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On the Photochemical Behavior of Some Xanthenes and Xanthones and the Photochemical Formation of Dixanthenes, Mono-, and Dihydroxydixanthenes*

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By ultraviolet spectrometric measurements we studied the photochemical behavior of xanthene, xanthone, 9, 9′-dihydroxydixanthene and dixanthene in aerated and deaerated ethanolic solutions in the range of concentration $5\cdot10^{-3}$ M to 10^{-4} M by Osram-HBO 200- and Hanau TQ 81- lamps. We found: Xanthenes are photostable similar to monoacridans in the absence of oxygen; in the presence of oxygen photooxidation to the corresponding xanthones takes place. The xanthones are photochemically unstable; in oxygen free solvents containing H-atoms, like methanol, ethanol, benzene, cyclohexane, dioxane, they are reduced to xanthenes. In cyclohexane we found a soluble xanthene, 9-cyclohexylxanthydrol. In hexane there is formed a precipitate with a yield above 80%; this is the dimeric xanthene 9, 9′-dihydroxydixanthene. The photoreaction presumably is going over a diradical, H-atom transfer from the solvent and formation of a xanthydrol monoradical in the primary step and dimerization to the 9, 9′-dihydroxydixanthene. Irradiation of solutions of xanthone and xanthene in benzene furnish 9-hydroxydixanthene. Solutions of equal molarity of xanthone and acridan yield under irradiation also a solid photoproduct; this is 9, 9′-diacridan. The first step of reaction is photoreduction, where xanthene tranfers a H-atom to xanthone and the hydroxyxanthyl radical dimerizes with the xanthyl radical or the acridanyl radical dimerizes with themselves and forms the diacridan.

In connection with studies about the spectroscopy and photochemistry of the acridines and acridine dyes,[1-6] we also began a few years ago, to investgate the photochemical and spectroscopic behavior of the cations and dianions of the fluorescein dyes.[7-11] Decisive and accurate investigations on this photochemical special field were especially carried out by the Japanese researchers Imamura, Koizumi, Kato and others;[12-16] Lindqvist[17] and Grossweiner[18] also contributed by their flash photolytic experiments to the elucidation of the mechanism of photo-reduction respectively oxidation of some substances of this class of dyes.

Our own investigations are still being fully elaborated, and we hope that we can finish these studies in the next time. Similar to earlier experiments on the acridines,[19] we believe, that we

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[1] V. Zanker and P. Schmid, *Z. Phys. Chem., N. F.*, **17**, 11 (1958).

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[14] M. Imamura and M. Koizumi, ibid., **29**, 899 (1956); **29**, 913 (1956).

[15] M. Imamura, ibid., **30**, 249 (1957); **31**, 62 (1958).

[16] M. Koizumi, M. Imamura and Cow., ibid., **31**, 962 (1958); **33**, 262 (1960); **33**, 169 (1960); **35**, 16 (1962); **35**, 185 (1962); **35**, 1875 (1962); **38**, 1022 (1965); **38**, 1015 (1965).

[17] L. Lindqvist, *Arkiv Kemi*, **16**, 79 (1960). V. Kaoshe and L. Lindqvist, *J. Phys. Chem.*, **68**, 817 (1964).

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[19] V. Zanker, *Z. Phys. Chem. N. F.*, **52**, 2 (1954).

can analyze the absorption bands of di- and tetrahalide fluoresceins, starting from the parent substances of this dyestuff class and the monohydroxy derivatives. For this purpose we also have synthesized a series of xanthones, xanthenes, xanthydrols, and xanthylium cations and have carried out spectroscopic and photochemical experiments. The absorption spectroscopy and photochemistry of these compounds are very interesting for us, because so far we have had little knowledge about the parent substances of fluorescein and the other dyestuffs. On the other side the photochemical investigation of acridine and acridine cations lead us to the acridans and diacridans.[5,6] Analogously we could hope, to get similar results in the case of the xanthenes and xanthons. The results will be reported here in a short paper.

Experimental

The substances which we have used for our photochemical and spectroscopical investigations as xanthone, xanthene and the dixanthenes were prepared in optical purity by repeated crystallization out of hexane or ethanol. The solutions of a molarity of 10^{-3} to 10^{-4} were used and in most cases they were deoxygenized by repeated boiling and cooling under N_2-gassing. The last traces of oxygen were removed by aluminumtriethyl. The photolytical conversion was controlled spectrometrically by means of a Zeiss PM Q II and we also identified partly in this way the photochemical converted substances.

Results of the Photolytical Investigations and Discussion

As an example for the study of the photochemical behavior of the monoxanthenes we show at first a measurement of xanthene itself on Fig. 1. In the non-illuminated state this compound shows an electronic band with a vibrational structure at 34300 and 35500 cm^{-1}, classified in the terminology given by Platt[20] as a transition to the ^1L_b-state and at 40500 cm^{-1} it shows the transition to ^1L_a-state, mostly unstructured and of a higher intensity. Further to shorter wavelengths, we can see another very intensive band presumably due to the transition to the ^1B_b-state (^1B_b-band). Irradiating an air saturated ethanolic solution by a Mercury lamp HBO 200, an oxidation reaction quickly starts. In this case we see an increase but no decrease of the xanthene bands at 34000 to 35000 cm^{-1}. In the wavelength region longer than that of xanthene a new band appears and increases up to a yield of about 18%. Then this band decreases again and a second new band at 32000 to 33000 cm^{-1} arises. We suppose, that there is formed an intermediate out of xanthene and xanthone, but we have not yet identified this. In deoxygenized ethanolic and other polar and homopolar solutions the xanthenes, like the acridans, are photostable. Pure xanthone formed by photooxidation of the xanthene shows a spectrum as is shown on Fig. 2. Characteristic bands of it are an unstructured band at 29000 cm^{-1} and two bands

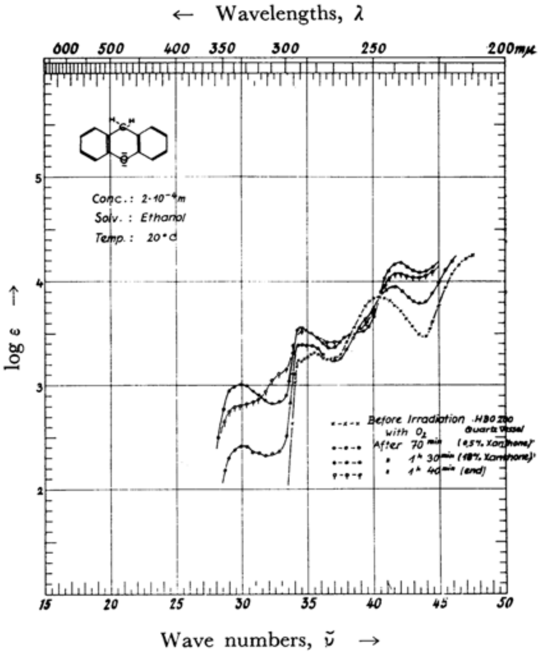

Fig. 1. Absorption spectra of xanthene during photolysis in oxygen containing solution.

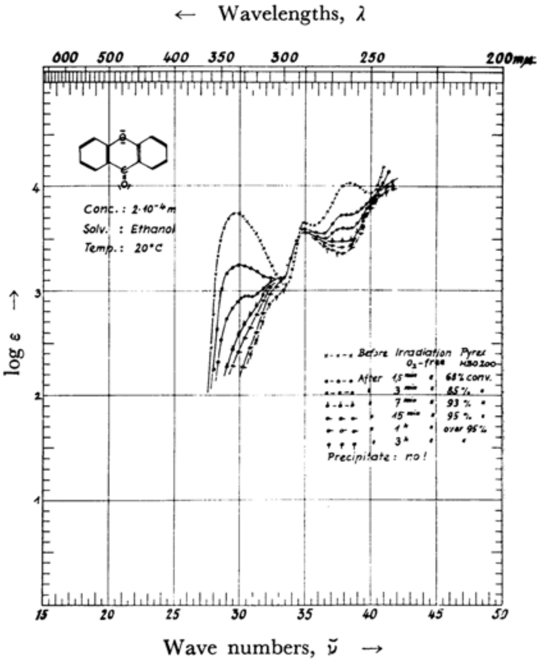

Fig. 2. Absorption spectra of xanthone during photolysis in oxygen free solution.

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[20] J. R. Platt, *J. Chem. Phys.*, **17**, 470, 484 (1949).

at 34700 and 38400 cm^{-1}. These intensive bands of the xanthone are responsible for the apparent rise of the xanthene bands under the photolysis in oxygen containing solutions. If a deoxygenized ethanolic solution of xanthone is illuminated in a pyrex vessel, xanthone undergoes quickly a photochemical reduction to xanthene, as is demonstrated by a very weak decrease of the band at 34500 cm^{-1}, the minimum at 38000 cm^{-1}, and the increase of the bands at 41000 to 42000 cm^{-1}. After an irradiation of 15 min. we reached a conversion of 95% out of 25 ml. solution and a concentration of 2×10^{-4} M: *we could not observe any formation of a solid photoproduct!*

In this case also, the band at 32000 to 33000 cm^{-1} is changed a little; this indicates again an intermediate between the generated xanthene and the xanthone.

If we irradiate an ethanolic solution of equal concentration in a quartz vessel, we get the same course of reaction; this is plotted on Fig. 3. Again we find that preferentially the formation of xanthene and an intermediate occurs. Under this condition we also find no precipitate or a solid product.

Proceeding from ethanol to dioxane as solvent and irradiating in a quartz vessel, no change in the reaction is detectable. This is shown on Fig. 4. The structure of the individual electronic transitions is indeed better resolved, but the photolysis itself is not influenced. We tried to separate the xanthene which was formed in these solvents. The crystallization from the oily residue was very bad and we were not successful. Always again we found bands at 32000 to 33000 cm^{-1}, indicating an unidentified intermediate.

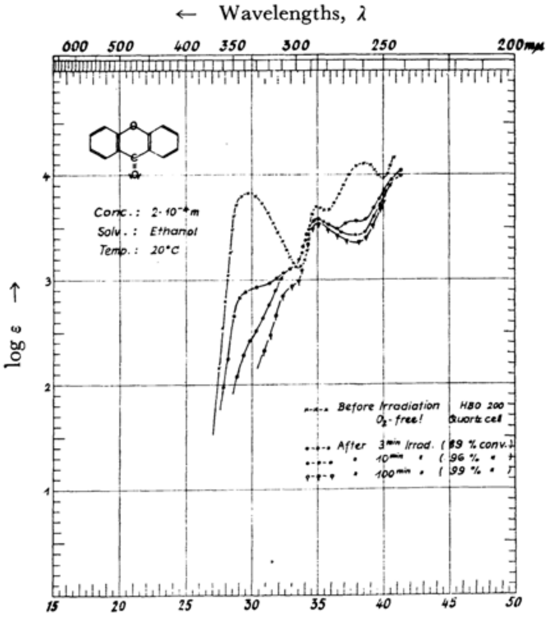

Fig. 3. Absorption spectra of xanthone during photolysis in oxygen free solution in a quartz cell.

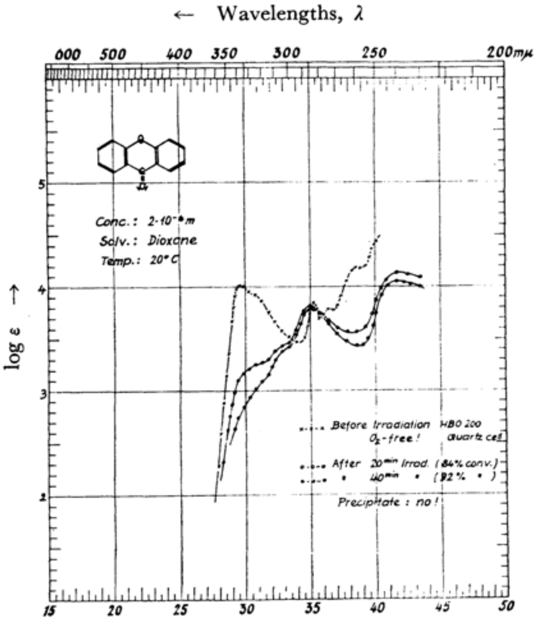

Fig. 4. Absorption spectra of xanthone during photolysis in oxygen free solution of dioxane.

Finally, our experiments to indentify the photolytical final product were successful. In this case we used a homopolar solvent, cyclohexane. We found the same course of reaction as for ethanol and dioxane, and again there was no formation of a solid product. If we remove here the greater part of cyclohexane out of the solution, we obtain a crystalline, colorless product. After repeated crystallization the constitution of the final product of the photolysis could be identified by elementary analysis, molecular weight and ultraviolet spectrum, as a 9-cyclohexylxanthydrol. This result is analogous to the behavior of acridine in deoxygenized cyclohexane or dioxane; we likewise have found for this compound a photochemical reduction to 9-cyclohexyl or 9-dihydroxanyl-substituted monoacridans. From this result we have to conclude, that the photoreactions of the xanthenes in ethanol, dioxane and other polar solvents also form similar soluble xanthydrols, with the corresponding solvent fragment in 9-C-position. But hitherto we could not isolate and identify these compounds.

If we use *n*-hexene as a solvent, we get the following somewhat surprising result. As plotted on Fig. 5, we observe a quick conversion from xanthone to xanthene. After 10 min. 95% are converted and we observe a precipitate of a solid photoproduct. After filtration and determination of the weight, we found over 80% of the substance which we had put in. The low solubility and the high melting

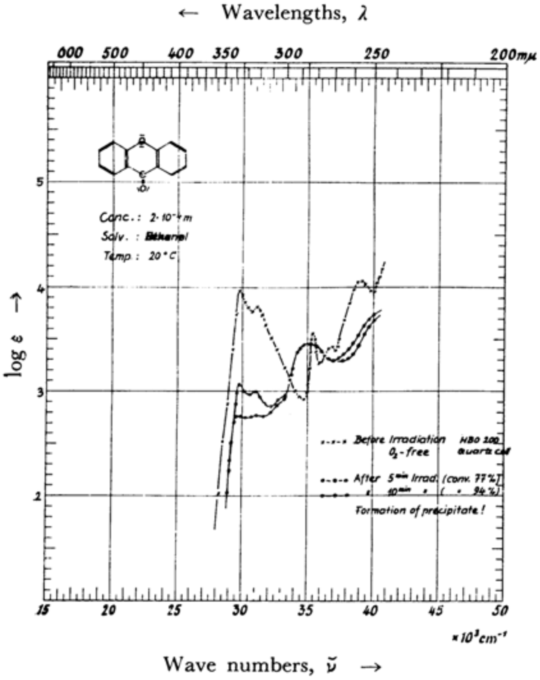

Fig. 5. Absorption spectra of xanthone during photolysis in oxygen free solution of hexane.

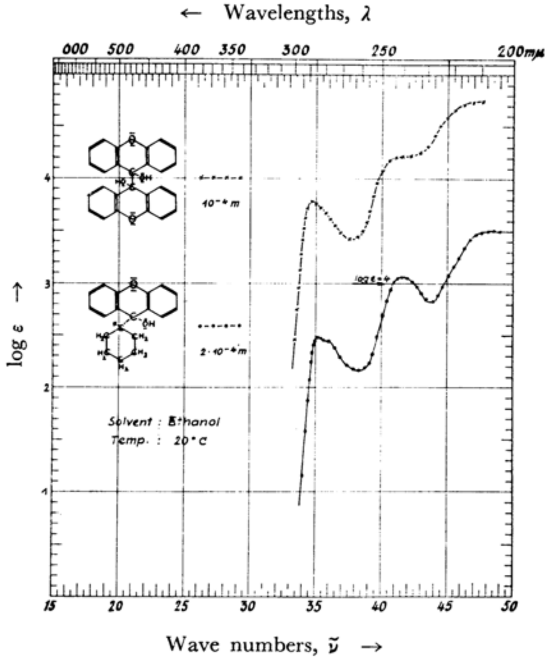

Fig. 6. Absorption spectra of 9, 9′-dihydroxydixanthene and 9-hydroxy-9-cyclohexylxanthene.

point of this substance gave us the first advice that in this case we had obtained a dimer. The elementary analysis and the determination of the molecular weight showed us, that we have here a double xanthydrol. By synthesis of a 9, 9′-dihydroxydixanthene according to literature[21] and by comparison with the photolytical substance, we found a complete agreement in ultraviolet and infrared spectrum, molecular weight and melting point. Thus we have proved, that this product is a 9, 9′-dihydroxydixanthene. From this we could show for the first time, that in the series of xanthones a photochemical dimerization out of equal building stones is also possible.

On Fig. 6 we demonstrate the ultraviolet spectra of 9-hydroxy-9-cyclohexylxanthene and 9, 9′-dihydroxy-9, 9′-dixanthene, which we have got in solutions of hexane and cyclohexane by photolysis. If we compare these spectra with the spectrum of xanthene, as plotted on Fig. 1, we see only a little difference in these two compounds against the parent substance. The dihydroxy derivative has the most intensive 0→0 transition of the ^1L_b-band, whereas the monohydroxy derivative shows 0→0 and 0→1 transitions of equal intensity; on the other hand, in the case of xanthene, the 0→1 transition is favored. In an opposite sequence, the intensity of this band increases from $\log\varepsilon=3.25$ over $\log\varepsilon=3.45$ to $\log\varepsilon=3.80$ of the dihydroxy derivative. From the appearance of their vibration structure, these three xanthenes are distinguishable. In the case of the dihydroxy derivative, also the minimum, following the ^1L_b-band, is most strongly marked.

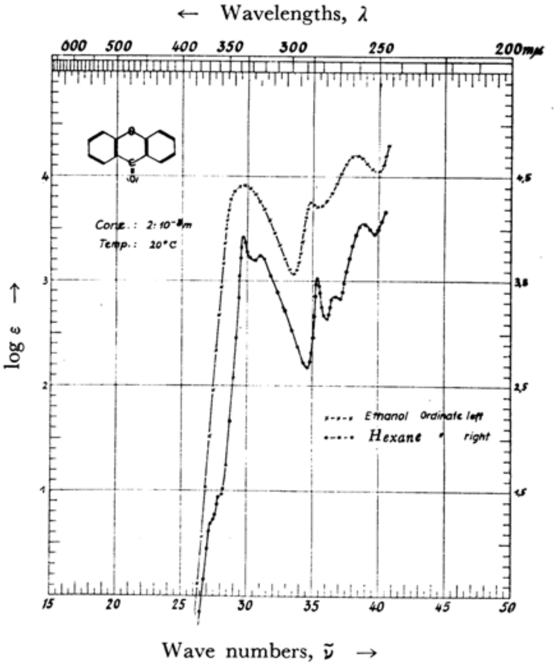

Fig. 7. Absorption spectra of xanthone in ethanol and hexane.

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[21] M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **49**, 253 (1927).

To the Mechanism of Photochemical Formation of Mono- and Dihydroxyxanthenes out of Xanthone.—The first information about the course of the photolysis of the xanthone, can be got from the spectrum of the xanthone itself. Therefore, we give the enlarged plotting, down to log $\varepsilon=0$, for various solvents, on Fig. 7. The spectrum, measured in the polar ethanol, displays a striking little structure and especially the band at the longest wavelengths is strongly broadened and without vibrational structure. On the contrary, all electronic transitions in hexane show a very well marked structure and the band at the longest wavelengths from 29000 to 33000 cm^{-1}, especially responsible for the primary process of the photoreaction, shows a well marked $0\rightarrow0$ transition with two exponentially decreasing vibration bands. We doubtless have here a $\pi\rightarrow\pi^*$ transition, with all three rings coupling aromatically. For the spectrum in hexane, we find in the wavelength region longer than that of the xanthenes two weak attendants at 27500 and 28000 cm^{-1}; these we have interprete as members of a $n\rightarrow\pi^*$ transition of absorption band.

We can expect such transitions for the compounds with heteroatoms on which lone pair electrons appear. A $n\rightarrow\pi^*$ transition in ethanol is not observable; but this does not mean, that this transition is not present. We think, that this transition is shifted to shorter wavelengths due to the rising polarity of the solvent and it is superposed with the intensive $\pi\rightarrow\pi^*$ absorption band. This also is consistent to $n\rightarrow\pi^*$ transitions; they are usually shifted to shorter wavelengths with increasing polarity of the solvent.

Superposition of two bands goes mostly together with a loss of structure. Generally we can explain the big differences of the spectra measured in ethanol and *n*-hexane as due to the interaction with the solvent molecules. In ethanol, the solvent molecules interact distinctly with the solute xanthone molecule; this interaction is especially specific to the polar carbonyl group. The xanthone molecule in hexane is free and displays a spectrum, similar to that in gas phase. Therefore, the explanation for the various behavior, seems to be given by a strong or a weak interaction with the solvent.

On Figs. 8 and 9, we have pointed out reaction schedules, set up to elucidate the photochemical reduction of xanthone or generally of the xanthones. As to the formation of monohydroxy and dihydroxydixanthenes (xanthydrols) respectively we have the following conception: xanthone absorbs at the free electron pair of the CO-group a quantum ($n\rightarrow\pi^*$ transition) and passes over to a diradical. The high affinity of a O-radical position to H-atoms is responsible for the transfer of an H-atom from solvents with H-atoms resulting the reductive formation of a xanthydrol- or a hydroxyxanthyl-radical. Simultaneously the solvent ethanol is oxidized to aldehyde. This C-radical has the tendence to react with other C-radicals and to form stable hydroxyxanthene molecules. Therefore, we can realize two ways of reaction: On the one side the combination of two equal xanthyl radicals to dihydroxydixanthyl, and on the other side an association of the xanthyl radical with a solvent radical generated at the H-atom transfer. As is mentioned above, the latter seems to be especially favoured in the case of strong interaction of the solvent molecule with the CO-group, where only a small distance holds permanently between CO-group and solvent molecule. On the other side the probability of association with an equal xanthyl radical is similarly high, and according to low solubility of the dimer, this aggregation is in the foreground.

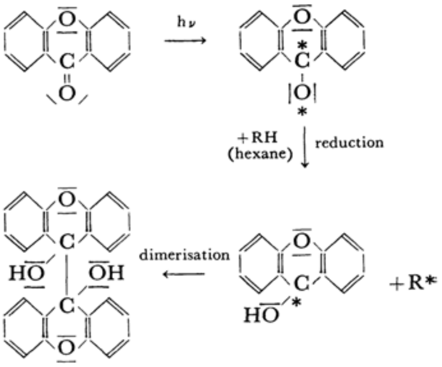

Fig. 8. Schedule of photoreaction of xanthone in solution of hexane.

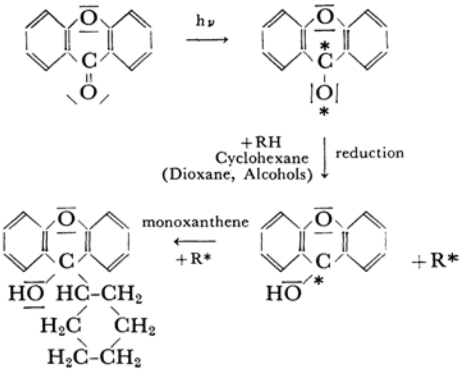

Fig. 9. Schedule of photoreaction of xanthone in solution of cyclohexane, dioxane and alcohols.

Photolytical Investigations on 9, 9′-Dihydroxy- and Dixanthenes.—In connection with the photochemical behavior of the diacridans, we were interested in the stability of the dixanthenes and in the question, if the dixanthenes, corresponding to the diacridans, decompose heterolytically to xanthylium cations and anions or to

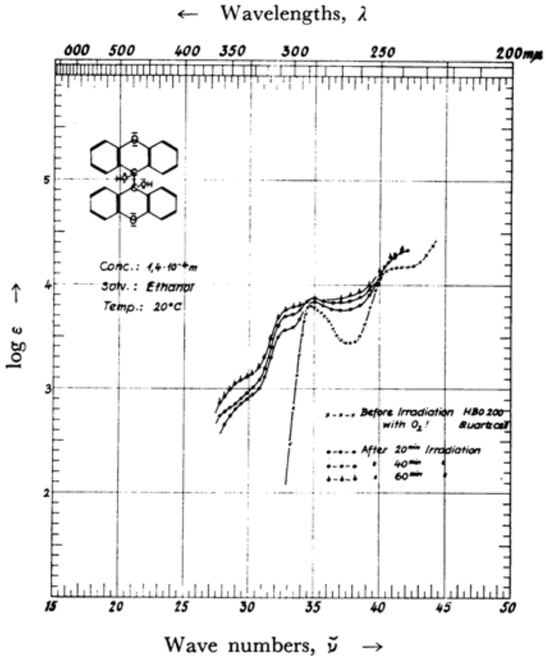

Fig. 10. Absorption spectra during photolysis of 9, 9′-dihydroxydixanthene in oxygen containing solution.

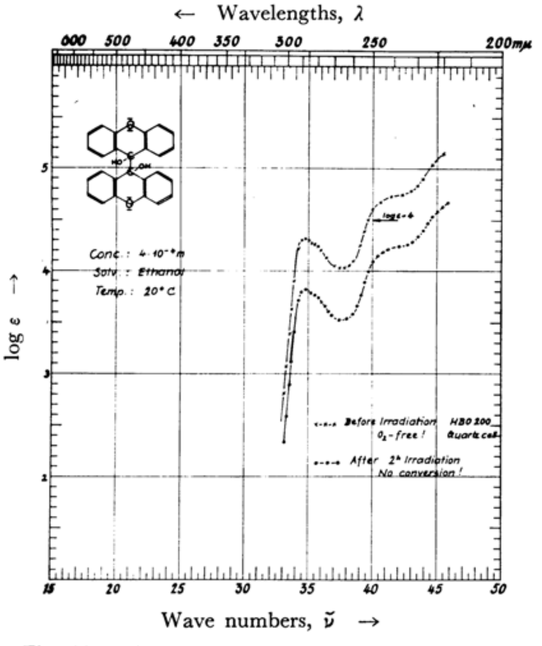

Fig. 11. Absorption spectra of 9, 9′-dihydroxydixanthene before and after irradiation.

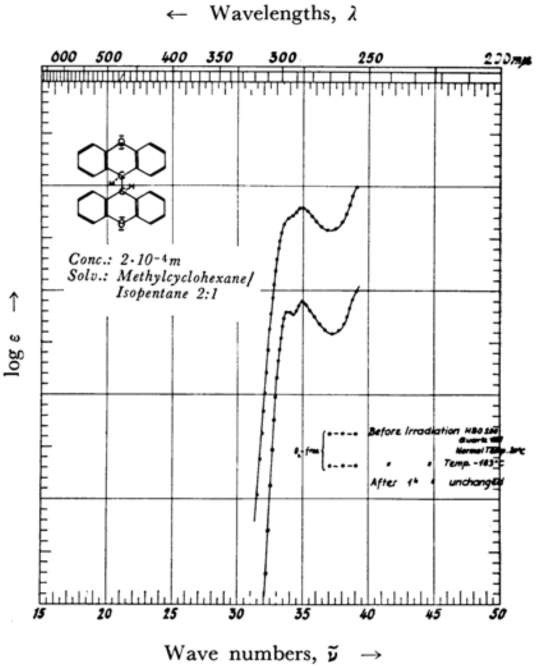

Fig. 12. Absorption spectra of dixanthene before and after irradiation.

xanthydrols (hydroxyxanthenes). In order to investigate this, we have irradiated air saturated and deoxygenized ethanolic solutions of 9, 9′-dihydroxydixanthene. The results of this investigation are plotted on Figs. 10 and 11.

In the case of oxygen containing solutions, we have obtained an oxidation to xanthone; this result if it is compared to the reaction of the diacridans but here the oxidation leads to the acridine and partly to acridan, is not extraordinary. This is proved by the appearnce of a band at 30000 cm^{-1}. As in the case of the photoreduction of xanthone or the oxidation of xanthene, here also appears another product absorbing at 33000 cm^{-1} This is like before but not yet identified in its constitution.

In deoxygenized solutions the dixanthenes are photostable. This is shown by the experiments, carried out on 9, 9′-dihydroxydixanthene and 9, 9-′dixanthene. The results are pointed out on Figs. 11 and 12. After an illumination of two hours by a HBO 200 mercury lamp at a concentration of $4 \cdot 10^{-4}$ M, no change is observable. The same result we have got for chemically synthesized 9, 9′-dixanthene. In this case also no photolytical reaction is detectable. This substance is so far not yet synthesized by photolysis.

This behavior of the dixanthenes differs from that of the diacridans. There we find photoinstability, with an exception of 9, 9′-diphenyldiacridan. Now we have the problem to understand the properties of these compounds out of their spectroscopic data. As was demonstrated in a previous paper, the monoacridans differ essentially from the diacridans by an absorption band situated in the long wave absorption region. The intensity of this band is $\log \varepsilon = 3.4 - 3.5$. The appearance of this band is indicative of $\pi \rightarrow \pi^*$-interaction between the two acridan nuclei of the diacridan, via the 9, 9′-bond. Light excitation especially affects this 9, 9′-bond and breaks it photochemically.

With the dixanthenes we miss completely such a band and they differ from the monoxanthene derivatives only little by intensity. This has been plotted on Figs. 11 and 12. The two chromophores are practically completely isolated from each other, and at the excitation no stressing of the 9, 9′-bond and no photosensibility is observable.

Photosynthesis of Further Dixanthenes.—Starting from the above mentioned results, which guided us to a reaction schedule shown before, we have supposed, that it may be possible to synthesize photolytically besides the symmetrical and unsymmetrical dixanthenes. Using a stronger H-donor than the solvent itself, we must get such products, if we would have the right conception. The stronger donor in the class of our compounds is the xanthene, respectively 9-alkyl- or 9-arylmonoxanthenes.

If we add equimolar amounts of xanthone and xanthene in benzene solution and irradiate this mixture, we get indeed a solid photoproduct. We determined the melting point and the molecular weight and found this to be a 9-*hydroxydixanthene*. This compound was prepared already photochemically by Schönberg;(22) we now synthesized this substnace by another idea. Including the other H-donors for this synthesis, we also used acridan as an H-donor. If we irradiate equimolar solutions of xanthone and acridan in benzene, we can quickly observe the precipitate of a colorless solid substance. After repeated crystallization, we have found from molecular weight, elementary analysis, and ultraviolet and infrared spectra, that here is formed a *9, 9′-diacridan*.

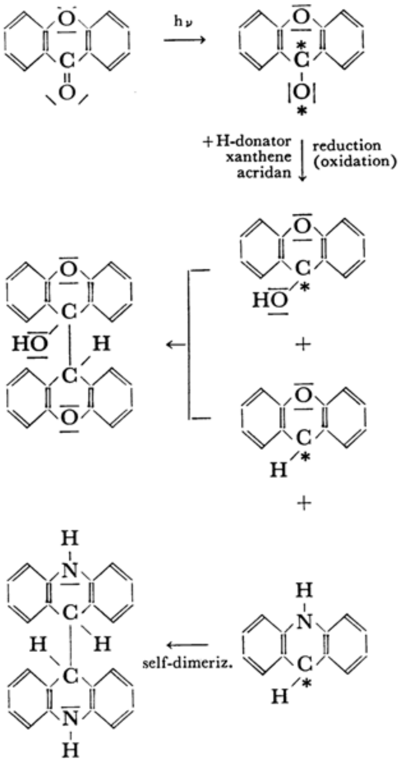

Fig. 13. Schedule of photoreaction of xanthone with xanthene resp. acridan.

In the last Fig. 13, we show a schedule to these dimerizations, which enlarges the mechanisms pointed out previously. Using suitable combination of filters, we irradiated only in the long wave absorption range of xanthone. This causes again the formation of a xanthone-diradical, fixed at the CO-group. This diradical takes over an H-atom from the stronger donor of xanthene and acridan and forms a 9-hydroxyxanthyl radical. The xanthene itself, which has the function as an H-donor, dismisses an H-atom and goes to a xanthyl radical. Combination of these two C-radicals yields the 9-hydroxydixanthene. In the second case, the xanthone diradical takes over an H-atom from the acridan and passes over to a 9-hydroxydixanthyl-radical. Simultaneously the acridan is oxydized to acridanyl-radical furnishing H-atoms. We could expect here also the formation of a mixed xanthylacridanyl dimer. But this is not occurring or presumably occurring little. The extraordinary low solubility of this substance ($4\cdot10^{-5}$ molar against $5\cdot10^{-3}$ molar of the dixanthenes) prevents the formation of a mixed product or the likewise possible dihydroxydixanthene.

So we have settled a bridge to the photolytical formation of diacridans and have found a new way, to synthesize this dimer diacridan.

We wish to express our thanks to the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie, Federal Republic Germany, for personal help and especially to Professor Masao Koizumi for his invitation to the informal meeting on photochemistry at Sendai, Septmeber, 1965, on which we could discuss the present results.

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22) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, **1944**, 67.