CHEMISTRY LETTERS, pp. 691-692, 1983.

SYNTHESIS OF A NEW PHOTO-STABLE SPIROPYRAN

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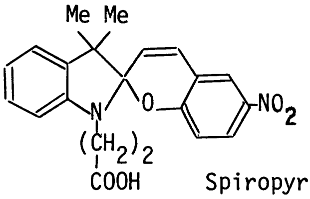
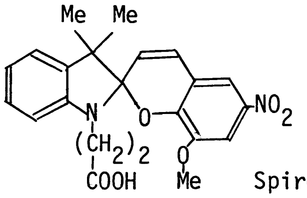
3',3'-Dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-indoline)-1'-propionic acid [I] was modified with a methoxy group at 8th position of the pyran ring. The stability of photoresponsive activity was 3.4 times higher than that of [I]. The new spiropyran is promising for the photocontrol of enzyme activity.

3',3'-Dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-indoline)-1'-propionic acid [I] has been synthesized and applied to the photocontrol of enzyme activity.1)-4) However, the photosensitivity of the spiropyran compound [I] decreased with successive utilization possibly due to the irreversible isomerization (photodegradation).5) Formerly, Gautron investigated the stability of several derivatives of 6-nitro-1',3',3'-trimethylspiro(2,2'-indolinyl-2*H*-benzopyran). It was shown that introduction of nucleophilic groups such as methoxy group or replacement of benzopyran ring by naphthopyran ring improved the stability of photoresponsive activity.6),7) Accordingly the stabilization of spiropyran was attempted by introducing a methoxy group to 8th position of the pyran ring of the compound [I]. 3',3'-Dimethyl-8-methoxy-6-nitrospiro(2*H*-1-benzopyran-2, 2'-indoline) -1'-propionic acid [II] was newly prepared from 1-(β-2-carboxyethyl)-3,3-dimethylindolenium iodide and 5-nitro-*O*-vanilline in the presence of piperidine.

The spiropyran compound [I] was prepared according to Namba et al.1) and used as a standard. The compound [II] was compared with the compound [I]. The values of Rf were 0.48 [I] and 0.47 [II] respectively when benzene-dioxane-acetic acid (100:15:1) mixture was used for thin layer chromatography. The specific absorptions of the compound [II] were relatively greater than those of compound [I] at 1448 - 1456 cm^{-1} and 2860 cm^{-1}. The peak at 3.78 ppm of H-NMR was assigned as three protons of the methoxy group. From these observations, the new compound [II] was assigned as a methoxy derivative of compound [I]. The compound [II] showed normal photochromism in dioxane and its photochromic property was remarkably affected by water, as shown in Fig. 1. When water



Spiropyran [I]



Spiropyran [II]

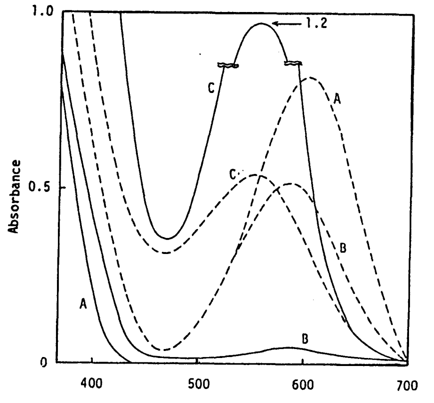


Fig.1 Spectral Change of Compound [II] due to UV Light Irradiation. Water Contents:(A)0%,(B) 0.34%,(C)0.88%. Spiropyran 10^{-4}M. Temp.21°C. (——)Before,(---)10 sec After Irradiation.

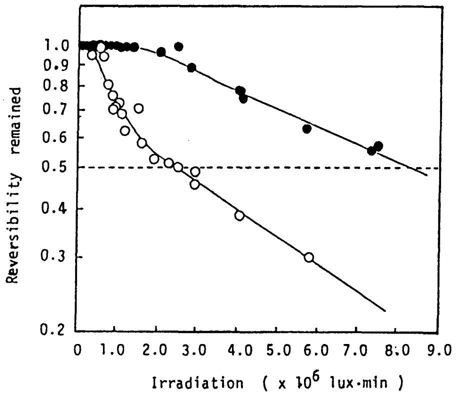


Fig.2 Stability of Photo Responsive Activity of Spiropyran Compounds [I] and [II]. (c) Compound [I] 10^{-4} M, (c) Compound [II] 10^{-4} M, Temperature 21°C.

mole fraction was above 0.8, the compound [II] showed reverse photchromism.

The stability of the photoresponsiveness was examined by flash illumination method. Spiropyran compound [I] (or [II]) was dissolved in dioxane (10^{-4} M) and transferred in a Thunberg tube and filled with nitrogen gas. The spectrum of the solution was measured with a rapid scan spectrophotometer after storage at 20℃ for 24h in the dark. Then the solution was irradiated for 10 sec (flash illumination) with near ultraviolet light. The spectrum was measured 10 sec after shielding of light. Optical densities before and after flash illumination at the absorbance peak were represented as $OD^{D}_{t=0}$ and $OD^{L}_{t=0}$ respectively. The difference of $OD^{D}_{t=0}$ and $OD^{L}_{t=0}$ was defined as the initial photoresponsive activity. After the continuous irradiation of visible light, the photoresponsive activity was measured as above. The difference of $OD^{D}_{t=t}$ and $OD^{L}_{t=t}$ was plotted against irradiation time (t). The life time (τ) of the spiropyran was determined from the equation : $(OD^{L}_{t=\tau} - OD^{D}_{t=\tau})/(OD^{L}_{t=0} - OD^{D}_{t=0}) = 1/2$. Photoresponsiveness of the compound [I] decreased markedly after 1.0×10^{6} lux•min irradiation as shown in Fig. 2. The half life time was estimated 2.5×10^{6} lux•min. On the other hand, the compound [II] retained more than 90 % of initial activity for more than 2.5×10^{6} lux•min, and the half life time of [II] was 8.5×10^{6} lux•min.

This improvement was attributed to the stabilization of opened ring structure of pyran in a similar manner to spiropyran derivatives prepared by Gauton.[7)] The ionic state of oxygen atom of opened pyran ring can be stabilized by introducing a methoxy group at the ortho or para position. Further developmental studies in this laboratory are being directed toward applying the new compound [II] to the photocontrol of synthetic reactions using hydrolyzing enzymes.

References

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(Received January 29, 1983)