Tetrahedron Letters No.40, pp. 3501-3504, 1970. Pergamon Press. Printed in Great Britain.

REVERSIBLE PHOTO-VALENCE ISOMERIZATION OF TROPONOIDS

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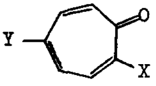
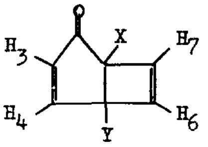
(Received in Japan 20 July 1970; received in UK for publication 28 July 1970)

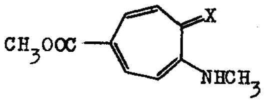
Most monocyclic troponoids are known to undergo the photochemical rearrangement to bicyclo-[3,2,0] hepta-3,6-dien-2-one derivatives (1), while tropone and 2-chlorotropone afford the dimeric products (2), and such photochemical products usually revert to original troponoids upon heating at high temperatures. However, we have found that the irradiation products (B) obtained from some of 2,5-disubstituted troponoids (A), unlike in the cases of 2,3- or 2,4-disubstituted troponoids, reverted in the dark back to original troponoids (A) even at lower than room temperature (3). A brief account of these interesting photochemical and thermal reactions are presented herein (4).



(A)



(B)



(C)

Cyclohexane solution of 5-phenyltropolone (I,A: X=OH, Y=Ph), set in a quartz Dewer vessel with transparent windows in three directions, was irradiated using a 500 W high pressure mercury arc lamp or a 500 W xenon lamp fitted with a cut-off filter. Exposure for 2 minutes to ultraviolet light of longer wavelengths than 290 nm at 16.5° resulted in a rapid decrease of the intensity of its absorption maxima, which gradually recovered in the dark to reach the same intensity with the original one as shown in Fig. 1.

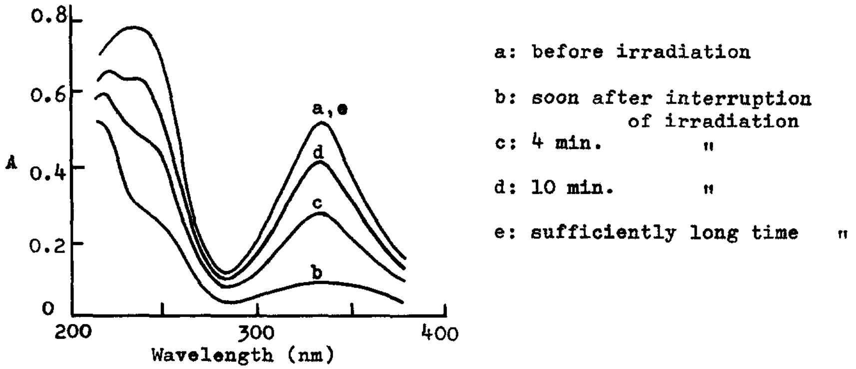


Fig. 1. Change of UV spectra of I

IR spectra showed that the photoproduct (II, B: X=OH, Y=Ph) has a strong absorption at 1718 cm^{-1} (cyclopentenone) and no band due to tropolone ring. Solution of the photoproduct can be kept at -45° without any change for a sufficiently long time, and concentrated solutions, which are necessary to measure NMR spectra, can be irradiated using specially designed quartz vessel which permit the solution to descend continuously in a thin film, thus preventing over-irradiation. NMR spectrum in $CDCl_3$ at -45° exhibited four doublets at τ=2.19(H_4), 2.93(H_6), 3.45(H_7) and 3.77(H_3) with J_{34}=6.3 and J_{67}=3.4 Hz, in addition to the signal due to a phenyl group. Comparison of these spectra with the irradiation products of tropolone methyl ethers (5), left no doubt for the structure B (X=OH, Y=Ph) for II. The reverse thermal reaction (II→I) described above can also be traced by IR or NMR spectra in which the absorptions due to II gradually decreased while those due to I increased. The change of the carbonyl region in IR spectrum of II is presented in Fig. 2.

The rate of this reaction, that is, the stability of II depends remarkably on the solvent used; the higher the polarity of the solvents, the smaller the rate constants. Activation energy of the reaction is 17, 17 and 24 kcal/mol in n-hexane, carbon tetrachloride and acetonitrile, respectively. Although oxygen and moisture have no effect on the rate, pH in aqueous solution shows a pronounced effect; the reaction may be so fast in the presence of caustic alkali that the photoisomerization (I→II) can not virtually be observed.

These isomerization reactions have been extended to various 2,5-disubstituted troponoids (6) in order to investigate the substituent effect of the reactions. It was deduced by comparison of their UV and IR spectra, the isomerization of the most other troponoids examined occurs in a similar manner as in the case of I. All the compounds, which show the easy reverse

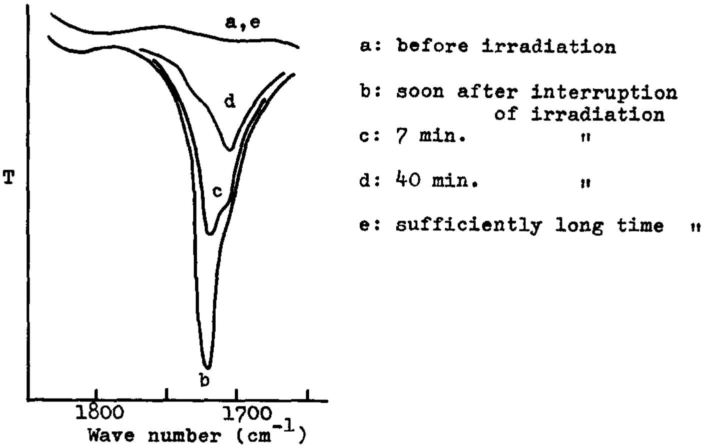


Fig. 2. Change of IR spectra (ν_{co} region) of I

isomerization (B→A), are shown in the Table 1 in order of the easiness of the reaction.

Table 1. Easiness of the reverse reaction (B→A)

Compounds (A)	X	Y	M.P.	Temp.
2-Methylamino-5-cyano-tropone	$NHCH_3$	CN	199°	-75°*
2-Amino-5-cyanotropone	NH_2	CN		-50°*
2-Methylamino-5-carboxy-tropone	$NHCH_3$	COOH	297°	-44°*
2-Methylamino-5-methoxy-carbonyltropone	$NHCH_3$	$COOCH_3$	176°	-33°*
2-Amino-5-phenyltropone	NH_2	C_6H_5		R.T.
5-Formyltropolone	OH	CHO		R.T.
5-Phenyltropolone	OH	C_6H_5		R.T.
5-Cyanotropolone	OH	CN		R.T.
5-Carboxytropolone	OH	COOH		R.T.
5-Methoxycarbonyltropolone	OH	$COOCH_3$		R.T.

*Temperature at which 50% of photoisomers in methanol were disappeared during 2 minutes. The other compounds were measured in n-hexane.

Tropolone and 2-aminotropones having the electron-withdrawal groups such as CN, COOH, $COOCH_3$, CHO and phenyl group at 5-position easily undergo the reverse reaction (B→A), the order of the easiness being roughly CN > COOH > COOMe > Phenyl. Aminotropones, especially 2-methylaminotropones react faster than the corresponding tropolones, and most of the methylaminotropone derivatives (shown in Table 1) appears at a glance to be resistant to the photoisomerization at room temperature. No reverse isomerization was detected for tropolone *with nitro, nitroso, arylazo or styryl group at 5-position at -80° to room temperature.*

Although 2-methylamino-5-methoxycarbonyltroponimine (C: X=NCH_3), m.p. 85°, and 2-methylamino-5-methoxycarbonyltropothione (C: X=S), m.p. 115°, undergo photochemical reactions, reverse thermal reactions were not observed at room temperature. On the other hand, 2-methoxy- and 2-dimethylamino-5-cyanotropones behave considerably differently upon irradiation both at room temperature and lower temperatures.

Further studies related to these reactions are in progress and details will be published elsewhere in near future.

Acknowledgement: Our sincere thanks are due to Sankyo Co. (Drs. G. Sunagawa and N. Soma) and professors K. Takase (Tohoku University) and H. Matsumura (Kumamoto University) for their generous gifts of various troponoids used in this study.

REFERENCES AND FOOTNOTES

1) For general references, see (a) O.L. Chapman, Advances in Photochemistry, 1, 323 (1963); (b) K.F. Koch, Advances in Alicyclic Chemistry, 1, 257 (1966); (c) D.J. Pasto, Organic Photochemistry, 1, 155 (1967).

2) T. Mukai, T. Tezuka and Y. Akasaki, J. Am. Chem. Soc., 88, 5025 (1966); A. Kende, ibid., 88, 5026 (1966); T. Tezuka, Y. Akasaki and T. Mukai, Tetrahedron Letters, 1967, 1397, 5003; A. Kende and J. Lancaster, J. Am. Chem. Soc., 89, 5283 (1967).

3) A part of the present result has been presented at the 20th and 22nd Annual Meeting of the Chemical Society of Japan (March, 1967 and March, 1969) T. Hirai and T. Kobayashi, Abstracts of Papers, Vol. III, p.194 and Vol. III, p.1748, respectively.

4) Very recently, Kimura and Mukai reported the similar isomerization of the irradiation products of 2-anilinotropone occured during 2 months at room temperature. M. Kimura and T. Mukai, the 3rd Symposium of the Chemical Society of Japan on the Chemistry of Nonbenzenoid Aromatic Compounds (Nov., 1969), Abstracts of Papers, p.40.

5) O.L. Chapman and D.J. Pasto, J. Am. Chem. Soc., 82, 3642 (1960); W.G. Dauben, K. Koch, S.L. Smith and O.L. Chapman, ibid., 85, 2616 (1963).

6) All new compounds are accompanied by their melting points and showed the correct analytical figures and spectroscopic properties.