109. *The Photochemistry of Some Aliphatic Nitroso-compounds.*

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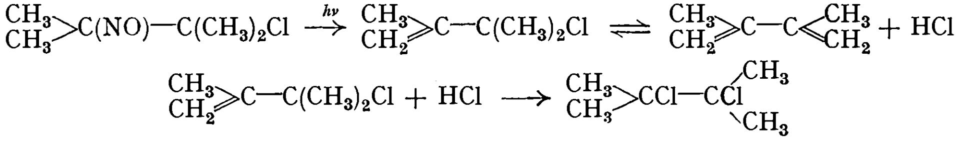
In a previous communication (J., 1935, 1679) an account has been given of the photolysis of two aliphatic nitroso-compounds, nitroso*iso*propylacetone, and β-nitroso-βε-dimethylhexane, which are decomposed in benzene solution by red light with unit quantum efficiency into olefins by the elimination of the radical NOH. We have now investigated the photochemistry in solution of the following chloro- and nitro-nitroso-compounds : tetramethylethylene nitrosochloride, $CMe_2(NO)\cdot CMe_2Cl$, 1-chloro-1-nitroso*cyclo*hexane, β-chloro-β-nitroso-γγ-dimethylbutane, $CH_3\cdot CCl(NO)\cdot CMe_3$, and β-nitro-β-nitrosopropane. Schmidt (*Ber.*, 1904, **37**, 547) observed that tetramethylethylene nitrosobromide decomposes in light to give tetramethylethylene dibromide and nitric oxide. This nitroso-compound is, however, also thermally unstable, and therefore inconvenient for quantitative photochemical investigation. The corresponding nitrosochloride is, on the other hand, stable in the dark, and is decomposed in solution by red light with a quantum efficiency of about unity to give mainly tetramethylethylene dichloride, nitrogen, and nitrous acid, together with tarry material, small amounts of olefin, and hydrochloric acid. These facts make it very probable that the primary photochemical process is, as in the cases previously described, the elimination of the radical NOH and the formation of olefin, the observed production of the dichloro-derivative resulting from a series of subsequent reactions :



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C(NO)-C(CH_3)_2Cl \xrightarrow{h\nu} \begin{matrix}CH_3\\CH_2\end{matrix}\!\geqslant C-C(CH_3)_2Cl \rightleftharpoons \begin{matrix}CH_3\\CH_2\end{matrix}\!\geqslant C-C\leqslant\!\begin{matrix}CH_3\\CH_2\end{matrix} + HCl$$

$$\begin{matrix}CH_3\\CH_2\end{matrix}\!\geqslant C-C(CH_3)_2Cl + HCl \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CCl-CCl\!\begin{matrix}\diagup CH_3\\ \\ \diagdown CH_3\end{matrix}$$

Most of the dimethylbutadiene is probably to be found in the gummy, intractable material.

The rate of photolysis of tetramethylethylene nitrosochloride was unaffected when the air in contact with the solutions was replaced by nitrogen or oxygen. The other nitroso-compounds investigated behaved differently. In the dark they were stable in the presence of oxygen, but on illumination in various solvents they underwent photo-oxidation with low quantum efficiencies to the corresponding nitro-compounds.

EXPERIMENTAL.

Preparation of Materials.—Tetramethylethylene nitrosochloride was prepared as described by Thiele (*Ber.*, 1894, **27**, 455); m. p. 121°.

1-Chloro-1-nitroso*cyclo*hexane has been prepared by Rheinboldt (*Annalen*, 1927, **455**, 300) by the action of nitrosyl chloride on *cyclo*hexanoneoxime. The following preparation is more convenient: 10 g. of *cyclo*hexanoneoxime were dissolved in dilute hydrochloric acid and cooled in ice. A fairly rapid stream of chlorine was passed through the solution until no more gas was absorbed. The blue oil that separated was taken up in ether, and washed with sodium bicarbonate solution and with water. After drying with anhydrous sodium sulphate, the ether was removed; the nitroso-compound distilled under diminished pressure as a purple oil with a very unpleasant smell, b. p. 58—59°/13 mm.

β-Chloro-β-nitroso-γγ-dimethylbutane, prepared from pinacolinoxime by a process exactly similar to that described above for chloronitroso*cyclo*hexane, formed very volatile, bright blue, diamond-shaped crystals, m. p. 119° (Rheinboldt, *loc. cit.*).

β-Nitro-β-nitrosopropane was prepared by a modification of Schmidt's method (*Ber.*, 1900, **33**, 875): 3·5 g. of acetoneoxime in 100 c.c. of ether were added to 10 g. of sodium nitrite in 50 c.c. of water, and the whole cooled in a freezing mixture. 24 G. of a 30% (by weight) solution of sulphuric acid in water were run in slowly with shaking, so that the ψ-nitrole was taken up in the ethereal layer as soon as it was produced. The ethereal solution was washed and dried as for 1-chloro-1-nitroso*cyclo*hexane, and finally distilled with a short fractionating column (owing to the volatility of the nitroso-compound) until colourless crystals appeared; m. p., after washing with cold dry ether, 76° (cf. Schmidt, *loc. cit.*).

Tetramethylethylene nitrosobromide and α-chloro-α-nitrosoethylbenzene were also prepared by analogous methods, but owing to their thermal instability their photo-kinetics were not investigated. It was found possible, however, by working rapidly to determine their absorption spectra in solution.

Molecular Weights.—The molecular weight of each nitroso-compound was determined cryoscopically in benzene and found either to be unimolecular (blue solids) or to diminish, after various lengths of time, in the way characteristic of aliphatic nitroso-compounds (colourless in the solid state) to a steady value corresponding to the unimolecular form. We quote one example:

0·1500 G. of β-nitro-β-nitrosopropane ($C_3H_6O_3N_2$ = 118) in 15·495 g. of benzene.

Time	35 mins.	115 mins.	15 hours
Depression of f. p.	0·340°	0·408°	0·434°
M	147·3	122·8	115·4

Absorption Spectra.—Preliminary experiments with all the nitroso-compounds investigated except tetramethylethylene nitrosobromide and α-chloro-α-nitrosoethylbenzene showed that Beer's law was obeyed in each of the solvents used in the photokinetic experiments. Colour densities D were determined in a 2-cm. absorption tube, with benzene solutions that had been allowed, in the cases of the thermally stable compounds, to stand overnight to ensure complete dissociation to the unimolecular forms. Data are in Table I. The extinction coefficient ε is defined by the relation $I_{\text{transmitted}}/I_{\text{incident}} = 10^{-\varepsilon cl} = 10^{-D}$; c is concentration in g.-mols./l. in a tube of length l cm.

Photokinetics.—*Apparatus.* The optical system used directed a parallel beam of light (diam., 2·7 cm.) from a 1500-watt filament lamp into the photo-cell (diam. 5·5 cm., thickness 1·0 cm., capacity about 25 c.c.). The voltage across the filament was maintained constant, and the radiation from the lamp showed no appreciable change, as measured with a thermopile, throughout the series of experiments. Owing to the fact that no colour filters are known that will transmit even approximately monochromatic light at wave-lengths within the range of those absorbed by the nitroso-compounds investigated, the only filter used was one to eliminate infra-red radiation.*

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* The filter solution contained 18 g. of $NiCl_2,6H_2O$, 50 g. of $FeSO_4,(NH_4)_2SO_4,6H_2O$, 6 c.c. of concentrated hydrochloric acid, and 3 c.c. of concentrated sulphuric acid per litre.

TABLE I.

Tetramethylethylene nitrosochloride.

λ	7500	7400	7300	7200	7100	7000	6900	6800	6700
ε	2·67	5·25	7·89	11·03	14·71	17·65	17·94	17·35	15·64
λ	6600	6500	6400	6300	6200	6100	6000	5800	5500
ε	12·75	10·30	8·68	7·59	6·45	5·15	4·01	2·45	1·03

$\epsilon_{\text{max.}} = 17{\cdot}94$ at 6900 A.

1-*Chloro*-1-*nitroso*cyclo*hexane.*

λ	7500	7400	7300	7200	7100	7000	6900	6800	6700	6600
ε	0·60	0·99	1·44	2·32	3·78	5·87	8·15	10·77	14·53	17·27
λ	6500	6400	6300	6200	6100	6000	5900	5800	5700	5600
ε	17·60	15·93	12·73	10·70	9·10	6·40	4·29	2·73	1·27	0·67

$\epsilon_{\text{max.}} = 17{\cdot}87$ at 6550 A.

β-*Chloro*-β-*nitroso*-γγ-*dimethylbutane.*

λ	7400	7300	7200	7100	7000	6900	6800	6700
ε	1·50	2·01	3·31	4·85	7·15	10·51	14·63	17·10
λ	6600	6500	6400	6300	6200	6100	6000	
ε	16·18	13·38	10·51	9·57	8·35	7·29	5·83	

$\epsilon_{\text{max.}} = 17{\cdot}10$ at 6700 A.

β-*Nitro*-β-*nitrosopropane.*

λ	7500	7400	7300	7200	7100	6900	6800	6700	6600
ε	0·02	0·58	1·12	1·60	3·47	6·52	12·41	17·31	19·92
λ	6550	6500	6400	6300	6200	6100	6000	5900	5500
ε	21·29	21·04	18·39	16·67	14·42	12·43	10·03	8·60	3·69

$\epsilon_{\text{max.}} = 21{\cdot}29$ at 6550 A.

Tetramethylethylene nitrosobromide.

λ	7500	7400	7300	7200	7100	7000
ε	1·15	4·26	6·71	11·43	15·14	17·11
λ	6900	6800	6700	6500	6400	6000
ε	17·76	16·16	12·88	8·57	5·66	2·58

$\epsilon_{\text{max.}} = 17{\cdot}76$ at 6900 A.

α-*Chloro*-α-*nitrosoethylbenzene.*

λ	7500	7400	7300	7200	7100	7000	6900	6800	6700
ε	0·44	0·78	1·23	1·60	2·48	3·66	4·94	8·42	11·77
λ	6500	6400	6300	6200	6100	6000	5900	5700	5500
ε	17·02	16·34	14·38	11·83	9·23	9·31	7·33	5·22	2·74

$\epsilon_{\text{max.}} = 17{\cdot}02$ at 6500 A.

The photo-cell contained a small piece of soft iron enclosed in glass, and was stirred by an electromagnetic device.

Solutions of the nitroso-compounds were made up in the various solvents so that their colour densities at the maximum of absorption were about 2, for at such concentrations the fraction of light absorbed is nearly 100% and changes only slowly with concentration. All solutions were kept in the dark for a time sufficient to ensure that dissociation into the unimolecular form was complete. The rate of disappearance of the blue nitroso-molecules when irradiated was followed by measurements of colour densities at some convenient wave-length with the Hilger–Nutting spectrophotometer.

In each case the relation between rate of photolysis and light intensity was determined directly by the interposition of a metal gauze in the irradiating beam of light, the ratio of light transmitted to that incident upon it being determined with a thermopile.

Lastly, the quantum efficiencies of the photochemical processes were found from a comparison of the mean amount of energy absorbed per minute by a solution as measured with the thermopile, and the number of g.-mols. of nitroso-compound destroyed per minute. Owing to the fact that all the nitroso-compounds investigated were found to obey Beer's law, the latter rate is given by $k = n\left(\frac{D_0 - D_1}{D_0}\right)\frac{1}{\partial T}$, where n = number of g.-mols. of nitroso-compound initially present in the photo-cell, D_0 is the initial colour density, and D_1 that after an interval of T

minutes. In all cases the mean value of $(D_0 - D_1)/\partial T$ was taken as that given by the slope of the straight-line plot of colour density against time.

We give our data for the photolysis of tetramethylethylene nitrosochloride in contact with air in some detail in order to indicate the kind of concordance attained, the number of measurements made, etc., in all our experiments, the results of which are summarised in Table II.

Tetramethylethylene nitrosochloride.

c = 0·5355 g. in 19·48 g. of benzene.

Time (mins.)	0	15	25	40	55
(i) D_{6700}	2·21	2·11	2·04	1·955	1·865
(ii) D_{6500}	1·540	1·465	1·420	1·363	1·310

These data give satisfactory plots of D against T, from which

$$\left.\begin{array}{l}\text{rate (i)} = 1{\cdot}02 \times 10^{-5}\ \text{g.-mol./min.}\\ \text{rate (ii)} = 0{\cdot}97 \times 10^{-5}\ \ \text{,,}\end{array}\right\}\text{mean } 1{\cdot}00 \times 10^{-5}\ \text{g.-mol./min.}$$

A piece of metal gauze was now interposed between the light source and the photo cell.

0·3832 G. of nitroso-compound in 18·90 g. of benzene.

Time (mins.)	0	30	60	90	120
D_{6700}	1·714	1·631	1·555	1·468	1·385

From the plot, which is a straight line, of D against T, the rate of photodecomposition is 0·41 × 10^{-5} g.-mol./min.; the ratio of transmitted to incident light, found with the thermopile, was 0·41. The rate of photolysis is thus proportional to the first power of the light intensity.

Quantum efficiency. Measurements with the thermopile showed that the mean absorption of energy during the run referred to above (no gauze present) was 0·391 cal./min., which leads to a quantum efficiency of very nearly unity (1·04) on the assumption that the mean frequency of the absorbed radiation is that of the wave-length at maximum absorption (6900 A.).

TABLE II.

Quantum efficiencies.

	Solvent.			
Substance.	C_6H_6.	$CHCl_3$.	MeOH.	EtOH.
Tetramethylethylene nitrosochloride	1·04	0·84	1·94	1·87
β-Chloro-β-nitroso-γγ-dimethylbutane	0·91	0·93	1·75	1·56
Chloronitroso*cyclo*hexane	0·81	—	2·42	2·17
β-Nitro-β-nitrosopropane	0·82	0·85	—	—

The above data show that the photolysis in contact with air of the four nitroso-compounds resembles quantitatively that of the nitroso-derivatives previously investigated (*loc. cit.*) in that the quantum efficiencies are in the neighbourhood of unity. The solvent influence which can cause a 2—3-fold variation in the apparent quantum efficiency is of the type already well known (Moelwyn-Hughes, " Kinetics of Reactions in Solution," pp. 71, 155).

Photo-oxidation.—The effect of oxygen on the photolysis of the nitroso-compounds was investigated by making successive determinations of the velocity of photo-reaction at constant light intensity with the solution in contact with nitrogen, air, or oxygen. The results are in Table III. Owing to the high volatility of the nitroso-compounds, it was found impossible effectively to " boil out " the solutions in contact with pure nitrogen or oxygen. The space above the solutions was therefore swept out as thoroughly as possible with these gases.

TABLE III.

Rate of photo-reaction at constant illumination (g.-mols./min. × 10^{-5}).

Substance.	Solvent.	Nitrogen.	Air.	Oxygen.
Tetramethylethylene nitrosochloride	C_6H_6	1·08	1·04	1·06
	MeOH	2·41	2·41	2·57
β-Chloro-β-nitroso-γγ-dimethylbutane	C_6H_6	$<0{\cdot}2$	0·87	1·71
	MeOH	0·81	1·67	2·41
Chloronitroso*cyclo*hexane	MeOH	2·22	3·25	—
β-Nitro-β-nitrosopropane	C_6H_6	$<0{\cdot}3$	0·82	0·89

The above figures show that the photolysis of tetramethylethylene nitrosochloride is unaffected by the presence or absence of oxygen. In the three other cases, however, the results indicate that a photo-oxidation of some kind occurs; an indication as to the nature of this oxidation is given by an examination of the products of the photo-reaction.

Products of the Photo-reactions.—Tetramethylethylene nitrosochloride. Benzene solutions, illuminated in either presence or absence of air, evolved a gas, identified as nitrogen, and ultimately became colourless. An aqueous extract of the solution was found to contain nitrous acid and traces of hydrochloric acid. The benzene was found to contain tetramethylethylene dichloride, $CMe_2Cl\cdot CMe_2Cl$, m. p. and mixed m. p. 160°. An intractable gummy material, together with some unsaturated substance (reaction with bromine), was also present.

β-Chloro-β-nitroso-γγ-dimethylbutane. Solutions in benzene or ethyl or methyl alcohol gave, on illumination in contact with air, the corresponding nitro-compound, m. p. and mixed m. p. 166°. In absence of air, very little photolysis occurred, even after prolonged irradiation.

*1-Chloro-1-nitroso*cyclo*hexane.* The illumination of a benzene solution of this substance resulted in the separation of a gummy material (this fact prevented the measurement of photokinetics in benzene solution). Separation did not occur in alcoholic solution, from which on dilution with water an oil separated. This, after drying in ether, distilled at 90°/13 mm.; this b. p. was unaffected by the addition of authentic chloronitro*cyclo*hexane. The main reaction is thus an oxidation of the nitroso- to the nitro-group. Traces of nitrous acid and hydrochloric acid indicated that the photo-oxidation is not the only reaction that occurs. This was confirmed by the exposure of a solution in ether to light, air being excluded. The nitroso-compound was ultimately transformed into a brown, insoluble, gummy material, with small quantities of nitrous and hydrochloric acids. No gaseous products were observed.

β-Nitro-β-nitrosopropane. Photo-oxidation in benzene yielded mainly ββ-dinitropropane (m. p. and mixed m. p. 53°). Photolysis occurred to some extent in absence of air, nitrogen being evolved; a satisfactory isolation of other products has, however, not yet been achieved.

SUMMARY AND OBSERVATIONS.

The aliphatic nitroso-compounds studied in the course of this and of the previous investigation (Anderson, Crumpler, and Hammick, J., 1935, 1679) resemble one another very closely in the way in which their solutions absorb light. The nearly symmetrical absorption curves are very similar in shape and are very little affected by change of solvent. Values for the extinction coefficients at the maximum of absorption in benzene are collected below, and show how little considerable variation in molecular weight and structure affects absorptive power.

Substance.	ε.	Substance.	ε.
Nitroso*iso*propylacetone	24·3	β-Nitroso-βε-dimethylhexane	20·0
Tetramethylethylene nitrosochloride	17·9	1-Chloro-1-nitroso*cyclo*hexane	17·9
Tetramethylethylene nitrosobromide	17·7	β-Nitro-β-nitrosopropane	17·1
β-Chloro-β-nitroso-γγ-dimethylbutane	17·1	α-Chloro-α-nitrosoethylbenzene	17·0

Although the molecules of these nitroso-compounds can all absorb very nearly the same amount of light energy by means of the nitroso-group, however, it is now clear that the activated molecule can behave in different ways depending on its structure and composition. First, we have the behaviour of nitroso*iso*propylacetone, β-nitroso-βε-dimethylhexane and, if our interpretation of its photochemistry is accepted, tetramethylethylene nitrosochloride; these substances on the absorption of 1 quantum of light energy eliminate the radical NOH in either the presence or absence of oxygen. Secondly, it appears from the examples so far examined that, if the carbon atom to which the nitroso-group is attached is also linked to an atom other than carbon (halogen or the nitro-group), then in the presence of oxygen a light-catalysed oxidation occurs with roughly unit quantum efficiency. In the absence of oxygen, these nitroso-compounds undergo photochemical decomposition to a greater or less extent. β-Chloro-β-nitroso-γγ-dimethylbutane and β-nitro-β-nitrosopropane appear slowly to eliminate NOH as in the case of the non-photo-oxidisable compounds. 1-Chloro-1-nitroso*cyclo*hexane undergoes a comparatively rapid photo-reaction that does not involve oxygen; practically no gas is evolved in the course of its transformation into the intractable material which is the only product that we have so far been able to isolate.

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