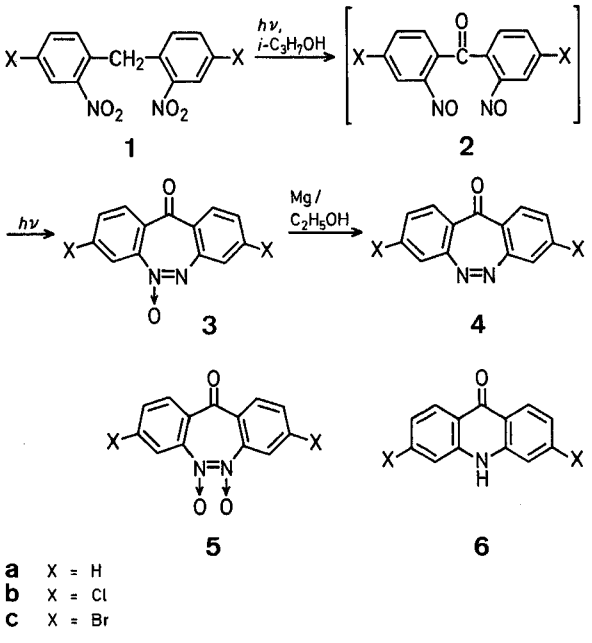
Photolysis of 2,2'-Dinitrodiphenylmethanes. A New Route to the Dibenzo[*c*,*f*][1,2]diazepine System

C. P. JOSHUA* and P. K. RAMDAS

Department of Chemistry, University of Kerala, Trivandrum, India-695001

Our interest in the photochemical reactions of dibenzo[*c*,*f*][1,2]diazepin-11-ones (**4**) necessitated the preparation of these compounds. One available method involves alkaline glucose reduction of 2,2'-dinitrobenzophenone[1]. The other one[2] uses the chromic anhydride oxidation of 11*H*-dibenzo[*c*,*f*][1,2]diazepines which in turn are obtained by lithium aluminium hydride reduction of 2,2'-dinitrodiphenylmethanes (**1**). Another feasible method appeared to be the photochemical intramolecular oxygen insertion and reductive coupling of **1**. Since photochemical reactions of dinitroarenes of this type have not been investigated so far, we examined the photochemical behaviour of a few of these compounds.

An isopropyl alcohol solution of **1a**[3] (0.024*M*) on irradiation with a 125W high-pressure mercury-quartz lamp for 25 h was found to yield 11-oxo-11*H*-dibenzo[*c*,*f*][1,2]diazepine 5-oxide (**3a**; 40%), 11-oxo-11*H*-dibenzo[*c*,*f*][1,2]diazepine 5,6-dioxide (**5a**; 20%), acridone (**6a**; 15%), and 2,2-dinitrobenzophenone (4%). Both *N*-oxides, **3a** and **5a**, were readily converted to **4a** in near quantitative yields by reduction with magnesium in ethanol. By extending the irradiation time to 30 h, the yield of **3a** was increased to 45% at the expense of **5a**. This relationship between **3a** and **5a** indicates that the reaction proceeds via the intermediate **2a**, formed by two successive oxygen insertion reactions. Photochemical reductive coupling of compound **2a** then yields **3a**. Due to the proximity of the two nitroso groups, photochemically unchanged **2a** forms **5a** by intramolecular dimerisation (probably as a dark reaction). The formation of acridone could be explained by photodissociation of one of the C—NO bonds in **2a** followed by coupling and photoreduction of the nitroxyl intermediate[4] thus formed. 2,2'-Dinitrobenzophenone possibly results from intermolecular photoredox reactions which occur to a small extent.



4,4'-Dichloro- and 4,4'-dibromo-2,2'-dinitrodiphenylmethanes (**1b** and **1c**)[2,5] were selected to test the generality of this interesting photo reaction. Analogous behaviour was observed for both and the *N*-oxides, **3b** and **3c**, were obtained

Table. Preparation and Properties of 11-Oxo-11*H*-dibenzo[*c*,*f*][1,2]diazepine 5-Oxides (**3**)

Product	M.p.	Yield (%)	I.R. (KBr) ν_{max} (cm^{-1})	U.V. (Ethanol) λ_{max} (nm)	Elemental Analysis				
3a[a]	204°[b]	45	1660, 1450, 1310	248, 337	$C_{13}H_8N_2O_2$ (224.1)	calc.	C 69.64	H 3.57	N 12.50
						found	69.51	3.70	12.41
3b	265°[c]	38	1680, 1455, 1305	230, 248, 336	$C_{13}H_6Cl_2N_2O_2$ (293.0)	calc.	C 53.26	H 2.05	N 9.57
						found	53.13	2.26	9.49
3c	278°[c]	35	1680, 1440, 1300	236, 250, 330	$C_{13}H_6Br_2N_2O_2$ (381.9)	calc.	C 40.86	H 1.57	N 7.34
						found	40.81	1.77	7.39

[a] ^{1}H-N.M.R. ($CDCl_3$): δ = 8.3–8.1 (m, $1H_{arom}$), 7.9–7.6 ppm (m, $7H_{arom}$).
[b] Recrystallised from ethanol.
[c] Recrystallised from benzene/petroleum ether.

as the major products. These could also be readily converted in ~100% yields to the corresponding dibenzodiazepinones (**4b** and **4c**) when reduced with magnesium in ethanol. The structures of the *N*-oxides **3** were established by elemental analyses and spectral data.

The following procedure is representative of the reactions described in this communication.

Irradiation of 2,2'-Dinitrodiphenylmethane (1a):
A solution of **1a** (1 g, 0.0039 mol) in isopropyl alcohol (160 ml) was irradiated for 30 h by immersing a Philips HPK 125W high pressure mercury-quartz lamp surrounded by a water cooled quartz outer jacket. Isopropyl alcohol was then distilled off from the photolysed solution and the residue chromatographed on a column of neutral alumina (65 g). Elution with petroleum ether gave unchanged **1a**; yield: 25 mg; followed by 2,2'-dinitrobenzophenone; yield: 40 mg; m.p. 188°; mixture m.p. 188° with an authentic sample[1]. Further elution with petroleum ether/benzene mixture (2:1 v/v) resulted in the separation of an yellow band. Evaporation of the eluate and recrystallisation of the residue from ethanol gave 11-oxo-11*H*-dibenzo[*c,f*][1,2]diazepine 5-oxide (**3a**); yield: 450 mg; yellow needles, m.p. 204°. Then the column was eluted with benzene/chloroform mixture (1:1 v/v). Removal of the solvent and crystallisation of the residue from acetic acid gave acridone (**6a**); yield: 210 mg; m.p. 354° (Ref[6], m.p. 354°). Final elution with chloroform yielded 11-oxo-11*H*-dibenzo[*c,f*][1,2]diazepine 5,6-dioxide (**5a**); yield: 100 mg; which crystallised from isopropyl alcohol as yellow needles; m.p. 181° (dec.).

$C_{13}H_8N_2O_3$	calc.	C 65.00	H 3.33	N 11.67
(240.1)	found	64.91	3.47	11.63

I.R. (KBr): $\nu_{max} = 1690, 1380, 1320\ cm^{-1}$.

U.V. (C_2H_5OH): $\lambda_{max} = 251, 317$ nm.

^1H-N.M.R. ($CDCl_3$): $\delta = 8–8.2(m, 2H_{arom}), 7.4\ 7.9$ ppm (m, $6H_{arom}$).

Mass spectrum: $m/e = 240\ (M^+)$.

Dibenzo[*c,f*][1,2]diazepin-11-one (4a):
11-Oxo-11*H*-dibenzodiazepinone-N-oxide (**3a**; 500 mg, 0.0022 mol) was refluxed with ethanol (50 ml) and finely divided magnesium ribbon (0.5 g) for $1^1/_2$ h and filtered. Concentration of the filtrate gave shining orange needles of dibenzo[*c,f*][1,2]diazepin-11-one (**4a**); yield: 450 mg (98%); m.p. 197° (Ref[1], m.p. 197°).

$C_{13}H_8N_2O$	calc.	C 75.00	H 3.85	N 13.46
(208.1)	found	74.93	4.02	13.35

Similarly prepared were: 3,8-dichlorodibenzo[*c,f*][1,2]diazepin-11-one (**4b**); yield: 98%; m.p. 234°.

$C_{13}H_6Cl_2N_2O$	calc.	C 56.33	H 2.17	N 10.11
(277.02)	found	56.16	2.33	10.19

and 3,8-dibromodibenzo[*c,f*][1,2]diazepin-11-one (**4c**); yield: 96%; m.p. 238°.

$C_{13}H_6Br_2N_2O$	calc.	C 42.64	H 1.64	N 7.64
(365.9)	found	42.50	1.73	7.65

The authors thank the C.S.I.R., New Delhi for the award of a Junior Research Fellowship to P.K.R.

Received: August 16, 1974

* To whom enquiries should be addressed

[1] R. B. Johns, K. R. Markham, *J. Chem. Soc.* **1962**, 3712.
[2] A. Catala, F. D. Popp, *J. Heterocyclic Chem.* **1**, 178 (1964).
[3] W. Theilackar, O. Korndorfer, *Tetrahedron Lett.* **1959**, 5.
[4] J. A. Maassen, H. Hittenhausen, T. deBoer, *Tetrahedron Lett.* **1971**, 3213.
[5] L. Mascarelli, B. Toschi, T. Zamboni, *Atti. accad. Licei.* [II] **19**, 338 (1910); *C. A.* **5**, 473 (1911).
[6] C. F. H. Allen, G. H. W. McKee, *Org. Synth., Coll. Vol.* II, 15 (1943).