaction medium forces us to add a small amount of tetrahydrofuran (*ca.* 3%) in order to ensure a homogeneous solution. The photoaddition occurred less rapidly than usual leading to the formation of, in addition to the expected photoadduct, some piperidine hydrochloride. The crude photoadduct was resolved to *syn*- and *anti*-4-piperidino-5-octanone oxime (Ie), the configurations of which were assigned by a comparison of their physical properties.

The photoaddition of N-nitrosopiperidine to styrene, an unsymmetrically substituted olefin, led to the known[5] *syn*-α-piperidinoacetophenone oxime (*syn* Id) and *anti* Id. The presence of both isomers in the crude product was easily demonstrated by two methylene singlets (ratio 6:1) in the nmr spectrum. The *anti* compound was apparently less stable as was witnessed by a partial isomerization to *syn* Id during silicic acid chromatography. This instability is probably caused by the intervention of the nonbonded interaction between hydroxyl group and *ortho* hydrogen of the aromatic ring while the oximino moiety strives to achieve the endowed stability through conjugation. The addition product with the alternative mode of orientation (leading to III) was not detected by various types of

(5) (a) The nomenclature for *syn* and *anti* configurations follow from the arbitrary rule adapted in ref 2 and 5b. (b) H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, **46**, 936 (1963).

(6) G. J. Karabatsos, R. A. Taller, and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 2327 (1963).

(7) W. F. Trager and A. C. Huitric, *Tetrahedron Letters*, 825 (1966).

(8) H. Saito and K. Nukada, *J. Mol. Spectry.*, **18**, 1 (1965).

TABLE II[a]

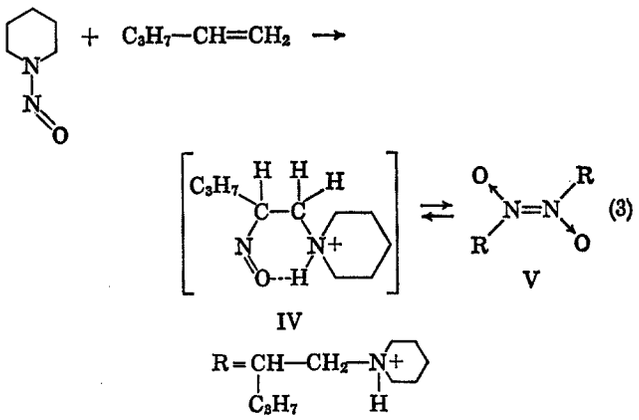
INFRARED AND NUCLEAR MAGNETIC SPECTRAL PARAMETERS

Compd	OH, cm^{-1}	Bohlman bands, cm^{-1}	C=N, cm^{-1}	900–1000-cm^{-1} region	Chemical shifts (τ), ppm CHN	Others
syn Ia	3200, 3100	2815, 2780	1660	970, 930	6.55 (T, 6)[b]	
anti Ib	3140, 3020	2800, 2740	1635	969, 921	6.91 (DD, 7.5, 4)[c]	
Ic[d]	3330, 3070	2850, 2450	1645	935, 985	6.81, 7.01	9.03 (T; 7)[e]
syn Id	3150, 3050	2815, 2775	1625	940, 977	6.26 (s)	2.35 (M)[b]
anti Id	3325, 3100	2825, 2785	1640	990, 945	6.67 (S)	2.40 (M)[f]
syn Ie	3300, 3150	2850, 2780	1650	960, 940	7.06 (T, 6)	
anti Ie	3350, 3120	2820, 2790	1645	962, 940	7.23 (T, 6.5)	
syn If	3200	2819, 2750	1612	940, 925	5.54 (DD, 8, 5)	2.30 (M)[f]
anti If	3180, 3060	2805, 2730	1595	962, 922	5.83 (DD, 8, 5.5)	1.53 (M)[f]
syn IIb	3350, 3250	2830, 2790	1656	975, 935	6.77 (T, 8)	7.69 (S[g]
anti IIb	3370, 3230	2825, 2780	1645	965, 925	7.22 (T, 7)	7.77 (S)[g]
syn IIg	3180, 3075	2830, 2780	1658	915, 979	7.34	7.76 (S)[g]

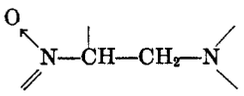
[a] The nmr spectra were taken in $CDCl_3$ unless specified otherwise and all infrared were taken in Nujol or liquid films. [b] The figures in brackets represent coupling constants. [c] The nmr was taken in a pyridine solution. [d] A liquid mixture of *syn*/*anti*, 1:7. [e] The nmr was taken in CCl_4. [f] The *ortho* proton. [g] N-methyl protons.

chromatography. A similar photoaddition to indene took place readily with the same exclusive orientation to give *syn*- and *anti*-2-piperidinoindanone oxime (If). The nmr spectra of If show that the nonequivalent methylene protons together with the methine proton form an ABX pattern. The summation of the spectra of *syn* If and *anti* If at τ 5.5–7.2 region (ABX system) corresponds well to the spectrum of the crude product at the same region indicating that the alternative mode of addition did not take place to a detectable extent. Thin layer chromatography of the crude product on alumina again shows only two spots corresponding to the *syn* If and *anti* If.

When the photoaddition of N-nitrosopiperidine to 1-pentene was followed by ultraviolet spectroscopy, the decrease of the 345-mμ absorption was complicated by a new and stronger (by a factor of 20) absorption at *ca.* 290 mμ, and simple zero-order kinetics could no longer be observed. The new peak (290 mμ) increased rapidly with a concomitant decrease at 345 mμ during the first 0.5 hr reaching the maximum shortly under these conditions. The optical density at 290 mμ decreases at a much slower rate from this time irrespective of irradiation. Interruption of the photolysis near the end point and work-up of the photolysate gave a small amount of the recovered nitrosamine, the expected photoadducts of 1-piperidino-2-pentanone oxime (Ic) and a crystalline hydrochloride. The crystalline hydrochlorides were readily converted to the non-crystalline hydrochlorides of Ic on heating in a 2-propanol solution. The corresponding free base of this crystalline hydrochloride was, however, easily liberated without causing a further transformation and could be recrystallized from pentane. The analysis and cryoscopic molecular weight determination showed this compound to be a dimer of the photoadduct and infrared showed the typical absorption for a C-nitroso dimer[9] at 1249 but with no absorption above 3100 cm^{-1}. Most of the primary and secondary C-nitroso compounds known so far have been shown to exist only as dimers, the structures of which have been established after extended investigations by various workers.[10] It has been further shown that most of the dimers possess the *trans* configuration unless a stringent



stereochemical demand forces a *cis* configuration.[9,11] The structure V was therefore assigned to 1-piperidino-2-nitrosopentane *trans* dimer. In agreement with this assignment the nmr spectrum at 100 Mc conspicuously showed the signals corresponding to the ABX system of protons of the following system in which the X



proton was further coupled to another methylene group. The methylene protons (AB portion of the ABX) were nonequivalent owing to the adjacent asymmetric carbon atom (see the Experimental Section). The methine proton was well shifted downfield (τ 4.28) possibly owing to the partial positive charge carried by the nitroso nitrogen atom.[12,13] It should be mentioned that Ic was isolated and analyzed as a *syn* and *anti* mixture (ratio 7:1). The nmr spectra of the crude product was free of signals at a field lower than τ 5.00 except for a diffused one for OH which was exchangeable with D_2O. This explicitly implied that the alternative photoadduct of type III was not formed since an aldoxime proton should resonate at the range τ 0–4.

(9) W. Lüttke, *Z. Elektrochem.*, **61**, 976 (1957).

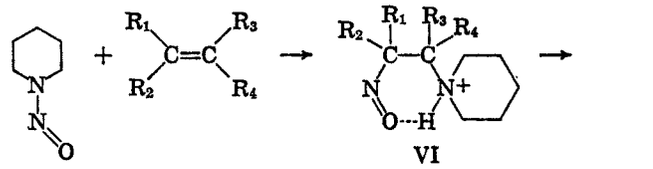
(10) For the recent review on C-nitroso compounds, see B. G. Gowenlock and W. Lüttke, *Quart. Rev.* (London), **12**, 321 (1958).

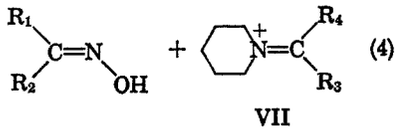
(11) J. M. Smith, *J. Chem. Soc.*, 1124 (1957).

(12) The unpublished data from this laboratory and the data in ref 13 show that the chemical shift of similar protons are generally in the region τ 4.3–4.8.

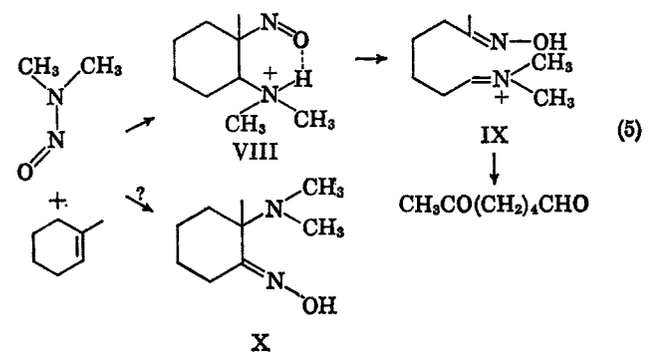
(13) M. Ohno, M. Okamoto, and K. Nukada, *Tetrahedron Letters*, 4047 (1964).

In an effort to prepare the α-*t*-nitroso derivative,[14] photoaddition was carried out on 2,3-dimethyl-2-butene (eq 4). A facile secondary reaction of the adduct (VI, $R_1 = R_2 = R_3 = R_4 = CH_3$), apparently catalyzed by an acid, took place to give acetone and acetone oxime. The photolysate was hydrolyzed and analyzed for the total yield of acetone. A similar photoaddition to α-methylstyrene, an unsymmetrically disubstituted olefin, followed exclusively the predictable orientation to give a C-nitroso intermediate (VI, $R_1 = C_6H_5$; $R_2 = CH_3$; $R_3 = R_4 = H$), which decomposes further to acetophenone oxime in better than 90% yield (eq 4). In this case, the other cleavage product was identified as dipiperidylmethane. If the same orientation holds true, the photoaddition of N-nitrosodimethylamine to 1-methylcyclohexene would yield neutral 6-ketoheptanal rather than X (eq 5). Experimentally, though





(4)



(5)

crude 6-keptopheptanal was obtained in good yield small amounts of basic products were also isolated. Except that the dimethylamino group was present in the basic products, its identity is still unknown.[15]

Discussion

In the presence of an acid, N-nitrosodialkylamines undergo a light-catalyzed decomposition for which the primary process has been demonstrated to be an elimination of hyponitrous acid monomer (HNO).[16,17] On the other hand, when the photolysis is run in a presence of cyclohexene, the addition of the nitrosamine across the carbon–carbon double bond takes place readily to form a 2-*t*-aminocyclohexanone oxime.[2] It is striking, however, that the expected products from the photoelimination of N-nitrosamines are not detected in the latter cases. Although there remain many uncertainties on the mechanisms, the remarkable difference in the products suggests that the photoaddition may follow a quite different but much faster primary process than the photoelimination. Superficially both photoreactions, however, share the same features in that (i) both light and an acid catalysis are required, (ii) the nitrogen–nitrogen bond of the nitrosamine is broken at certain stages, and (iii) the photoreactions are insensitive to a presence of oxygen.

The results indicate that N-nitrosodimethylamine and N-nitrosopiperidine generally add across a carbon–carbon double bond under the simultaneous catalysis of acid and light. Formally the mode of photoaddition can be represented as a breaking of the nitrogen–nitrogen bond at a certain stage followed by addition of nitroso and amino moieties to a carbon–carbon double bond to give a C-nitroso compound as the primary reaction product. A survey of literature shows that C-nitroso compounds may undergo various transformations under photolysis conditions namely, (i) tautomerization to oximes,[9] (ii) dimerization,[18] and (iii) light-catalyzed elimination[19] of HNO. In the present work the first two types of products were isolated but the occurrence of the last type of reaction was not detected. Further a fourth reaction pathway typical to the present C-nitroso intermediate will be discussed later.

All olefins carrying at least one hydrogen at each carbon atom of the double bond give α-*t*-amino oximes as the photoadduct attesting to the ready irreversible tautomerization of the secondary C-nitroso compound under the photolytic conditions (eq 1, 2, and 3). A reverse tautomerization, *e.g.*, oxime to C-nitroso compound, is thermodynamically not feasible and has never been observed. Alternatively, instead of undergoing a tautomerization, a C-nitroso compound can spontaneously attain an equilibrium state with a stable dimer in which the equilibrium heavily favors the dimer under ordinary conditions.[18] It should be pointed out that, while rate of dimerization is dependent on the concentration of C-nitroso compound, that of tautomerization is not. Furthermore the latter is an acid-catalyzed reaction while the former is not. In the event that the conditions are such that the dimerization is faster than the tautomerization, a photoadduct should accumulate as a dimer which should exhibit a typical ultraviolet absorption[10,18] at the 280–290-mμ region. Such a situation has been observed in the photoaddition to 1-pentene leading to the isolation of the *trans*-C-nitroso dimer, V. In the formation of Id and If spectroscopic evidence of dimer formation is not observed indicating that fast tautomerization taking place. These fast tautomerizations are to be expected in view of the migrating hydrogen being benzylic and finds a parallel in the keto–enol tautomerism of aceto acetates.[20] In some other cases, a weak, transient absorption at 280–290-mμ region has been detected.

The fourth type of reaction pathway is typical to the specific structural features associated with the present photoadduct, namely, a C-nitroso compound carrying

(14) A part of this work has been published as a communication: Y. L. Chow, *J. Am. Chem. Soc.*, **87**, 4642 (1965).

(15) The possibility that the basic product is derived from subsequent cyclization from structure IX can not be excluded at this stage.

(16) Y. L. Chow, *Can. J. Chem.*, **45**, 53 (1967); *Tetrahedron Letters*, 2333 (1964).

(17) E. M. Burgess and J. M. Lavanish, *ibid.*, 1221 (1964).

(18) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955); 1670 (1956); and the earlier papers.

(19) K. D. Anderson, C. J. Crumpler, and D. L. Hammick, *ibid.*, 1679 (1935).

(20) J. B. Conant and A. F. Thompson, Jr., *J. Am. Chem. Soc.*, **54**, 4039 (1932).

a tertiary amino group at the α position. It has been recognized that the monomer–dimer equilibrium of tertiary alkyl nitroso compounds is sensitive to changes in environment.[10,18] With an ammonium group readily available in the vicinity, the present C-nitroso intermediate is expected to assume a hydrogen-bonded monomeric form, *e.g.*, IV and VI. Since the tautomerization is blocked in the photoadduct VI, an alternative pathway will be the intramolecular proton transfer with concomitant breaking of the carbon–carbon bond as indicated in eq 4. Thus in this manner acetone (87% yield as 2,4-dinitrophenylhydrazone) was produced from 2,3-dimethyl-2-butene *via* acetone oxime and the immonium salt of acetone VII.

Orientation.—The question of the orientation is readily answered from the results of the photoaddition to styrene and indene in which the amino moiety attached itself to the less substituted carbon atom and the carbon atom farthest from the benzene ring in the double bond. The nitroso group turns up as the oximino group at the benzylic carbon atom as shown in Id and If. Thus, whatever are the factors controlling this photoaddition, superficially the amino group resembles the cationic species in an acid-catalyzed addition reaction. Be it a free-radical or an ionic pathway, a phenyl group conjugated with a double bond is known to exert an overwhelming directive effect on the orientation of an addition reaction. A better test of orientation can be provided by the photoaddition to 1-pentene where the conjugative effect of a phenyl group is absent. In this case the same orientation is observed which appears to discount the importance of an electronic effect. It is pertinent to point out that a photoexcited nitrosamine molecule is a high-energy species and therefore will be expected to be less discriminative in directing the attack. From this point of view, the directive effect shown by a mere alkyl group is indeed very remarkable, and is tentatively ascribed to the steric and inductive effects of the alkyl group working in the same direction.

For the photoaddition to α-methylstyrene, which subsequently undergoes the cleavage reaction, the orientation is predictably in one direction to give acetophenone oxime. The isolation of dipiperidylmethane substantiates the intermediacy of the methylene piperidylium salt (VII, $R_3 = R_4 = H$) and thus lends proof to the proposed cleavage pathway. The major part of the photoaddition to 1-methylcyclohexene follows the same preference of orientation and cleavage pathway to yield the expected 6-ketoheptanal. The minor product, which is recovered as the basic fraction, is tentatively assigned the structure IX arising from the alternative orientation.[15]

Stereochemistry.—Since it is obvious that a *trans*-C-nitroso dimer is isolable under controlled conditions, an investigation on the stereochemistry of the photoadduct is now possible provided that a suitably substituted olefin which also gives a *trans* dimer can be found. Although the photoaddition of either nitrosamine takes place readily with a series of cyclic olefins, the C-nitroso compounds derived from cyclohexene and *cis*-cyclooctene apparently do tautomerize much faster than dimerization leading to exclusive formation of oximes. A limited formation of the dimer from cyclopentene photoaddition was observed as witnessed by the appearance of a low peak at 295 mμ. The dimer, however, could not be isolated since the tautomerization is fairly rapid. The photoaddition to *trans*-4-octene proceeds too slowly to be useful for the purpose of preparing the dimer. The faster tautomerization for the adducts derived from these disubstituted olefins in comparison to that derived from 1-pentene is certainly due to an increased steric compression. Such compression brings the protonated amine and nitroso group closer for an efficient intramolecular proton-catalyzed tautomerization. Work is underway to find conditions in which the dimer formation is favored.

Reactivity.—From the good zero-order kinetics shown by the photoaddition reaction it is clear that the light energy is the limiting factor in promoting the addition. Accordingly, the rates of the addition of N-nitrosopiperidine as well as N-nitrosodimethylamine to cyclic olefins, styrene, and indene vary little. On the assumption that both photodecomposition of nitrosamines and photoaddition to olefins take place concurrently in the photolysis system, the reactivity of olefins should be reflected by the yield of photoadducts. Unfortunately, the yields of the photoadducts to the above olefins vary very little and give little indication of the reactivity. It is only in the case of acyclic internal olefin, *trans*-4-octene, that a decrease in the addition rate (by a factor of *ca.* 5) is noticeable and the yield of the adduct is accordingly lower. This low reactivity may be attributed to the two bulky alkyl groups disposed in the *trans* configuration hindering a bimolecular approach of the addenda. The formation of piperidine hydrochloride in this case suggests that the alternative photoreaction, *e.g.*, the light-catalyzed decomposition,[21] occurs when the photoaddition is slow. It is interesting to point out that a similar steric effect can also be observed with a hinderance associated with a nitrosamine. Thus photoaddition of N-nitroso-2-methylpiperidine[22] to styrene was shown to proceed more slowly and give poor yields of the expected adduct. With respect to the reactivities in general, it is pertinent to mention that both aminium[4] and amine radical[3] show marked enhancement in their reactivity toward a conjugated olefin while they react sluggishly with unconjugated olefins

Experimental Section

Microanalyses were performed by Dr. C. Daessle, Montreal, and by Miss D. Roberts, Microanalysis Laboratory, Chemistry Department, University of Alberta. Melting points were determined on a Fisher-Johns hot stage and were uncorrected. Infrared spectra were recorded in Nujol mull with a Perkin-Elmer Model 421 and an Unicam SP-200. Ultraviolet spectra were recorded on a Cary Model 14 and an Unicam SP-800 recording spectrophotometer. The nmr spectra were obtained with a Varian A-56-60 instrument and are reported in τ values using internal tetramethylsilane standard; coupling constant (J) are given in cycles per second (cps). Decoupling experiments were performed with a Varian HR-100 spectrometer.

Material.—The CP grade olefins were used as supplied without further purification with exceptions of styrene and indene that were distilled under a reduced pressure (14 mm) before being used. The nitrosamines were prepared according to the standard

(21) Generally, the photoelimination of HNO prevails over the light-catalyzed denitrosation in the N-nitrosopiperidine photolysis. In the present case, piperidine hydrochloride (from denitrosation) appears to predominate over 2-piperidone oxime (from photoelimination). It is not clear why the presence of *trans*-4-octene reverses the trend.

(22) Y. L. Chow and C. Colon, unpublished observation.

procedures as described previously[1] and distilled. The analytical reagent grade solvents were used without purification.

General Procedure of Photoaddition.—The general procedure as described previously was followed. A nitrosamine (*ca.* 0.05 mole), an olefin (1 to ~3 mole equiv), a reagent grade methanol (*ca.* 300 ml), and concentrated hydrochloric acid were placed in a Pyrex photolysis apparatus. In the water-jacketed inner sleeve a Hanovia ultraviolet lamp (Type 54A36, 140 w) was placed. The apparatus was externally cooled by placing in an ice bath. The solution was agitated with a magnetic stirrer and a slow stream of nitrogen. Unless specified otherwise, the photolysis was continued until the nitrosamine absorption at 350 mμ was no longer observable. At suitable intervals an aliquot portion of the photolysate was pipetted out and was properly diluted for spectroscopic measurement in the 250–400-mμ region. The decrease of the peak followed a zero-order kinetics up to 75% completion. The time required for complete photolysis was obtained by extrapolation to 0 point of the optical density. As a control experiment the 0-hr sample was kept in a dark ice box and its optical density was checked again at the end of the photoaddition. This optical density and shape of the curve were shown to be the same as the 0 hr.

For working up of the reaction mixture, the major part of the solvent was removed under vacuum at temperatures lower than 50°. In some cases, the hydrochlorides of the photoadducts crystallized out immediately and were recrystallized from a suitable solvent. In other cases, the residue was treated with cold water. The excess olefins if there were any, were removed by ether extractions. On basification of the aqueous phase the basic photoadduct was freed and was extracted if it was an oil or filtered if it was a solid. These crude photoadducts were either vacuum distilled, chromatographed, or recrystallized in order to affect purifications. Generally, a small sample was further recrystallized from a suitable solvent followed by sublimation to afford an analytical sample. The analyses are listed in Table I.

Photoaddition of N-Nitrosopiperidine. A. To Cyclopentene.—The nitroso compound (5.5 g, 48 mmoles), cyclopentene (4 g, 59 mmoles), and concentrated hydrochloric acid (4.2 ml) were photolyzed in methanol (300 ml). On photolysis a new absorption at 295 mμ appeared at the beginning which then decreased as the irradiation continued to consume the 345-mμ peak. Upon working up of the photolysate some unreacted N-nitrosopiperidine (320 mg) was isolated in the neutral portion and the free base of the photoadduct (Ia, 5.70 g) was isolated. *syn* Ia was recrystallized from methanol, mp 152–154°.

In a separate experiment the same amounts of the reactants were photolyzed in methanol (480 ml) until the 345-mμ absorption disappeared. The basic fraction (7.84 g, 89%) isolated was shown by the infrared spectroscopy to be *syn* Ia slightly contaminated by the corresponding ketone (1745 cm^{-1}).

B. To *cis*-Cyclooctene.—The nitroso compounds (5.3 g, 46.5 mmoles) *cis*-cyclooctene (10 g), and concentrated hydrochloric acid (8 ml) were photolyzed in methanol (280 ml). On evaporation of methanol to *ca.* 40 ml, the hydrochloride of the photoadduct (*anti*-Ib) crystallized out (10.3 g) and was recrystallized from ethanol, mp 218–222°. The free base was obtained by neutralization of the salt with a potassium carbonate solution and recrystallized from methanol, mp 163–165°. A small basic fraction obtained after removal of *anti* Ib salt was shown by nmr spectrum ($CDCl_3$) to contain mostly *anti* Ib (τ 6.72) and a barely visible triplet at τ 7.21. The yield was 94%.

C. To 1-Pentene.—The nitroso compound (6.7 g, 59 mmoles), 1-pentene (15 g), and concentrated hydrochloric acid (8.5 ml) were photolyzed in methanol (280 ml). After a 1-hr photolysis, a new intense peak appeared at 290 mμ which completely swamped the 340-mμ absorption of the nitrosamine. The photolysis was continued for 2-hr. After evaporation and trituration of the residue with a small amount of acetone a crystalline hydrochloride V (8.2 g) was obtained. The mother liquor, after removal of this salt, was worked up to afford the crude base of the photoadduct Ic (3.68 g) which consisted of *syn* and *anti* isomers in a ratio of 1.9:1.3 as shown by the corresponding nmr signals (for CH_2 next to the amino group) at τ 6.74 and 7.03. This crude product was also slightly contaminated by the corresponding ketone as shown by the infrared absorption at 1710 cm^{-1}. On distillation under 0.2 mm the ketone distilled as a forerun followed by a fraction of *syn* Ic and *anti* Ic mixture distilled at 84–87°. The latter mixture was sublimed at 82° (bath temperature) (0.05 mm) to give a resin with an *anti*/*syn* ratio of 7:1. The combined yield was 97%.

An attempt to recrystallize the crystalline hydrochloride of V from 2-propanol caused a transformation to syrupy hydrochloride of Ic which liberated a mixture of *syn* and *anti* Ic on treatment with an aqueous potassium carbonate solution. The free base (V) was liberated by a treatment with potassium carbonate in an aqueous solution and recrystallized from pentene: mp 101–102°, infrared absorption at 3010, 2800, 2780, 1455, 1249, and 1185 cm^{-1}; the nmr spectrum in CCl_4 at 100 Mc showed signals at τ 4.28 (Ha), 7.20 (Hb), and 7.91 (Hc) with the coupling constants J_{ab} = 9.5 cps, J_{bc} = 12.5 cps, J_{ac} = 4 cps, and τ 9.18 (3 H, triplet, J = 5 cps). The cryoscopic molecular weight (in $CHCl_3$) was found to be 373.6 (calcd for $C_{20}H_{40}N_4O_2$, 368.6).

To Styrene.—The nitroso compound (5.8 g, 51 mmoles), freshly distilled styrene (35 ml), and concentrated hydrochloric acid (5 ml) were photolyzed in methanol (270 ml). About 80% of the 345-mμ absorption disappeared in 1 hr and the photolysis was stopped in 1.5 hr. The excess styrene was extracted as the neutral fraction and distilled. The amount of the nondistillable, polymeric substance remaining in the flask (50 mg) was about the same as that of a control experiment which was run in an absence of N-nitrosopiperidine and without irradiation. The crude free base (11.05 g, 95%) was a solid showing the CH_2N proton singlets (CCl_4) at τ 6.37 and 6.70 with a ratio of 6:1. Recrystallization from methanol and then from cyclohexane gave *syn* Id: 117–117.5° (lit.[23] mp 117–118°); the nmr shows a signal at τ 6.26 (2 H, singlet). The crystals recovered from the mother liquor is a mixture of *syn* and *anti* Id as shown by the nmr spectrum. Alumina chromatography of the residue from the mother liquor gave *syn* Id and then *anti* Id (less than 10% of the crude) by chloroform elution. When the *anti* Id (110 mg) was rechromatographed on a silicic acid column, *syn* Id (24 mg) and *anti* Id (40 mg) were obtained. *anti* Id was recrystallized to give white crystals, mp 133–134° (lit.[23] mp 133–135°).

To *trans*-4-Octene.—The nitroso compound (3.0 g, 26 mmoles), *trans*-4-octene (4.7 g), and concentrated hydrochloric acid (2.2 ml) were photolyzed in methanol (280 ml) containing tetrahydrofuran (10 ml) for 1.5 hr. The residue from partial evaporation of the solvents was triturated with acetone to give piperidine hydrochloride (450 mg). Extraction of the acidic solution with ether gave a fraction (400 mg) which was not investigated. The free base of the photoadduct (3.2 g, 53.5%) contained a trace of the corresponding ketone as could be seen from the infrared spectrum at 1710 cm^{-1}. This peak disappeared on treatment with hydroxylamine hydrochloride and sodium acetate. A part of this free base (1 g) was chromatographed on a basic alumina (30 g) column. Elution with benzene gave *syn* Ie (700 mg) as an oil which showed only one spot on a silica gel tlc plate and was sublimed for an analysis. Continued elution with $CHCl_3$–10% methanol gave a fraction containing *anti* Ie (97 mg) which showed the infrared spectrum to be very similar to the *syn* Ie except for the region at 900–1000 cm^{-1} and a slight shift of other peaks.

To Indene.—The nitroso compound (5.5 g, 48 mmoles), indene (13.2 g), and concentrated hydrochloric acid (5 ml) were photolyzed in methanol (280 ml) for 3 hr. The crude free baes of the photoadduct (10.35 g, 93%) shows nmr signals at τ 1.49 and 2.25 with the ratio 4:6. By fractional recrystallization from ether, the crude product was separated to *syn* and *anti* If fractions. The fraction corresponding to *anti* If was recrystallized from ether, mp 171–174°, and *syn* If was recrystallized from cyclohexane, mp 101–103°. While the former could not be sublimed at 90° (0.3 mm) dec, the latter was easily sublimed under the same condition. *anti* If exhibited the nmr signals at τ 5.83 (1 H) and 6.78 (2 H) (for ABX system of methine and methylene protons), 1.53 (1 H, *ortho* proton) and −0.02 (1 H, hydroxyl). *syn* If showed the corresponding signals at τ 5.54 and 6.94 (ABX system) and 2.30 and −2.64.

To 2,3-Dimethyl-2-butane.—The nitrosamine (6.21 g), 2,3-dimethyl-2-butene (10 ml), and concentrated hydrochloric acid (8 ml) were photolyzed in methanol (280 ml). The photolysate was divided in two equal portions (165 ml).

To the first portion water (20 ml) was added and distilled to collect 150 ml of the distillate. To the distillate (20 ml) the calculated amount of Brady's reagent was added to give a yellow precipitate. The precipitate was recrystallized once from methanol to give acetone 2,4-dinitrophenylhydrazone (1.512 g), mp and mmp 124–126°.

(23) H. P. Fischer and C. A. Grob, *Helv. Chem. Acta*, **45**, 2528 (1962).

The second portion was evaporated under vacuum to give a residue which was triturated with ether to give crystalline piperidine hydrochloride (800 mg), mp 221–227°. The ether solution was evaporated and the residue (875 mg) was sublimed three times to give acetone oxime, mp and mmp 56–58°.

To α-Methylstyrene.—The nitrosamine (5.76 g), α-methylstyrene (6.31 g), and concentrated hydrochloric acid (8 ml) were photolyzed in methanol (450 ml). The photolysate was evaporated under vacuum and then the residue was diluted with water (50 ml). The neutral and the basic fractions were extracted with ether and were worked up in an usual manner. The residue from the neutral extraction gave acetophenone oxime on crystallization from Skellysolve B, mp and mmp 56–58° (3.3 g). The mother liquor was treated with hydroxylamine hydrochloride (1 g) and sodium acetate (2 g) in ethanol to give an additional amount of the oxime (1.6 g). The total yield was 91%.

The basic extract (2.92 g) was distilled at 48–50° (0.5 mm), the infrared and nmr spectra of which were found to be superimposable with dipiperidylmethane prepared according to Knoevenagel's method.[24]

Photoaddition of N-Nitrosodimethylamine. To Cyclohexene.—The nitroso compound (7.2 g, 97.5 mmoles), cyclohexene (16.4 g, 0.2 mole), and concentrated hydrochloric acid (12 ml) were photolyzed in methanol (480 ml). The crude free base of photoadduct IIg (13.10 g, 85%) showed an infrared absorption at 1705 cm^{-1} which disappeared on oximation with hydroxylamine hydrochloride and sodium acetate in methanol. Purification was done by recrystallization from cyclohexane and finally by sublimation, mp 111–113° (lit.[25] mp 120°).

To *cis*-Cyclooctene.—The nitroso compound (3.7 g, 50 mmoles), the cyclooctene (11 g, 100 mmoles), and concentrated hydrochloric acid (8.5 ml) were photolyzed in ethanol (500 ml) for 2.5 hr. On evaporation to a small volume, the hydrochloride of the photoadduct IIb crystallized out (5.81 g) and was recrystallized from a methanol–acetone mixture, mp 204–205°. This salt was dissolved in water and was neutralized with K_2CO_3 solution to give *anti* IIb, mp 84–85°. An additional amount of the free base (3.92 g, the combined yield 97%) was isolated as an oil and was sublimed three times for analysis. The nmr spectrum of the sublimed material as well as that of the crude product, shows two methyl signals of nearly the same intensity at τ 7.77 and 7.69 indicating this is a mixture of *syn* and *anti* Ib. Chromatography of this fraction on a silicic acid column gave the *syn* isomer as the first compound to be eluted, mp 71–73°. Continuing elution gave a mixture of the isomers and then the *anti* isomer.

To 1-Methylcyclohexene.—The nitrosamine (3.74 g), 1-methylcyclohexene (5 g), and concentrated hydrochloric acid (10 ml) were photolyzed in a tetrahydrofaran (230 ml)–water (80 ml) mixture. The photolysate was set aside at room temperature overnight and evaporated under vacuum. The neutral and the basic fractions were extracted with ether and were worked up as usual. Various efforts to purify the basic fraction (746 mg) were not successful. The neutral fraction (3.85 g) was distilled at 103–105° (13 mm) to give a liquid (3.59 g) with infrared peaks at 2730 and 1710 cm^{-1} and nmr signals at τ 0.25 (1 H, triplet, J = 1 cps) 7.56 (4 H, two triplets), and 7.91 (3 H, singlet). The bishydrazone of this liquid was prepared and recrystallized from an ethyl acetate–ethanol mixture, mp 196–198°.

Anal. Calcd for $C_{19}H_{20}N_8O_3$: N, 22.94. Found: N, 23.09.

Registry No.—*syn* Ia, 10591-86-3; *anti* Ib, 10591-87-4; hydrochloride of *anti* Ib, 10591-88-5; *syn* Ic, 10591-89-6; *anti* Ic, 10591-90-9; *syn* Id, 10591-91-0; *anti* Id, 10591-92-1; *syn* Ie, 10591-93-2; *anti* Ie, 10591-94-3; *syn* If, 10591-95-4; *anti* If, 10591-96-5; *syn* IIb, 10591-97-6; *anti* IIb, 10591-98-7; hydrochloride of *anti* IIb, 10591-99-8; *syn* IIg, 10592-00-4; V, 10592-01-5; bishydrazone of 6-ketoheptanal, 10592-02-6.

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Photochemical Reactions with Phenols. I. The Photochemical Reaction of Benzophenone with 2,6-Di-*t*-butylphenol

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Benzophenone has been found to react photochemically with 2,6-di-*t*-butylphenol in the presence of a catalytic amount of mineral acid to yield 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane. A multistep mechanism of this new reaction has been established by either trapping or isolating all probable intermediates.

Among the representatives of light-sensitive, phenyl-substituted carbonyl compounds, benzophenone has received considerable attention. Although its photochemical transformation into benzpinacol had been observed by Ciamician and Silber[1] as early as 1900, during recent years a deeper insight into the primary steps of the photochemical reactions of benzophenone has been gained.[2–5] The mechanism of the photochemical pinacolization[6–10] as well as the scope and limitation of triplet energy transfer reactions[11–13] of benzophenone are now fairly well understood, and new reactions are sometimes predictable.

In the course of a study on the oxidation of phenols[14] the photochemical reaction of benzophenone with 2,6-di-*t*-butylphenol has been investigated since it appeared interesting and worthwhile to apply photoexcited benzophenone as a novel oxidizing agent. This paper describes a new photochemical reaction of benzophenone found in the course of this investigation.

Results

Irradiation of a methanol solution of benzophenone (I) and 2,6-di-*t*-butylphenol (II) containing a catalytic

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