ISOMERISATION AND DECOMPOSITION OF

ALKYLARYLDIAZOSULPHIDES BY LIGHT

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It is known that irradiation of E-isomers of diazosulphonates[1] and diazocyanides[2] gives Z-isomers as photoisomerisation products. The light experiments with E-alkyl(ar)-aryldiazosulphides[3] do not exclude the possibility that decomposition products as well as Z-isomers might be formed by irradiation. The only light reaction products observed with E-diazosulphones[4] and E-aryldiazosulphides[3,5] are decomposition products. Van Beek et al.[7] remark that both isomers of alkylaryldiazosulphides are light sensitive, but further information is not given. Hence for the several groups of diazo compounds the light reaction may be different and it is not clear whether alkylaryldiazosulphides isomerise or decompose by the action of light or show both reactions simultaneously.One of the main difficulties in studying the light reactions of diazo compounds has been the non availibility of the Z-isomer. Since we were able to prepare both E- and Z-isomers of several alkylaryldiazosulphides we decided to study the light reactions with pure E- as well as pure Z-isomer solutions of 4-cyano-(D-I),4-nitro-(D-II),3,5-dichloro-4-dimethylaminobenzenediazo tert. butyl sulphide (D-III) and phenyldiazo tert. butyl sulphide (D-IV). The conditions of the experiments[8] were chosen so that the thermal decomposition and/or thermal isomerisation reaction of the Z- and the E-isomers were negligible in all the experiments described below[9].

We found that both isomers are light sensitive. Curiously the light reaction products are dependent on the wavelength of irradiation. With light of 405nm starting with a methanol solution of pure Z- or E-isomer, only mixtures of these two stereo-isomers were observed with TLC or NMR[10]. After irradiation of pure Z-isomer solutions in methanol[10] with light of 300nm E-isomers and the decomposition products: sulphide, di-sulphide and (substituted)benzene were observed. After irradiation with light of 300nm of pure E-isomer solutions in methanol the Z-isomer was observed as the only photo-product, when the absorption of light of 300nm by the Z-isomer was negligible.

Further evidence of the isomerisation and decomposition reactions was obtained with UV-VIS-Spectroscopy. Using light of 405 or 435nm and methanol solutions of the pure Z- or E-isomers the spectra showed isosbestic points in both cases at the wave-lengths for which the extinction coefficients of the two isomers are identical.After

prolonged irradiation of the two solutions the same photoequilibrium was reached[10].
With light of 365, 330 and 300nm the spectra of the irradiated solutions of E-isomers
showed in the beginning the same isosbestic points as those observed after irradiation
with 405nm. After prolonged irradiation however,the changes in the spectra are no longer
in agreement with those observed at 405nm. With corresponding pure Z-isomer solutions
the spectra even in the beginning behaved differently from those observed with light of
405nm. Careful experiments revealed isosbestic points in the beginning but at different
positions, the extinction also changed in a different way , indicating the occurrence
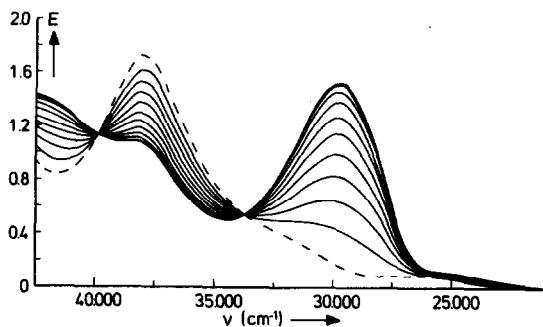of other light reaction products (Fig. I- Fig. II).

Fig. I
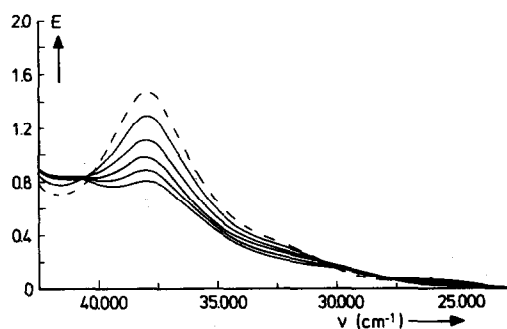Z-D-I irradiated with light of 405nm

Fig. II
Z-D-I irradiated with light of 330nm

   Similar results were obtained when these experiments were performed in acetonitrile
or n-heptane. The above mentioned results suggested a reaction mechanism as presented in
Fig. III.

   The isosbestic points are obtained because the differences between the extinctions
(ΔE) at these wavelengths (λ_i) after several periods of irradiation (Δt) are equal to
zero ($\Delta E_{\lambda_i}=0$). The remaining ΔE_{λ_j} ($j \neq i$) values are not equal to zero, but there may be
distinct relations between these ΔE_{λ_j} values. For instance, the quotients of the ΔE_{λ_n}
and ΔE_{λ_m} ($m \neq n \neq i$) may be independent of the period of irradiation. Calculations[11] show
that this relation is found when the concentrations of the observable compounds are
related to each other to such an extent that for each wavelength of measurement (λ_j) the
ΔE_{λ_j} values may be described by using the extinction coefficients of the observable com-
pounds at λ_j and the concentration of only one compound. In other words the concentrations
of the observable compounds must be correlated to each other by a number of linear in-
dependent equations (R) so that the difference between the number of observable com-
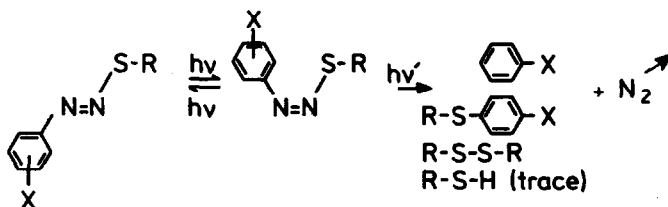

Fig. III: R= alkyl, X= substituent of benzene ring, ν=435, 405, 365, 330 or 300nm,
        ν'= 365, 330 or 300nm.

pounds (S) and R is 1. When these $\Delta E_{\lambda j}$ values are plotted against each other for two different wavelengths for several Δt values a straight line must be obtained(ED diagram).

The irradiation of pure E and pure Z solutions of D-II and D-III in methanol with light of 405, 330 and 300nm were plotted as ED diagrams. When light of 405nm was used straight lines were obtained in the ED diagrams (Fig.IV). This is in agreement with the mechanism of Fig.III, because at each wavelength only the E and the Z are observed:S=2. The sum of the concentrations of $E(c_E)$ and $Z(c_Z)$ is always equivalent to the starting concentration (c_0):R=1. In the beginning of irradiation when light of 300 or 330nm was used straight lines were obtained in the ED diagrams,but on further irradiation deviations from these lines were observed(Fig.V-Fig.VI). On ground of the mechanism proposed in Fig.III straight lines must be obtained when the isomer which occurs as photoproduct does absorb the light of 330 or 300nm to a negligible extent[12]. Deviation from linearity occurs when the amount of light of 300 or 330nm absorbed by the photoproduct becomes appreciably and this isomer reacts further. Calculations[11] show that in this case straight lines must be obtained when $\frac{\Delta E_{\lambda n}}{\Delta E_{\lambda m}}$ is plotted against $\frac{\Delta E_{\lambda k}}{\Delta E_{\lambda m}}(n \neq m \neq k)$ for different periods of irradiation (EDQ diagram, S-R=2)[12]. This is indeed observed for D-II and D-III in methanol(Fig.VII).

When pure E solutions in methanol were used the slopes of the straight lines in the ED diagrams for each wavelength pair are independent of the wavelength of irradiation. The values of these slopes are quantitatively into agreement with a E to Z photoisomerisation only[11]. Direct photodecomposition of the E can therefore be excluded. When pure Z solutions were used the values of these slopes are dependent on the wavelength of irradiation and indicated photoisomerisation and decomposition by light of 300 or 330nm.

Not only the observed isosbestic points,but also the observed variations in the extinctions of the solutions of alkylaryldiazosulphides after several periods of irradiation are quantitatively into agreement with the mechanism of Fig.III. Hence,photoisomerisation occurs from the Z-and the E-isomer,the photodecomposition products are formed only when the Z-isomer absorbs light of wavelength 365nm.
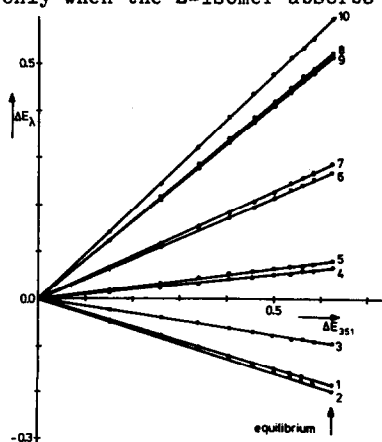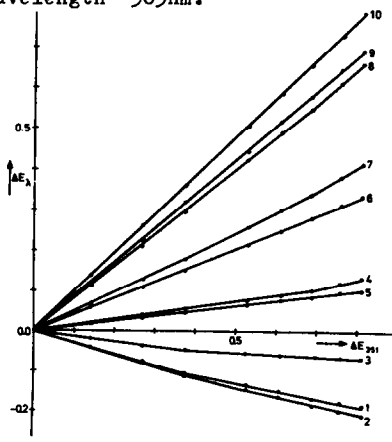

Fig.IV: ED diagram of E-D-II in methanol using light of 405nm. Fig.V: ED diagram of E-D-II in methanol using light of 330nm. ΔE_λ: 1:$\Delta E_{298.5}$; 2:ΔE_{290}; 3:$\Delta E_{307.5}$; 4:$\Delta E_{317.5}$; 5:ΔE_{392}; 6:$\Delta E_{377.5}$; 7:ΔE_{328}; 8:$\Delta E_{363.5}$; 9:ΔE_{340}; 10:ΔE_{345}.

Fig.VI

Fig.VII
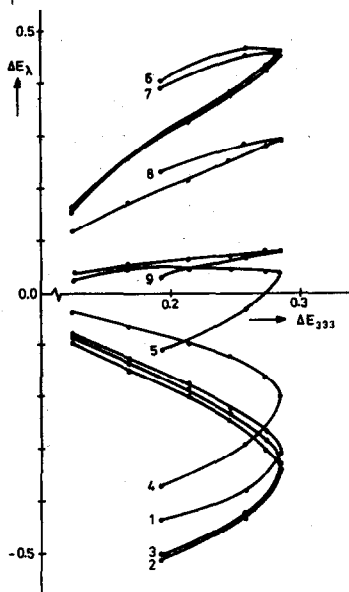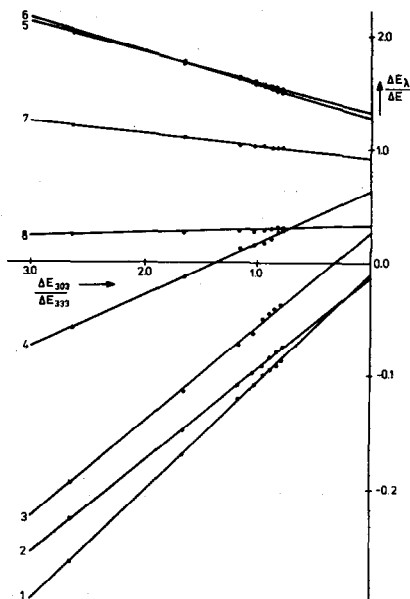
Fig.VI: ED diagram and Fig.VII: EDQ diagram of Z-D-II in methanol using light of 330nm.
Fig.VI: ΔE_λ: 1: E_{290}; 2:ΔE_{294}; 3:ΔE_{303}; 4:$\Delta E_{312.5}$; 5:$\Delta E_{322.5}$; 6:ΔE_{345}; 7:ΔE_{357}; 8:$\Delta E_{370.5}$ 9:$\Delta E_{384.5}$. Fig.VII:$\Delta E=\Delta E_{333}$;ΔE_λ: 1:ΔE_{290}; 2:ΔE_{294}; 3:$\Delta E_{312.5}$; 4:$\Delta E_{322.5}$;5:ΔE_{345}; 6: ΔE_{357}; 7:$\Delta E_{370.5}$; 8:$\Delta E_{348.5}$.

Notes:

1. H.Jonker, T.P.G.W.Thijssens, L.K.H. van Beek, Rec.Trav.Chim., 87, 997,(1968).
2. H.Zollinger,"Azo and Diazo Chemistry",Interscience Publishers,New York,(1961),p.62.
3. H. van Zwet, E.C. Kooyman, Rec.Trav.Chim., 86, 993,(1967).
4. M.Kobayashi, S.Fujii, H.Minato, Bull.Chem.Soc.Jap., 45, 2039,(1972).
5. The experimental conditions by which Van Zwet (3) observed only decomposition products excluded the observation of the Z as light reaction product (6).
6. T.Yamada, Bull.Chem.Soc.Jap., 43, 1506,(1970).
7. L.K.H. van Beek,J.R.G.C.M. van Beek,J.Boven,C.J.Schoot,J.Org.Chem.,36,2194,(1971).
8. Solutions of recrystallized Z or E were irradiated with a grating monochromator in combination with glass filters at room temperature. For spectroscopic work the concentrations were between 0.5×10^{-4} and 2.0×10^{-4} mole/l. Further details will be published elsewere.
9. J.Brokken-Zijp, H.v.d.Bogaert, Tetrahedron, 29, 4169,(1973).
10. On ground of the thermal instability of Z-D-IV the reaction was studied in n-heptane.
11. Detailed calculations are given by H.Mauser,Zeitschr.Naturforsch.,23b,1025,(1968).
12. In the beginning of irradiation of a pure Z solution the absorbing compounds above 250nm are sulphide(R) substituted benzene(B), Z and E: S=4, $c_0=c_E+c_Z+c_R+c_B$, $\frac{c_B}{c_R}$ and $\frac{c_E}{c_B+c_R}$ are constant: R=3. But after further irradiation this last equation lapse and R becomes 2. The constancy of the relation $\frac{c_B}{c_R}$ was verified for D-II and D-III in methanol with NMR. In the beginning of irradiation of a pure E solution the absorbing compounds are E and Z: S=2, but after further irradiation Z reacts further then S=4 and R=2.