108. *The Photolysis of Some Chloronitroso-compounds.*

By Stotherd Mitchell, Konrad Schwarzwald, and George K. Simpson.

The method described by Mitchell and Cameron (J., 1938, 1964) for measuring quantum efficiencies (γ) with red light has been improved and applied to the photolysis (in methyl alcohol and in the absence of oxygen) of γ-chloro-γ-nitrosovaleric acid (I) and β-chloro-β-nitroso-αδ-diphenylbutane (II). Some data are also included for 1-chloro-1-nitroso*cyclo*hexane (III) and β-chloro-β-nitroso-γγ-dimethylbutane (IV) previously examined by Hammick and Lister (J., 1937, 489).

When the wave-length of the light coincided with that of maximum absorption, we found $\gamma \gtrsim 1$ for (I) and (III) but $\gamma < 1$ for (II) and (IV). At shorter wave-lengths, however, γ became $\gtrsim 1$ for (II) and (IV) also. In all cases, hydrogen chloride was split off. The energy requirements for its elimination are discussed.

Rheinboldt and Dewald (*Annalen*, 1927, **455**, 300) prepared a number of chloronitroso-compounds and found that, when dissolved in organic solvents and exposed to light and air, they were oxidised to the corresponding nitro-compounds. These authors do not appear to have noticed that photolysis can take place in the absence of oxygen. Mitchell and Carson (J., 1936, 1005) obtained a mixture of β-chloro-β-nitroso- and γ-chloro-γ-nitroso-hexane by the photochemical action of nitrosyl chloride on *n*-hexane. A solution of this mixture in methyl alcohol gradually lost its blue colour when exposed to red light in sealed tubes, oximes and hydrogen chloride being produced. Anderson, Crumpler, and Hammick (J., 1935, 1679) and Hammick and Lister (J., 1937, 489) investigated the action of light on several substances containing the nitroso-group. Measurements of the quantum efficiencies of 1-chloro-1-nitroso*cyclo*hexane (III) and of β-chloro-β-nitroso-γγ-dimethylbutane (IV) are included in the later communication. With methyl alcohol as solvent, the values 2·41 and 1·74 were obtained for these two compounds, respectively. Unfortunately, steps were not taken to exclude oxygen from the reaction vessels when these measurements were made, and additional experiments showed that photochemical action takes place (but at a reduced rate) when no oxygen is present. Mitchell and Cameron (J., 1938, 1964) studied the photolysis of β-chloro-β-nitrosobutane in the absence of oxygen, and found that in methyl-alcoholic solution the quantum efficiency was 1·2. The products were examined and the reaction mechanism was discussed.

We are interested in chloronitroso-compounds because some of them appear to be suitable for asymmetric photochemical experiments, and we have now prepared two new ones, *viz.*, *γ-chloro-γ-nitrosovaleric acid* (I) and *β-chloro-β-nitroso-αδ-diphenylbutane* (II). These substances are both blue solids which dissolve in organic solvents to give simple molecules. We have investigated their products of photolysis, and made a number of quantum efficiency measurements using methyl alcohol as solvent. No dark reaction was detected in any of the experiments. The results obtained were similar to those already found for β-chloro-β-nitrosobutane, so we extended our investigations to the two chloronitroso-compounds used by Hammick and Lister (*loc. cit.*) to see if they would behave in the same manner. We did not examine the products of photolysis of these compounds, however, beyond confirming that an appreciable amount of hydrogen chloride is liberated in each case.

(I.) $CH_3{\cdot}CCl(NO){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ $CH_2Ph{\cdot}CCl(NO){\cdot}CH_2{\cdot}CH_2Ph$ (II.)

(III.) $C_5H_{10}{>}CCl{\cdot}NO$ $CH_3{\cdot}CCl(NO){\cdot}CMe_3$ (IV.)

Table I contains the quantum efficiency data. Using approximately monochromatic light of wave-length (λ_1), coinciding with that of maximum absorption in each case, we found that the quantum efficiency (γ) was about 1 for (I) and (III), but only 0·78 and 0·62 for (II) and (IV), respectively. The absorption curves for all four substances are unsymmetrical when plotted on a wave-length scale, and on the short-wave side of (II) and (IV) there is a very distinct bulge due to a second component (cf. Mitchell and Simpson, J., 1940, 784). The absorption data for (I) and (II) are set out in Table II. For (III) and (IV) our readings (in methyl alcohol) are so similar to those (in benzene) recorded by

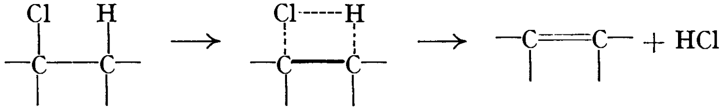
Hammick and Lister (*loc. cit.*) that it is unnecessary to publish them. We also determined the quantum efficiencies of (II) and (IV), using in each case light of wave-length (λ_2) corresponding to the head of the short-wave component of the absorption band. Under these conditions we obtained values in the neighbourhood of unity for both substances.

TABLE I.

Substance.	Wave-length, A.	Temp. of filter.	G./100 c.c. of soln.	Time of irradiation, mins.	Cals. absorbed.	G.-mols. decomposed, × 10^4.	γ.*	HCl, %.
(I)	6550 (λ_1)	15·4°	7·000	240	9·16	2·22	1·05	97·1
(II)	6580 (λ_1)	15·2	6·464	153	5·43	0·98	0·78	99·6
	6100 (λ_2)	18·7	6·223	600	9·93	2·34	1·10	
(III)	6540 (λ_1)	15·5	6·931	180	7·42	1·63	0·96	95·0
(IV)	6700 (λ_1)	14·2	6·678	250	10·29	1·51	0·62	89·6
	6140 (λ_2)	18·4	6·992	580	9·50	1·90	0·93	

* $\gamma = [(\text{g.-mols. decomposed})/(\text{cals. absorbed})] \times [(2{\cdot}847 \times 10^8)/\lambda]$.

The results lead us to the conclusion that in the photolysis of chloronitroso-compounds an activated molecule is first produced by the absorption of one quantum (*i.e.*, 42—47 kg.-cals./g.-mol. for the wave-length range 670—610 mμ), the absorption taking place through the nitroso-group. Hydrogen chloride is then split off. This necessitates the breaking of the bonds C–H and C–Cl. From the approximate values for these bond energies given by Pauling ("The Nature of the Chemical Bond," 1940, p. 53), 153·8 kg.-cals./g.-mol. would be required. The energy supplied by the light is not nearly enough to break these two bonds, but if we take into consideration the heat of formation of hydrogen chloride (102·7 kg.-cals.) and the energy (41·4 kg.-cals.) furnished by the formation of C=C from C–C, then plenty of energy is available for the reaction.* We may suppose that the elimination of hydrogen chloride is preceded by a transition state in which a preliminary link is formed between the chlorine atom and a neighbouring hydrogen atom, with compensating adjustments in the adjacent bonds (weakening of C–Cl and C–H, and strengthening of C–C).



In the cases where the quantum efficiency is less than 1, some deactivation probably takes place. We should expect deactivation to be favoured by the presence of the phenyl groups in (II), and to a greater extent by the proximity to the absorbing radical of the CMe_3 group in (IV). Even with these two compounds the quantum efficiency becomes approximately equal to unity for the shorter wave-lengths. Thus, although a certain amount of energy is always dissipated, at the shorter wave-lengths (where the light quantum contains more energy) there is still enough left to cause each of the absorbing molecules to split off hydrogen chloride.

EXPERIMENTAL.

Preparation of γ-Chloro-γ-nitrosovaleric Acid (I).—The oxime of lævulic acid was dissolved in ether, and chlorine passed into the solution until the white precipitate of the resulting hydrochloride had all reacted. The resulting greenish solution was shaken with dilute aqueous potassium hydrogen carbonate until it was blue. It was then washed with water, dried over anhydrous sodium sulphate, and the ether distilled off. The remaining blue oil solidified on cooling; it crystallised from hexane in dark blue plates, m. p. 33° [Found: C, 36·2; H, 4·9; N, 8·7; Cl (by Stepanow's method), 21·2. $C_5H_8O_3NCl$ requires C, 36·3; H, 4·9; N, 8·5; Cl, 21·4%]. After several weeks' standing some decomposition had taken place.

Preparation of β-Chloro-β-nitroso-αδ-diphenylbutane (II).—β-Hydroxy-αδ-diphenylbutane,

---

* Further evidence for this is given by the thermal decomposition of (II), in which hydrogen chloride is also split off. We found from measurements of the reaction rates at 70°, 80°, and 90° (using 4·16% solutions in methyl alcohol) that the energy of activation E (in the equation $k = Ae^{-E/RT}$) was 29—30 kg.-cals.

prepared from β-phenylethylmagnesium chloride and phenylacetaldehyde, was oxidised to αδ-diphenyl-β-butanone (cf. Tiffeneau, Orékhoff, and Levy, *Bull. Soc. chim.*, 1931, **49**, 1846). The oxime prepared in the usual manner from this ketone is a mixture of two stereoisomers and has not a sharp m. p.; by repeated crystallisation from alcohol the m. p. was raised to 121°. The chloronitroso-compound obtained from the lower-melting mixture and from the highest-melting sample had the same m. p., so for our purpose it was not necessary to isolate one form of the oxime. The mixture was therefore dissolved in ether, and chlorine passed in as described above. The blue oil remaining after washing, drying, and distilling off the ether solidified at once, and was crystallised from alcohol; it had m. p. 46° [Found : C, 70·2; H, 5·6; N, 5·1; Cl (by Stepanow's method), 13·1. $C_{16}H_{16}ONCl$ requires C, 70·2; H, 5·85; N, 5·1; Cl, 13·0%]. This *compound* is quite stable and has been kept for several months without showing any signs of decomposition.

Absorption Spectra.—The absorption due to the nitroso-group was examined in each case with a Spekker photometer used along with a Hilger glass spectrograph (E 495) in which wave-lengths from 3,600 to 10,000 A. are recorded on a 10″ × 4″ plate : Ilford long-range plates were very suitable. A ribbon filament lamp (6 v., 16 amp.) served as light source. Data for the two new chloronitroso-compounds are in Table II, where ε represents molecular extinction coefficients, and λ wave-lengths in A.

TABLE II.

Absorption of γ-chloro-γ-nitrosovaleric acid in methyl alcohol.

Concn. 0·0806M, l = 1 cm.

λ	7460	7040	6955	6900	6850	6825	6765	6705	6680	6640	6590
ε	2·48	3·72	4·96	6·20	7·44	8·69	9·93	11·16	12·41	13·65	14·89
λ	6470	6420	6355	6280	6225	6125	6010	5905	5820	5690	5350
ε	14·89	13·65	12·41	11·16	9·93	8·69	7·44	6·20	4·96	3·72	2·48

Absorption of β-chloro-β-nitroso-αδ-diphenylbutane in methyl alcohol.

Concn. 0·0649M, l = 1 cm.

λ	7300	7200	7130	7075	7015	6950	6850	6800	6770	6760
ε	1·54	3·08	4·62	6·17	7·71	9·25	10·78	12·33	13·87	15·41
λ	6740	6710	6690	6650	6630	6500	6445	6400	6370	6345
ε	16·95	18·49	20·03	21·57	23·12	23·12	21·57	20·03	18·49	16·95
λ	6315	6265	6130	6035	5960	5895	5800	5700	5500	5200
ε	15·41	13·87	12·33	10·78	9·25	7·71	6·17	4·62	3·08	1·54

Products of Photolysis.—(a) *Hydrogen chloride.* The products of photolysis could not be isolated so completely as had been done for β-chloro-β-nitrosobutane (Mitchell and Cameron, *loc. cit.*). In every case, however, hydrogen chloride was found in amounts varying between about 90 and 100% of that theoretically possible. The results shown in Table I (last col.) were obtained from 5% solutions of the chloronitroso-compounds in methyl alcohol (the latter having been freed as far as possible from dissolved oxygen by bubbling in nitrogen and then distilling it in an atmosphere of nitrogen). The solutions, contained in sealed tubes and kept cool by circulating water, were illuminated by several electric lamps. When the blue colour had faded completely, the tubes were opened, and the amount of chloride in 5 c.c. of each solution was estimated by Volhard's method with 0·1N-silver nitrate.

(b) *Other products from γ-chloro-γ-nitrosovaleric acid.* After complete photolysis of a 5% solution of γ-chloro-γ-nitrosovaleric acid in methyl alcohol, as described above, the solvent was removed under reduced pressure, and a yellow oil remained. When this was shaken with dry ether, a solid product separated, and on crystallisation from a mixture of alcohol and ether this had m. p. 114° [Found : C, 39·7; H, 6·9; N, 7·7; *M*, ebullioscopic in alcohol (Menzies's method), 182. $C_6H_{12}O_3NCl$ requires C, 39·7; H, 6·7; N, 7·7%; *M*, 181·5]. These results and the general properties of the substance led us to believe that it was the *oxime hydrochloride* of *methyl lævulate.* This was confirmed by preparing a specimen of the compound, which had m. p. 115° and showed no depression in a mixed m. p. The ethereal solution from which this product had been isolated was washed with cold dilute potassium hydroxide until neutral and dried over anhydrous sodium sulphate. After distillation of the ether, a small amount of liquid, b. p. 90°/30 mm., was obtained. It formed a 2 : 4-dinitrophenylhydrazone, m. p. 139° (Found : C, 46·5; H, 4·5; N, 17·6. Calc. for $C_{12}H_{14}O_6N_4$: C, 46·5; H, 4·5; N, 18·1%), undepressed on admixture with the corresponding hydrazone prepared from methyl lævulate, m. p. 139°. The presence of a small amount of methyl lævulate, formed doubtless from the first product, was therefore established. We were unable to isolate any other products.

The photolysis of γ-chloro-γ-nitrosovaleric acid appears to be similar to that of β-chloro-β-nitrosobutane. As with the latter compound, after 1 mol. of hydrogen chloride is eliminated, two of the resulting unsaturated residues probably combine to form a double molecule. On standing, esterification takes place with the methyl alcohol, and the water thus set free reacts with the double molecule, liberating the oxime hydrochloride of methyl lævulate. Unfortunately, the product from the other half of the double molecule could not be isolated.

(c) *Other products from* β-*chloro*-β-*nitroso*-αδ-*diphenylbutane.* A 5% solution of the chloronitroso-compound in methyl alcohol was exposed to light as described above. When the photolysis had gone to completion the solution was faintly green. Removal of the solvent gave a greenish oil mixed with a white solid. The oil was washed out by a little methyl alcohol, and the white solid crystallised from methyl alcohol; a product melting over the range 115—122° was obtained (Found: C, 80·6; H, 7·2; N, 6·2; *M*, 236. Calc. for $C_{16}H_{17}ON$: C, 80·3; H, 7·1; N, 5·8%; *M*, 239). The product was submitted to steam distillation in presence of dilute sulphuric acid, and an oil was obtained which crystallised on standing. After crystallising from light petroleum it had m. p. 43°, undepressed on admixture with αδ-diphenyl-β-butanone. The solid product of photolysis is therefore the oxime of this ketone. Examination of the green oil led only to the isolation of a small amount of αδ-diphenyl-β-butanone. To test for formaldehyde, the solution after photolysis was submitted to steam distillation. The first part of the distillate, diluted with water, slowly formed a crystalline precipitate with dimedone; recrystallised from alcohol, this had m. p. 188—189°, undepressed on admixture with the derivative from formaldehyde.

In this photolysis, therefore, we have no evidence of the formation of a double molecule. It seems likely that the two atoms of hydrogen necessary to convert the unsaturated residue (remaining after hydrogen chloride is split off) into the oxime of αδ-diphenyl-β-butanone are obtained from the solvent, with the production of formaldehyde.

Quantum Efficiencies.—The procedure was essentially that described by Mitchell and Cameron (*loc. cit.*), but the use of more suitable instruments permitted a reduction in the time of irradiation. An automatic carbon arc was again employed as light source. For most of the experiments, approximately monochromatic light was obtained from it by means of a single Christiansen filter together with a red glass filter. The former was immersed in a thermostat, and by regulating the temperature, the wave-length of maximum transmission was made to correspond to the wave-length (λ_1) for which the solution under investigation showed maximum absorption. The concentration of the solution was selected in each case so that at least 99% of the light was absorbed. For the experiments at the shorter wave-lengths (λ_2) two Christiansen filters were used in series, and the red filter was replaced by a yellow one. The energy measurements were made with a large-surface Moll thermopile and a Cambridge d'Arsonval galvanometer having a resistance of 10 ohms. The two rectangular apertures each 2·6 × 1 cm. (see diagram in paper by Mitchell and Cameron, p. 1965) were replaced by circular apertures of 2 cm. diameter, and the exposed parts of the thermopile and reaction cell were each 1·8 cm. in diameter. A cylindrical cell of 4 c.c. capacity and 1 cm. thickness was used for all but the experiments of 6100 and 6140 A. For these, a similar cell of 7·91 c.c. capacity and 2 cm. thickness was employed. In all experiments the cells were filled completely with solution and were closed with well-ground stoppers to prevent access of air during the irradiation. The Weston photronic cell (used with a recording galvanometer to give the variations in intensity of the light) was tested for fatigue with a constant light source (a filament lamp run at constant voltage from large capacity accumulators). In general, there was a slight fatigue effect of a few units % during the first hour or so, but thereafter it was usually negligible. To make allowance for any such effect we measured the *T*/*P* ratio at the beginning and end of each pair of carbons. Our photoelectric colorimeter for determining the amount of decomposition was improved by using a Cambridge short-period galvanometer having a resistance of 600 ohms.

Further work on chloronitroso-compounds is in progress.

We thank the International Student Service for a maintenance grant (to K. S.), and the Carnegie Trust for a scholarship (to G. K. S.) and for a research grant (to S. M.) with which the glass spectrograph was purchased. We are also indebted to Mr. J. M. L. Cameron, who performed the micro-analyses.

UNIVERSITY OF GLASGOW.

[*Received, July* 25*th*, 1941.]