

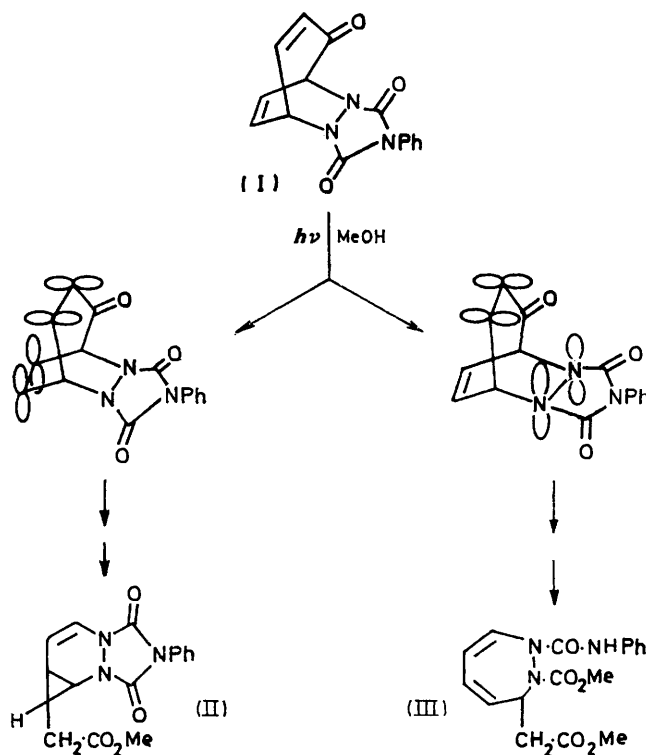
Studies of Heteroaromaticity. Part LIX.¹ Further Investigations of the Cycloaddition Reactions of Tropone with Azo-dienophiles and the Photochemical Behaviour of the Adducts

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The reactions of tropone with phthalazine-1,4-dione and 4,4-diethylpyrazoline-3,5-dione give the normal $[4 + 2]\pi$ -cycloadducts (V) and (VII), in 38 and 18% yield, respectively. Irradiation of the adducts (V) and (VII) and the tropone-*N*-phenylmaleimide adduct (XIV) in protic solvents gives one photo-product in high yield in each case. These photoproducts are formed by addition of the solvents to the initially formed ketens, thus providing an efficient synthesis of heterotricyclic compounds.

RECENTLY, cycloaddition reactions of azo-dienophiles such as 4-phenyl-1,2,4-triazoline-3,5-dione,²⁻⁴ phthalazine-1,4-dione,⁵⁻⁷ 4,4-diethylpyrazoline-3,5-dione,^{8,9} and others¹⁰ have been extensively studied. In a previous paper,¹¹ we reported the reaction of tropone with 4-phenyl-1,2,4-triazoline-3,5-dione and the photochemical behaviour of the adduct (I) to give two photoisomeric products (II) and (III) by different $[3,3]$ -sigmatropic rearrangements. This behaviour stemmed from the fact that the triazolinedione system (I) has the *cis*-configuration, with the nitrogen atoms having substantial sp^2 character.⁸ As a continuation of this work, we have prepared a series of compounds containing the 6,7-diazabicyclo[3,2,2]nona-3,8-dien-2-one

system, and have also studied their photochemistry. This paper deals with the reactions of tropone with



¹ Part LVIII, T. Sasaki, K. Kanematsu, and A. Kakehi, *Tetrahedron*, in the press.

² R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. (C)*, 1967, 1905.

³ (a) A. B. Evinin and D. R. Arnold, *J. Amer. Chem. Soc.*, 1968, **90**, 5330; (b) A. B. Evinin, D. R. Arnold, L. A. Karnischky, and E. Strom, *ibid.*, 1970, **92**, 6218.

⁴ E. K. Gustorf, D. V. White, B. Kim, D. Hess, and J. Leitich, *J. Org. Chem.*, 1970, **35**, 1155.

⁵ R. A. Clement, *J. Org. Chem.*, 1960, **25**, 1724.

⁶ T. J. Kealy, *J. Amer. Chem. Soc.*, 1962, **84**, 966.

⁷ O. L. Chapman and S. J. Dominianni, *J. Amer. Chem. Soc.*, 1966, **31**, 3862.

⁸ A. B. Evinin, A. Y. Lam, and J. J. Blyskal, *Tetrahedron Letters*, 1969, 4497.

⁹ B. T. Gillis and R. A. Izydore, *J. Org. Chem.*, 1969, **34**, 3181.

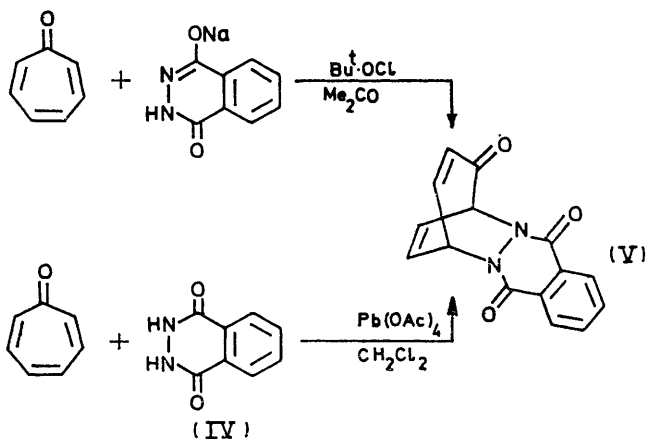
¹⁰ E. Fahr and H. Lind, *Angew. Chem.*, 1966, **78**, 376.

¹¹ (a) T. Sasaki, K. Kanematsu, and K. Hayakawa, *Chem. Comm.*, 1970, 82; (b) *J. Chem. Soc. (C)*, 1971, 2142.

phthalazine-1,4-dione and 4,4-diethylpyrazoline-3,5-dione, and the photochemical behaviour of the adducts.

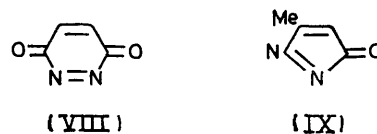
The azo-dienophiles, derived from the oxidation of the dihydrophthalizinedione (IV) and 4,4-diethylpyrazolidine-3,5-dione (VI) with *t*-butyl hypochlorite, reacted with tropone in acetone (-50°) and dioxan (room temperature) to afford the 1:1 adducts (V) and (VII), in 38 and 18% yield, respectively.

The reaction of phthalazine-1,4-dione, prepared by the



oxidation of the dihydro-derivative (IV) with lead tetraacetate, and tropone in methylene chloride also gave the adduct (V), but in lower yield (4%). Compound (V) was identified by its i.r. and n.m.r. spectra. Its mass

compound (I) except for the signals of the two additional ethyl groups. The mass spectrum showed a characteristic molecular ion peak at m/e 260 and an intense peak at $M-154$ (m/e 106, loss of $C_7H_{10}N_2O_3$ by a retro-Diels-Alder fragmentation). Compounds (V) and (VII) were concluded to be normal [$\pi 4_s + \pi 2_s$] cycloadducts. Treatment of tropone with pyridazine-3,6-dione (VIII)⁶ or 5-methylpyrazol-3-one (IX)¹² under various conditions did not give any products.



Irradiations of the adduct (V) in methanol and in acetonitrile-water at room temperature for 45 min with a high pressure 100 W mercury lamp in a Pyrex vessel under nitrogen gave one product in each case [(XIIa) or (XIIb)], in 93 and 88% yield, respectively.

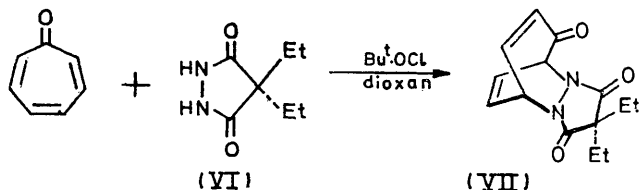
Elemental analysis and mass spectroscopy (M^+ , 298; similar pattern to the spectrum of a photo-product formed from tropone and diethyl azodicarboxylate,¹³ showed the product from methanol to be a methyl ester, which was formed by addition of methanol to an initially formed keten (X). The n.m.r. spectral data of compound (XIIa) are in the Table. The photo-product (XIIb) was similarly shown to be a carboxylic acid.

N.m.r. spectra of photoproducts, τ ($CDCl_3$)

| Compd. | H _a | H _b | H _{c,d} | H _e | CH ₂ | R | Others | Coupling constant (Hz) |
|---------|----------------|----------------|------------------|----------------|-----------------|--------------------------------|--|---|
| (XIIa) | 2.52(d) | 4.57(dd) | 7.88—8.11(m) | 6.15(t) | 7.67(m) | 6.40(s) ^a | 1.77(2H, m, ArH), 2.32 (2H, m, ArH) | J_{AB} 9.0 J_{BC} 3.5 J_{DE} 6.5 |
| (XIIIa) | 3.04(d) | 4.75(dd) | 7.95—8.38(m) | 6.42(t) | 7.82(m) | 6.30(s) ^a | 7.95—8.38(4H, m, CH_2CH_3), 9.17 (6H, m, CH_2CH_3) | J_{AB} 8.0 J_{BC} 3.0 J_{DE} 6.0 |
| (XIIIb) | 3.02(d) | 4.75(dd) | 7.87—8.38(m) | 6.38(t) | 7.75(m) | 5.88(q) 8.76(t) ^b | 7.87—8.38(4H, m, CH_2CH_3), 9.07 (6H, m, CH_2CH_3) | J_{AB} 7.8 J_{BC} 3.6 J_{DE} 5.5 |
| (XVIa) | 4.24(dd) | 3.92(dd) | 7.98—8.50(3H,m) | | 7.76(m) | 6.32(s) ^a | 2.64(5H, m, ArH), 6.67(2H, m, bridgehead) | J_{AB} 10.2 J_{BC} 5.5 J_{AC} 2.0 |
| (XVIb) | 4.20(dd) | 3.91(dd) | 8.12—8.47(3H,m) | | 7.67(m) | 2.58—2.76 ^c (1H) | 2.65(5H, m, ArH), 6.64(2H, m, bridgehead) | J_{AB} 8.8 J_{BC} 4.5 J_{AC} 2.0 |

^a Methyl ester. ^b Ethyl ester. ^c Carboxylic acid (overlapping with ring protons).

spectrum showed a characteristic molecular ion peak at m/e 266 and an intense peak at $M-160$ (m/e 106,



loss of $C_8H_4N_2O_2$ by a retro-Diels-Alder fragmentation). The n.m.r. spectrum of (VII) is very similar to that of

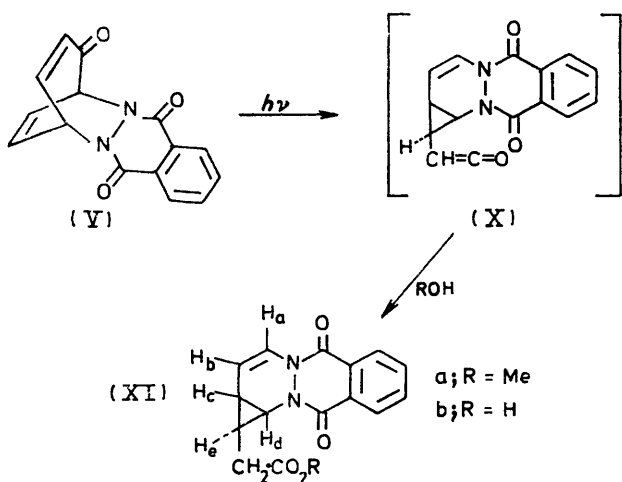
Irradiation of compound (VII) in methanol under the same conditions gave a single product, which was shown to be a methyl ester (XIIIa) by elemental analysis and spectroscopy (Table).

Interestingly the adduct (VII), in ethanol, was slowly converted into the ethyl ester (XIIIb) at room temperature with a half-life of 2 weeks. When refluxed in ethanol, compound (VII) was completely converted into the ethyl ester (XIIIb). The structure of (XIIIb)

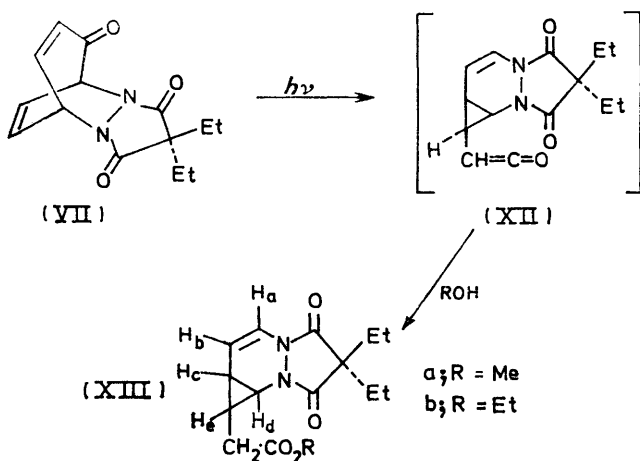
¹² B. T. Gillis and R. Weinkan, *J. Org. Chem.*, 1967, **32**, 3321.

¹³ O. L. Chapman, M. Kane, J. D. Lassila, R. L. Laesch, and H. E. Wright, *J. Amer. Chem. Soc.*, 1969, **91**, 6856.

was confirmed by the n.m.r. spectrum [by comparison with that of (XIIIa)]. Thus, the product (XIIIb)



was formed by addition of ethanol to the thermally formed keten (XII).

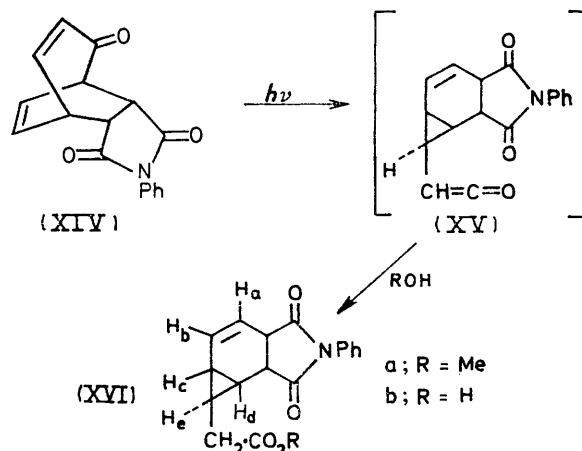


Analogously, irradiations of compound (XIV)¹⁴ in methanol and in water-acetonitrile under the same conditions in each case afforded one product [(XVIa) or (XVIb)] in 90 and 94% yield, respectively. The structures (XVIa) and (XVIb) were confirmed by elemental analyses and spectral data (Table). The stereochemistry of these cycloadducts [(I), (V), and (VII)] was examined by variable temperature n.m.r. spectroscopy. However, the spectra show no temperature dependence down to -40° . This indicates that the configurations of the nitrogen atoms are either planar, which is the preferred explanation, or are pyramidal but rapidly inverting.⁸

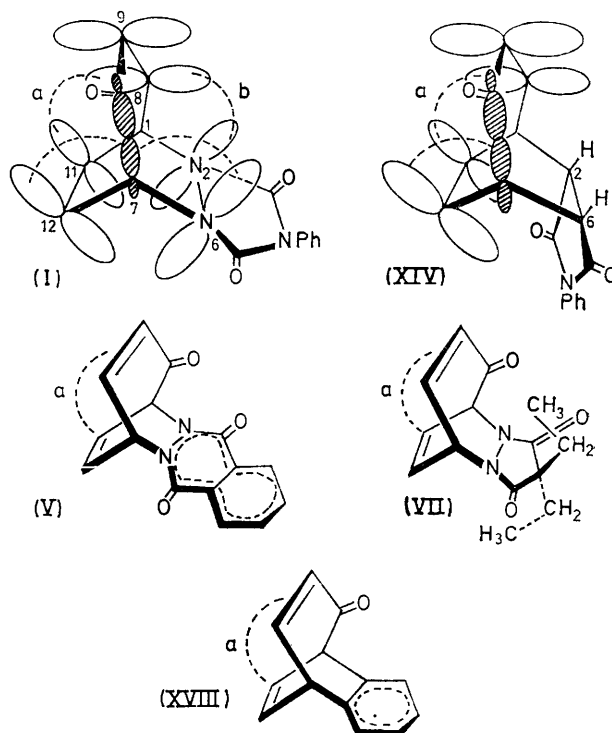
Experimentally, in the case of the photolysis of compound (I), two photoproducts (II) and (III) were independently obtained from competitive [3,3]-photorearrangements,^{11b} whereas irradiation of compounds (V), (VII), and (XIV) gave only one product. This

¹⁴ J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *J. Amer. Chem. Soc.*, 1955, **77**, 4401.

indicates that nitrogen-nitrogen bonding in structures (V) and (VII) does not participate in the photorearrangement as in compound (I). Since the lower chemical shifts of the bridgehead protons of compound (V) compared with those of (I) and (VII) suggest a sub-



stantial diamagnetic effect of the ring current and, therefore, stabilization of the lone-pair electrons of the nitrogen atoms by delocalization (Figure), participation of nitrogen-nitrogen bonding in the rearrangement is energetically unfavourable. Similar behaviour has been observed in the rearrangement of the tropone-benzene adduct (XVIII).^{3,15} In the case of compound



(VII), such an electronic effect was not observed in the n.m.r. spectrum, but instead the steric effect of the

¹⁵ A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *J. Amer. Chem. Soc.*, 1969, **91**, 6858.

two ethyl groups gives the same effect. The two ethyl groups cover the pyrazolinedione portion from both sides and participation of nitrogen–nitrogen bonding in the [3,3]-photorearrangements is restricted. In the case of compound (XIV), the C(2)–C(6) bond has no sp^2 -character and therefore, interaction of p orbitals of the C(11)–C(12) double bond with the bridged olefin and the C(7)–C(8) σ -bond is only possible *via* path a in the Figure.

From these facts, we conclude that interaction of p orbitals in the excited state is important in determining the course of the photorearrangement.

EXPERIMENTAL

M.p.s were measured with a Yanagimoto apparatus. Microanalyses were performed with a Perkin-Elmer 240 elemental analyser. U.v. spectra were determined with a JASCO ORD-UV-5 recorder. N.m.r. spectra were taken with a JEOL C-60-XL spectrometer and with a Varian A60 recording spectrometer, with tetramethylsilane as internal standard. I.r. spectra were taken with a JASCO-IR-S spectrophotometer. Mass spectra were obtained with a Hitachi RMU-D double-focusing spectrometer operating at an ionization potential of 70 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 100–150°.

6,7-Phthaloyl-6,7-diazabicyclo[3,2,2]nona-3,8-dien-2-one (V).—(a) *Oxidation by t-butyl hypochlorite.* To a suspension of the sodium salt of 2,3-dihydrophthalazine-1,4-dione (1.74 g) in dry acetone (30 ml) at -77° , was added t-butyl hypochlorite (1.2 g). After vigorous stirring for 3 h at -50° , tropone (1.0 g) was added. After additional stirring for 6 h at -50° , the precipitate was filtered off and evaporation to dryness at reduced pressure followed by chromatography on silicic acid and recrystallization from ethyl acetate gave the adduct (V) (1.0 g) as yellow crystals, m.p. 272–274° (Found: C, 67.8; H, 3.95; N, 10.6. $C_{15}H_{10}N_2O_3$ requires C, 67.65; H, 3.8; N, 10.5%), ν_{\max} (KBr) 1690, 1640, and 1604 cm^{-1} , m/e 266 and 106, τ ($CDCl_3$) 1.74 (2H, m, ArH), 2.27 (2H, m, ArH), 2.86 (1H, q, J 11.4 and 8.0 Hz, HC=), 3.08 (1H, dd, J 9.0 and 6.5 Hz, HC=), 3.47 (1H, dd, J 9.0 and 6.5 Hz, HC=), 4.13 (1H, dd, J 11.4 and 1.5 Hz, HC=), 3.63 (1H, t, J) 8.0 and 6.5 Hz), and 3.75 (1H, dd, J 6.5 and 1.5 Hz).

(b) *Oxidation by lead tetra-acetate.* A suspension of the dihydrophthalazinedione (IV) (0.81 g) in methylene chloride (20 ml) containing tropone (0.53 g) was treated with lead tetra-acetate (2.30 g) and stirred vigorously at room temperature until no more of the salt was consumed (20 g). The brown solid was filtered off and the solution was evaporated to dryness under reduced pressure, to give the adduct (V) (0.055 g).

4,4-Diethyl-2,6-diazatricyclo[5,3,2,0^{2,6}]dodeca-9,11-diene-3,5,8-trione (VII).—4,4-Diethylpyrazoline-3,5-dione was prepared by oxidation of 4,4-diethylpyrazolidine-3,5-dione (VI) with t-butyl hypochlorite in acetone and was used without isolation. After vigorous stirring of the dione for 3 h at -50° , tropone (0.68 g) in dioxan (20 ml) was added at room temperature. The colour was discharged gradually. After stirring for 1 day, evaporation to dryness at reduced pressure followed by chromatography on silica

gel the adduct (VII) (0.18 g) was obtained as a yellow oil, n_D^{20} 1.5248, ν_{\max} (film) 2970, 2920, 1730, 1690, and 1685 cm^{-1} , m/e 260 and 106, τ ($CDCl_3$) 2.93 (1H, q, J 12.0 and 7.0 Hz, HC=), 3.15 (1H, t, J 8.2 Hz, HC=), 3.63 (1H, t, J 8.2 and 6.8 Hz, HC=), 4.07 (1H, dd, J 12.0 and 1.5 Hz, HC=), 4.52 (1H, t, J 8.2 and 7.0 Hz), 4.57 (1H, dd, J 6.8 and 1.5 Hz), 8.41 (4H, m, $2 \times CH_2-CH_3$), and 9.18 (6H, m, $2 \times CH_2-CH_3$).

Irradiation of Compound (V).—(a) *In methanol.* The adduct (V) (0.60 g) was irradiated in methanol (60 ml) for 45 min with a high-pressure 100 W mercury lamp in a Pyrex vessel under nitrogen. Evaporation to dryness at reduced pressure and recrystallization from methanol gave methyl 2,3-phthaloyl-2,3-diazabicyclo[4,1,0]hept-4-en-7-ylacetate (XIa) (0.63 g) as pale yellow needles, m.p. 151–152° (Found: C, 64.25; H, 4.75; N, 9.25. $C_{16}H_{14}N_2O_4$ requires C, 64.4; H, 4.75; N, 9.4%), ν_{\max} (KBr) 1730, 1650, and 1604 cm^{-1} , m/e 298 and 266.

(b) *In water-acetonitrile.* The adduct (V) (0.16 g) was irradiated in water-acetonitrile (1:1) (50 ml) under the same condition as in (a). A similar work-up gave 2,3-phthaloyl-2,3-diazabicyclo[4,1,0]hept-4-en-7-ylacetic acid (XIb) (0.15 g) as yellow prisms, m.p. 231–232° (Found: C, 63.2; H, 4.3; N, 9.6. $C_{15}H_{12}N_2O_4$ requires C, 63.3; H, 4.25; N, 9.85%), ν_{\max} (KBr) 3080–2800, 1710, 1640, and 1604 cm^{-1} , m/e 284 and 225. The n.m.r. spectrum of the compound was not taken because of insolubility in $CDCl_3$.

Irradiation of Compound (VII).—The adduct (VII) (0.09 g) was irradiated in methanol (40 ml) under the same conditions as above. Evaporation and chromatography on silicic acid gave methyl 8,10-dioxo-9,9-diethyl-1,7-diazatricyclo[5,3,0,0^{2,4}]dec-5-en-3-ylacetate (XIIIa) (0.085 g) as a yellow oil, n_D^{24} 1.5254 (Found: C, 61.68; H, 6.85; N, 9.7. $C_{15}H_{20}N_2O_4$ requires C, 61.65; H, 6.9; N, 9.6%), ν_{\max} (film) 2970, 2920, 1730, 1700, 1685, and 1640 cm^{-1} , m/e 292 and 260.

Thermal Reaction of Compound (VII).—Refluxing the adduct (VII) (0.03 g) in ethanol (5 ml) for 1 week and evaporation to dryness followed by chromatography on silicic acid gave ethyl 8,10-dioxo-9,9-diethyl-1,7-diazatricyclo[5,3,0,0^{2,4}]dec-5-en-3-ylacetate (XIIIb) (0.02 g) as a yellow oil, n_D^{22} 1.5121, ν_{\max} (film) 2980, 2930, 1730, 1720, 1690, and 1640 cm^{-1} , m/e 306 and 260 [fragmentation pattern is similar to that of (XVIIIa)].

Irradiation of Compound (XIV).—(a) *In methanol.* The adduct (XIV) (0.50 g) was irradiated in methanol (80 ml) under the same conditions; work-up as above afforded methyl 8,10-dioxo-9-phenyl-9-azatricyclo[5,3,0,0^{2,4}]dec-5-en-3-ylacetate (XVIa) (0.50 g) as needles, m.p. 106–108° (Found: C, 69.2; H, 5.5; N, 4.2. $C_{18}H_{17}NO_4$ requires C, 69.45; H, 5.5; N, 4.5%), ν_{\max} (KBr) 1770, 1740, 1710, and 1600 cm^{-1} , m/e 311 and 279.

(b) *In water-acetonitrile.* The adduct (XIV) (0.30 g) in water-acetonitrile (1:1) (60 ml) was irradiated under the same conditions; similar work-up gave 8,10-dioxo-9-phenyl-9-azatricyclo[5,3,0,0^{2,4}]dec-5-en-3-ylacetic acid (XVIb) (0.30 g) as prisms, m.p. 185–187° (Found: C, 68.8; H, 5.2; N, 4.65. $C_{17}H_{15}O_4N$ requires C, 68.65; H, 5.1; N, 4.7%), ν_{\max} (KBr) 3240–2930, 1770, 1730, 1700, and 1600 cm^{-1} , m/e 297.