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Photochemical reactions of 2-bromotropone and 2,7-dibromotropone with 9,10-dicyanoanthracene

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The photochemical reactions of 2-bromotropone and 2,7-dibromotropone with 9,10-dicyanoanthracene gave products with anthracene, anthracenone, and dihydroanthracene skeletons both in polar and non-polar solvents. These products were formed by attack of water contaminated in the solvent, by attack of the troponoid, and by attack of the solvent used in the reactions, respectively, on a reaction intermediate. In a mixed solvent of benzene and methanol, a benzaldehyde derivative with a tribenzo-2-oxabicyclo[3.2.2]nonane system was obtained. This result was informative about the reaction mechanism, and suggested the formation of an [8+4]π cycloadduct with a tribenzo-2-oxabicyclo[3.2.2]nonane system between the troponoid as the 8π component and the 9,10-dicyanoanthracene as the 4π component. In non-polar benzene, a new tetrabromodihydroanthracene derivative was obtained together with anthracenone and anthracene derivatives. It was proved by the reaction in benzene-d_6 that the new product was formed by attack of benzene-d_6.

Introduction

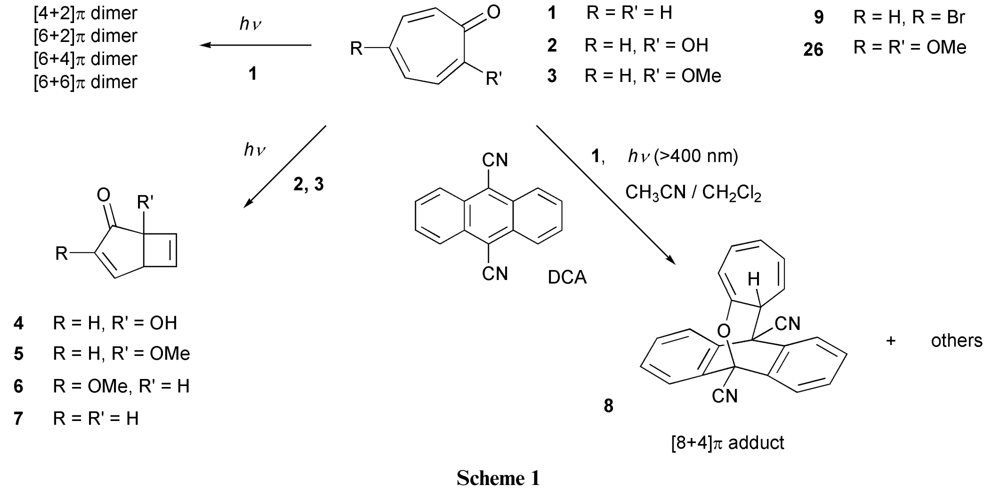
The photochemistry of troponoids was investigated under various conditions more than four decades ago; tropone (**1**) gives [4+2], [4+6], [6+2], and [6+6] photodimers under various reaction conditions[1] while tropolone (**2**)[2a] and 2-methoxytropone (**3**)[2b] give 1-substituted bicyclo[3.2.0]heptadienone photoisomers (**4** and **5**) (Scheme 1), and both did not give rise to photodimerization. In an acidic medium, **3** gave a 3-substituted bicyclo[3.2.0]heptadienone (**6**) and **1** afforded bicyclo[3.2.0]heptadienone (**7**).[3,4] The reaction mode of **3** is dependent on the medium. *Ab initio* calculations on **1** showed that **1** has the n,π* lowest excited state in neutral conditions and the π,π* lowest excited state in an acidic medium.[4]

Recently, we reported the photochemical reaction of **1** and 9,10-dicyanoanthracene (DCA) by irradiation of DCA with a longer wavelength than 400 nm.[5] From the reaction in a mixed solvent of polar acetonitrile and dichloromethane, an [8+4]π adduct (**8**) was obtained *via* an electron transfer process together with the products *via* an energy transfer process although the electron transfer process is endothermic ($\Delta G = +1.2$ kcal mol^{-1}). In non-polar benzene, however, only the adducts *via* an energy transfer process were obtained. The polarity of the reaction media and the nature of the substituents are quite influential on the photochemical reactions.[6] In this paper, we report the photochemical reactions of DCA and 2-bromotropone (**9**) and 2,7-dibromotropone (**10**) both in non-polar solvents such as benzene and in polar solvents such as acetonitrile and dichloromethane.

Results and discussion

Irradiation in polar solvents

When a dichloromethane solution of **9** and DCA was irradiated for 3 h by means of a Hg lamp through an aqueous $NaNO_2$ layer to cut off shorter wavelengths than 400 nm, two products (**11** and **12**) were obtained in 62 and 25% yields together with 78% recovery of **9** (Scheme 2). The yield was based on the consumed starting material. It is observed from the mass spectrum that the major product **11** has a molecular weight with a value corresponding to a bromide ion and a cyano group being eliminated from a 1 : 1 adduct between **9** and DCA. The NMR spectra indicated that **11** had a symmetrical structure with no



Scheme 1

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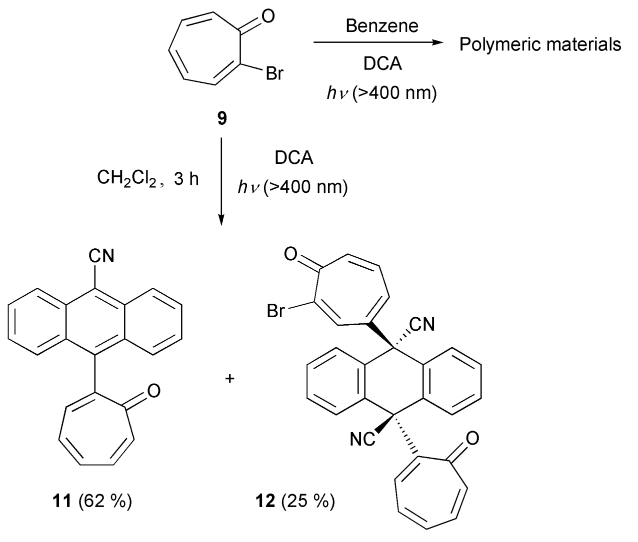
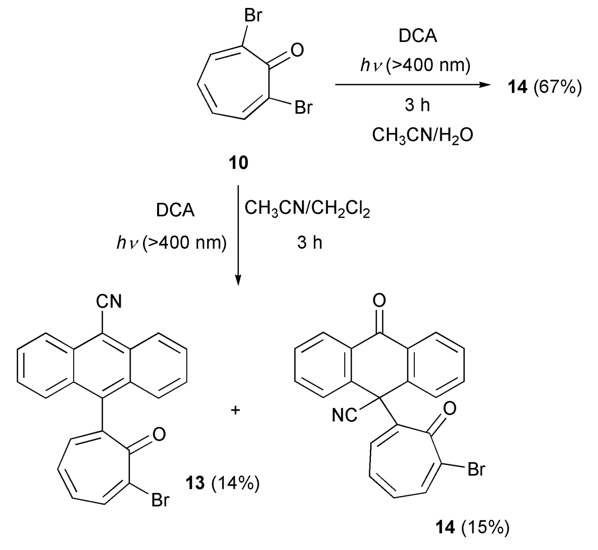


Scheme 2



Scheme 3

sp^3-protons and carbons and with five consecutive olefinic protons [7.20–7.24 (2H, m), 7.28 (1H, dd, J = 12.1, 0.9 Hz), 7.34 (1H, dd, J = 8.4, 1.1 Hz), and 7.37 (1H, ddd, J = 12.1, 8.4, 1.3 Hz)] on a tropone ring which were assigned from the values of the vicinal coupling constants.[7] From this evidence, the structure was determined to be 9-cyano-10-(7-oxocyclohepta-1,3,5-trienyl)anthracene. The mass spectrum of the minor product **12** showed that it has a molecular weight corresponding to a hydrobromic acid molecule being eliminated from a 2 : 1 adduct between **9** and DCA. Product **12** also has a symmetrical structure from the NMR spectral evidence. The X-ray crystallographic analysis confirmed that **12** is 9,10-dicyano-9-(6-bromo-5-oxocyclohepta-1,3,6-trienyl)-10-(7-oxo-cyclohepta-1,3,5-trienyl)-9,10-dihydroanthracene (Fig. 1). The crystallographic data are shown in Table 1. When a dichloromethane solution of **9** was irradiated without DCA by a 400 W Hg lamp, the solution gradually changed to a brownish one to give polymeric materials. The reaction of **9** and DCA in benzene gave only polymeric materials together with unreacted **9**.

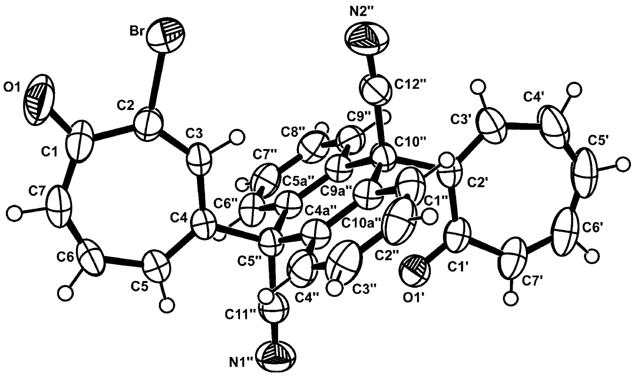


Fig. 1 ORTEP drawing of **12** with 50% probability displacement ellipsoids.

Next, irradiation of 2,7-dibromotropone (**10**) and DCA for 3 h in a 1 : 1 mixture of acetonitrile and dichloromethane under the above conditions afforded two products (**13** and **14**) in 14 and 15% yields, respectively (Scheme 3). From the mass spectrum, product **13** has a molecular weight corresponding to a bromide ion and a cyano group being eliminated from a 1 : 1 adduct between **10** and DCA. The NMR spectra indicated that **13** had a symmetrical structure with no sp^3-protons and carbons. From this evidence, the structure was determined to be 9-cyano-10-(7-oxo-6-bromocyclohepta-1,3,5-trienyl)anthracene, a bromo derivative of **11**. Similarly, the NMR spectra of **14** showed that it has a symmetrical structure with four tropone ring protons [7.01 (1H, ddd, J = 10.8, 9.2, 0.7 Hz), 7.40 (1H, ddd, J = 10.8, 9.0, 0.7 Hz), 8.08 (1H, dd, J = 9.2, 0.7 Hz), and 8.59 (1H, dd, J = 9.0, 0.7 Hz)], two carbonyl signals at δ 175.8 and 181.1, and one sp^3-carbon atom at 50.4, which suggested that the structure is 9,10-dihydro-10-cyano-10-(7-oxo-6-bromo-cyclohepta-1,3,5-trienyl)anthracen-9-one. Both structures of **13** and **14** were confirmed by X-ray crystallographic analyses (Figs. 2 and 3). The formation of **14** suggested the attack of

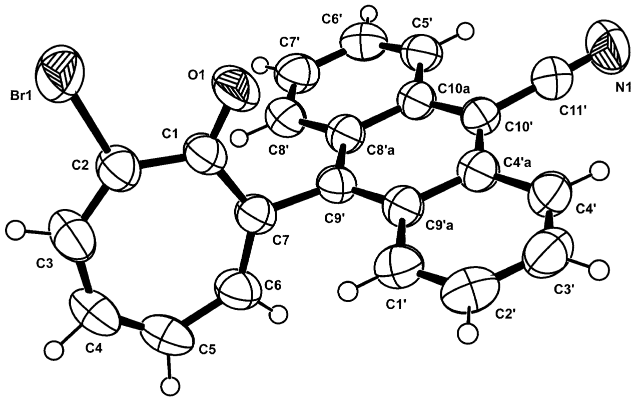


Fig. 2 ORTEP drawing of **13** with 50% probability displacement ellipsoids.

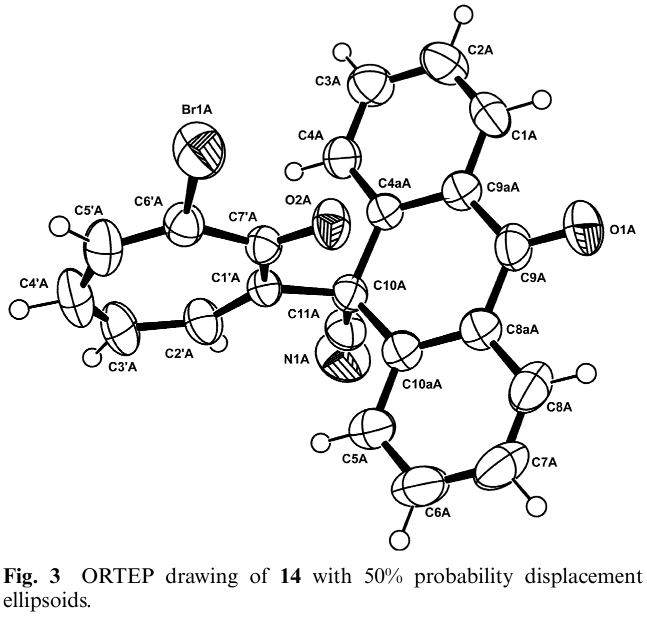
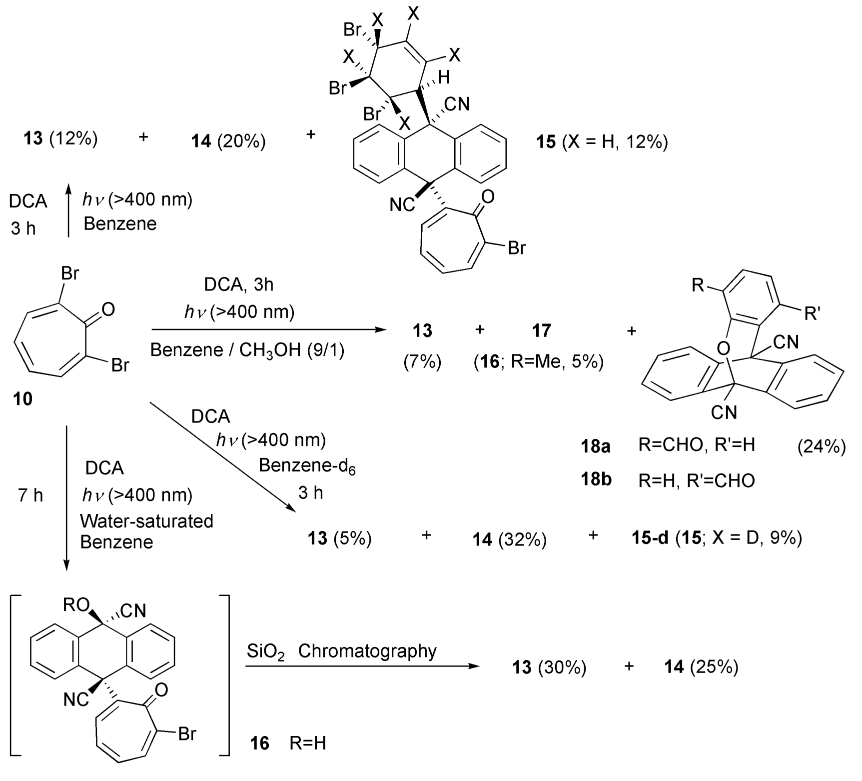


Fig. 3 ORTEP drawing of **14** with 50% probability displacement ellipsoids.

Table 1 Crystallographic data for **12**, **13**, **14**, and **15**

	12	**13**	**14**	**15**
Formula	$C_{30}H_{17}BrN_2O_2{\cdot}C_6H_6$	$C_{22}H_{12}BrNO$	$2{\cdot}(C_{22}H_{12}BrNO_2){\cdot}C_6H_6$	$C_{29}H_{18}Br_4N_2O$
Formula weight	595.47	386.25	882.58	730.09
Crystal color	Brownish yellow	Brownish yellow	Colorless	Yellow
Crystal size/mm	0.35 × 0.30 × 0.18	0.35 × 0.26 × 0.23	0.60 × 0.45 × 0.35	0.30 × 0.25 × 0.25
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/n$
a/Å	10.889 (2)	16.772 (3)	13.614 (3)	11.026 (2)
b/Å	28.960 (5)	7.698 (1)	13.721 (6)	23.928 (4)
c/Å	9.213 (2)	25.944 (6)	13.427 (3)	9.7068 (11)
a, β, γ/deg	106.59 (2)	94.46 (2)	a = 104.95 (2) β = 108.12 (2) γ = 111.56 (2)	β = 91.854 (12)
V/Å^3	2784.3 (9)	3339.5 (11)	2010.8 (11)	2559.6 (7)
Z	4	8	2	4
D_{calc}/g cm^{-3}	1.421	1.536	1.458	1.895
μ/mm^{-1}	2.299	3.417	2.952	7.889
No. of reflections	5067	3171	7365	4854
No. of obsd refl. [$I > 2\sigma(I)$]	3815	2577	6938	4341
No. of refined parameters	370	227	524	325
Refinement	F^2 (*SHELXL93*)	F^2 (*SHELXL93*)	F^2 (*SHELXL93*)	F^2 (*SHELXL93*)
$R[F^2 > 2\sigma(F^2)]$	0.048	0.0428	0.0457	0.053
$wR(F^2)$	0.1446	0.1214	0.1275	0.1441



Scheme 4

water on a reaction intermediate. When a mixed solvent solution of acetonitrile and water (9 : 1) with **10** and DCA was irradiated, only **14** was obtained in 67% yield.

Irradiation in non-polar solvents

Irradiation of **10** and DCA in benzene gave three products (**13**, **14** and **15**) in 12, 20, and 12% yields, respectively (Scheme 4). From the mass spectrum, **15** was a tetrabromo derivative. The ^{1}H NMR spectrum suggested that **15** had eight benzene ring protons, four tropone ring protons, and six consecutive protons [3.88 (1H, dd, J = 9.6, 3.5 Hz), 4.22 (1H, dd, J = 9.6, 8.7 Hz), 4.36 (1H, t, J = 9.6 Hz), 4.73 (1H, dd, J = 8.7, 2.4 Hz), 5.72 (1H, ddd, J = 10.4, 3.5, 2.4 Hz), and 6.30 (1H, dt, J = 10.4, 2.4 Hz)], which were assigned to a hexasubstituted cyclohexene ring from the splitting patterns of the signals. The X-ray single crystallographic analysis determined that the structure of **15** is 9,10-dicyano-9-(6-bromo-7-oxocyclohepta-1,3,5-trienyl)-10-(4,5,6-tribromocyclohex-2-enyl)-9,10-dihydroanthracene (Fig. 4).

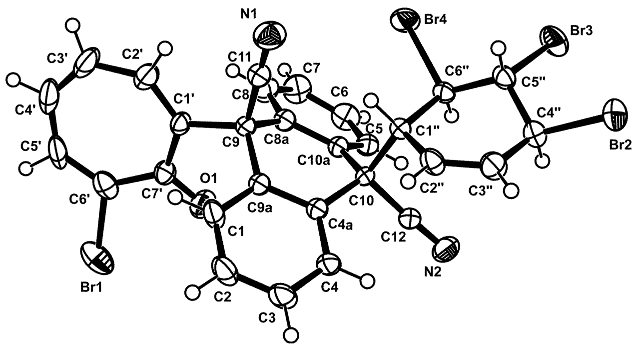


Fig. 4 ORTEP drawing of **15** with 50% probability displacement ellipsoids.

In order to clarify the intermediate, we investigated the reaction of **10** and DCA in benzene saturated with water. The ^{1}H NMR spectrum of the crude product **16** showed olefinic signals at 7.06 (1H, ddd, J = 11.0, 9.2, 0.7 Hz), 7.42 (1H, ddd, J = 11.0, 8.8, 0.7 Hz), 8.14 (1H, dd, J = 9.2, 0.7 Hz), and 8.53 (1H, J = 8.8, 0.7 Hz), which were assigned to a 2,7-disubstituted tropone system, together with the signals of a dihydroanthracene structure. After silica gel chromatography of the crude product **16**, products **13** and **14** were obtained in 30 and 25% yields, respectively, which suggested formation of cyanohydrin **16**.

When a mixed solution of benzene and methanol (9 : 1) of **10** and DCA was irradiated, three products (**13**, **17**, and **18**) were obtained in 7, 5, and 24% yields, respectively. The ^{1}H NMR spectrum of **17** was similar to that of **16** except for a methoxyl signal at δ 3.05. Product **17** should be the methyl ether of **16**. Since the NMR spectra of the major product **18** indicated it to have a symmetrical structure with two cyano groups and a 1,2,3-trisubsituted benzaldehyde moiety, **18** was determined to be a benzaldehyde derivative with a 2-oxatribenzobicyclo-[3.2.2]nonane system. There are two possibilities, however, for the structure of product **18**; one is **18a** and the other **18b**. The difference between them is the position of the formyl group. In the ^{1}H NMR spectrum of 3-methoxy-2-methylbenzaldehyde,[8] a reference compound for **18b**, the doublet signal assigned to the *ortho*-proton of the methoxyl group appears at the highest position (δ 7.09) amongst the aromatic region and the triplet one appears at 7.33. Although we could not find a ^{1}H NMR spectrum of a reference compound for **18a** such as 3-methyl-2-methoxybenzaldehyde, the triplet signal at the *para* position should be highest. The ^{1}H NMR spectrum of aldehyde **18** indicated that the chemical shift of the triplet is highest among the benzaldehyde ring protons. This implied that the structure of the aldehyde must be **18a**. Mechanistic considerations supported this conclusion.

Mechanistic considerations

The fluorescence quenching of DCA with **9** and **10** was efficient in acetonitrile and obeyed the Sterm–Volmer equation as shown in Fig. 5. From the slope of the plot of I_0/I *vs.* [**9**] and the lifetime of DCA (τ = 15.3 ns in acetonitrile),[9] the k_q value for **9** was determined to be 1.01 × 10^{10} M^{-1} s^{-1}. Similarly the value for **10** was 2.13 × 10^{10} M^{-1} s^{-1}. These values show the reaction to be close to diffusion control.

Possible mechanisms for the photoreactions of troponoids with DCA are shown in Scheme 5. The isolation of product **18a** with an oxabicyclo[3.2.2]nonane system was quite informative about the reaction mechanism because it strongly suggested the formation of an [8+4]π product between halotropones (**9** and **10**) and DCA in the reactions. We have reported that the reaction of tropone **1** and excited DCA in polar solvents gave an [8+4]π product **8** *via* an electron transfer process as shown by sensitized and quenching experiments together with the products formed *via* an energy transfer process.[5] Since the substituent effect of a bromine atom on the potential is reported to be 0.185 V in acetonitrile in a monosubstituted benzoquinone[10] and the oxidation potential of **1** was 1.95 V and the reduction potential of DCA was −1.05 V *vs.* Ag/AgCl in acetonitrile,[5] the oxidation potentials of compounds **9** and **10** are calculated to be 2.14 and 2.32 V *vs.* Ag/AgCl. From these data, electron transfer processes would seem to hardly occur in the present cases. Therefore, we proposed that excited DCA reacts with halotropones **9** and **10** to give the [8+4]π adduct **19** through an energy transfer process, which is equivalent to a tropylium ion (**20**: * = +) or a radical species (**20**: * = ·).

In the presence of methanol, a methoxide anion attacks on the carbon bearing a bromine atom to give a 7,7-disubstituted cycloheptatriene **21**, which gave **18a** through a norcaradiene intermediate **22**. Therefore, the formation of **18a** is reasonable. When the solvent is contaminated by water, the water can attack the carbon atom bearing a cyano group to lead to cyanohydrin **16**, which gave the product **14** by elimination of HCN whereas products **11** and **13** would be formed through elimination of the CN group close to the tropone ring as HOCN. In dichloromethane, 2-bromotropone **9** attacked **20** to give **12** through intermediate **23**.

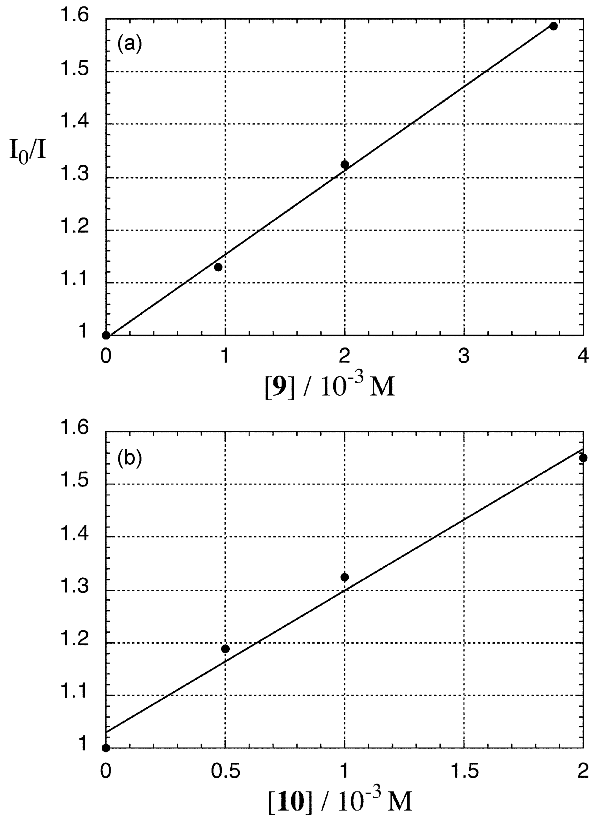


Fig. 5 Stern–Volmer plots of fluorescence of DCA with (a) **9** and (b) **10** in acetonitrile.

It is interesting to disclose the origin of the tribromocyclohexene moiety of **15**. There are two possibilities; one is from **10** and the other from benzene. We irradiated a hexadeuterated benzene solution of **10** and DCA, which afforded three products, **13** (5%), **14** (32%), and **15-d** (9%). The signals of the cyclohexene part of **15** completely disappeared in the spectrum of **15-d** as shown in Fig. 6. Therefore, benzene attacks the radical **20** to give a pentadienyl radical **24**.[11] Next, a bromide radical produced from the [8+4]π adduct **19** attacks the less hindered middle carbon atom of the pentadienyl radical system of **24** to give a cyclohexa-1,4-diene structure **25**, to which a bromine adds from the less hindered site of one of the double bonds to give **15**.

Finally, when an acetonitrile solution of 2-methoxytropone (**3**) and DCA was irradiated by means of a Hg lamp through an

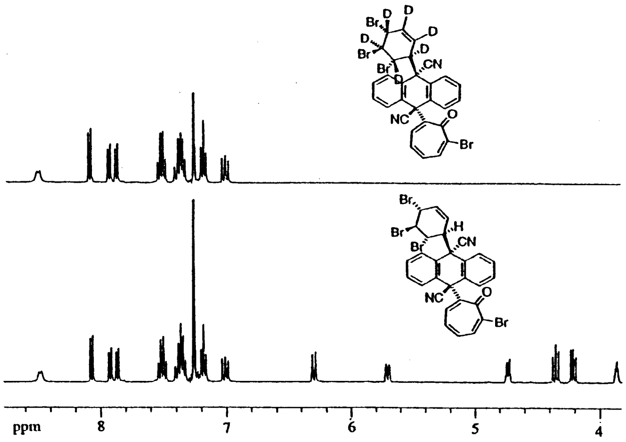
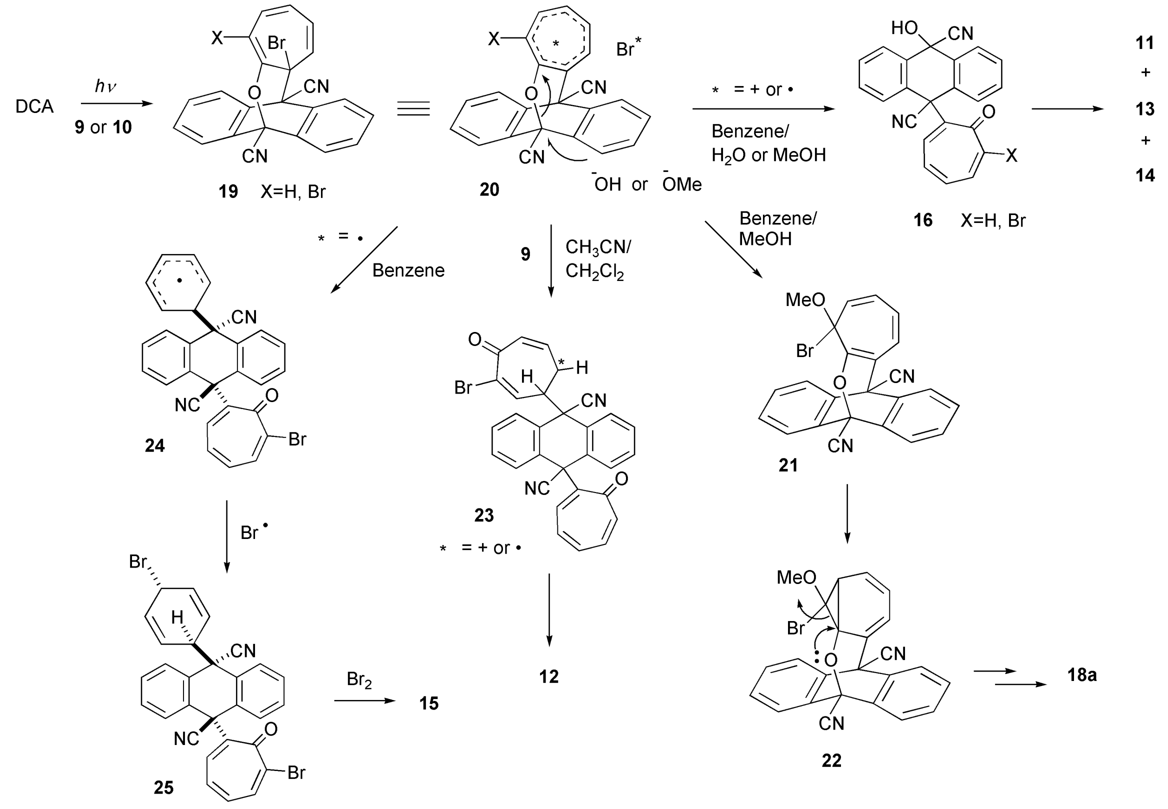


Fig. 6 ^{1}H NMR spectra of **15-d** (upper) and **15** (lower).



Scheme 5

aqueous $NaNO_2$ layer, no reaction occurred. Similarly, 2,5-dimethoxytropone (**26**) and DCA also gave no product under similar conditions. Reactivity of troponoids with electron-donating substituents with the excited DCA, therefore, was low.

In summary, we observed new types of photochemistry in the field of troponoids, where a tropylium ion was involved giving anthracene and anthracenone derivatives in polar media whereas radical reactions gave the products incorporating benzene when this was used as the reaction media.

Experimental

The elemental analyses were performed at the elemental analysis laboratory of Kyushu University. The melting points were obtained on a Yanagimoto micro melting point apparatus and are uncorrected. The NMR spectra were measured on JEOL GSX 270H, LA 400, and LA 600 spectrometers in $CDCl_3$; the chemical shifts are expressed in δ units. The mass spectra were measured with JEOL 01SG-2 and JMS-700 spectrometers. The IR spectra were recorded on a JASCO IR-A102 spectrometer with KBr disks. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.

Photoreaction of 2-bromotropone (9) and DCA

a) In dichloromethane. A dichloromethane solution (100 ml) of **9** (250 mg) and DCA (308 mg) was irradiated for 3 h under a nitrogen atmosphere by means of a 400 W high-pressure mercury lamp through 0.7 M $NaNO_2$ solution. After evaporation of the solvent, the residue was chromatographed on a silica gel column (hexane–AcOEt) to give **11** (55.9 mg, 62%) and **12** (18.8 mg, 25%) together with recovered **9** (195.9 mg). **11**: Yellow plates, mp 136–138 °C (decomp). ^{1}H NMR ($CDCl_3$): δ 7.20–7.24 (2H, m), 7.28 (1H, dd, J = 12.1, 0.9 Hz), 7.34 (1H, dd, J = 8.4, 1.1 Hz), 7.37 (1H, ddd, J = 12.1, 8.4, 1.3 Hz), 7.50 (2H, ddd, J = 8.8, 6.6, 1.1 Hz), 7.69 (2H, ddd, J = 8.6, 6.6, 1.1 Hz), 7.79 (2H, d, J = 8.6 Hz), and 8.47 (2H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 106.4, 117.3, 125.9 (2C), 126.5 (2C), 126.7 (2C), 126.8 (2C), 128.8 (2C), 133.2 (2C), 133.6, 135.2, 136.2, 139.1, 141.4, 142.6, 150.4, and 186.2; IR (KBr) 3052, 2210, 1629, 1579, 1522, 1459, 1439, and 763 cm^{-1}; MS m/z (%) 307 (63), 279 (100), 278 (62) and 149 (23); HRMS Found: 307.0994. Calcd for $C_{22}H_{13}ON$: 307.0997. **12**: Brownish yellow crystals, mp 187–189 °C (decomp). ^{1}H NMR ($CDCl_3$–C_6D_6): δ 6.45 (1H, dd, J = 12.1, 8.1 Hz), 6.52 (1H, dd, J = 10.6, 7.3 Hz), 6.56 (1H, d, J = 11.9 Hz), 6.67 (1H, dd, J = 12.1, 8.8 Hz), 6.70 (1H, dd, J = 12.1, 8.8 Hz), 6.84 (1H, d, J = 12.3 Hz), 7.00 (2H, dd, J = 8.1, 7.1 Hz), 7.07 (2H, dd, J = 7.9, 7.3 Hz), 7.18–7.26 (4H, m), 7.49 (1H, s), 7.79 (1H, d, J = 8.8 Hz), and 8.27 (1H, d, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$): δ 50.4, 51.1, 120.2, 120.8, 127.5 (2C), 128.3 (2C), 129.8, 130.0 (2C), 130.1 (2C), 130.2 (2C), 131.2, 131.6, 132.2, 134.4, 135.3, 135.7, 136.2, 137.5, 138.8, 143.4, 143.5, 146.0, 150.8, 179.9, and 180.7; IR (KBr) 3068, 3032, 2230, 1632, 1591, 1510, and 755 cm^{-1}; MS m/z (%) 518 (100), 516 (98), 438 (20), 437 (22), 333 (24), 307 (36), 306 (29), 305 (30), 304 (35), 279 (44), 278 (36), 277 (34), 228 (76), 149 (36), and 77 (32); HRMS Found: 516.0450 and 518.0447. Calcd for $C_{30}H_{17}O_2N_2Br$: 516.0474 and 518.0454.

X-Ray crystallographic analysis of 12. Monoclinic single crystals of **12** crystallized with a molecule of benzene. The measurement was made on an Enraf-Nonius FR590 diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of 23 ± 2 °C using the ω–2θ scan technique to a maximum 2θ value of 129.9°. The structure was solved by a direct method[12] (*SIR92*), and was refined using full-matrix least squares[13] (*SHELXL93*) based on F^2 of all independent measured reflections. All H atoms were located at ideal positions and were included in the refinement, but restrained to ride on the atom to which they are bonded. Isotropic thermal factors of H atoms were held fixed to 1.2 times or 1.5 times U of the riding atoms. The crystallographic data are listed in Table 1.†

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† CCDC reference numbers 203118–203121. See http://www.rsc.org/suppdata/ob/b3/b300922j/ for crystallographic data in .cif or other electronic format.

b) In benzene. A benzene solution (100 ml) of **9** (92.5 mg) and DCA (114 mg) was irradiated for 3 h under the same conditions. Only polymeric materials were formed together with recovered **9** (10 mg).

Photoreaction of 2,7-dibromotropone (10) and DCA

a) In a 1 : 1 mixture of acetonitrile and dichloromethane. A 1 : 1 mixture of acetonitrile and dichloromethane (100 ml) of **10** (264 mg, 1 mmol) and DCA (228 mg, 1 mmol) was irradiated under the same conditions. After evaporation of solvents, the residue was chromatographed on a silica gel column to give **13** (28.5 mg, 17%) and **14** (30.6 mg, 18%) together with recovered **10** (153 mg). **13**: Brownish yellow crystals, mp 236–237 °C (decomp). ^{1}H NMR (CDCl$_3$): δ 7.06 (1H, ddd, J = 10.8, 9.5, 1.1 Hz), 7.27 (1H, ddd, J = 10.8, 8.6, 0.9 Hz), 7.40 (1H, dd, J = 8.6, 1.1 Hz), 7.50 (2H, m), 7.70 (4H, m), 8.37 (1H, dd, J = 9.5, 0.9 Hz), and 8.48 (2H, dd, J = 8.4, 1.4 Hz); ^{13}C NMR (CDCl$_3$): δ 106.5, 117.3, 125.9 (4C), 126.3 (2C), 127.0 (2C), 128.7 (2C), 132.5 (2C), 133.1 (2C), 138.5, 139.5, 141.3, 143.9, 146.0, and 179.3; IR (KBr) 3050, 2210, 1619, 1583, 1440, 1352, and 767 cm^{-1}; MS *m*/*z* (%) 387 (25), 385 (23), 306 (16), 278 (71), 250 (21), 139 (34), and 125 (100); HRMS (FAB) Found [M + H]$^+$: 386.0185 and 388.0176. Calcd for C$_{22}$H$_{13}$ONBr: 386.0181 and 388.0161. **14**: Colorless crystals, mp 218–220 °C (decomp). ^{1}H NMR (CDCl$_3$): δ 7.01 (1H, ddd, J = 10.8, 9.2, 0.7 Hz), 7.34 (2H, m), 7.40 (1H, ddd, J = 10.8, 9.0, 0.7 Hz), 7.57 (4H, m), 8.08 (1H, dd, J = 9.2, 0.7 Hz), 8.46 (2H, m), and 8.59 (1H, dd, J = 9.0, 0.7 Hz); ^{13}C NMR (CDCl$_3$): δ 50.4, 120.1, 126.1 (2C), 128.5 (2C), 129.3 (2C), 131.4 (2C), 131.9, 133.3, 133.8 (2C), 135.5, 137.6, 138.9, 143.8, 146.4 (2C), 175.8, and 181.8; IR (KBr) 3034, 2215, 1667, 1597, 1455, 1325, 759, and 744 cm^{-1}; MS *m*/*z* (%) (FAB) 403 (100), 401 (100), 322 (32), 218 (53), and 190 (63); HRMS (FAB) Found [M + H]$^+$: 402.0116 and 404.0117. Calcd for C$_{22}$H$_{13}$O$_2$NBr: 402.0130 and 404.0110. Found: C, 65.87; H, 3.08; N, 3.52%. Calcd for C$_{22}$H$_{12}$O$_2$NBr: C, 65.59; H, 3.00; N, 3.48%.

X-Ray crystallographic analysis of 13 and 14. The monoclinic single crystals of **13** crystallized and the triclinic single crystals of **14** crystallised with two molecules of **14** and a molecule of benzene, were analyzed as detailed for **12**. The crystallographic data are listed in Table 1.

b) In a 9 : 1 solution of acetonitrile and water. A 9 : 1 mixture of acetonitrile and water (10 ml) of **10** (6.6 mg) and DCA (5.7 mg) was irradiated under the same conditions. After evaporation of solvents, the residue was chromatographed on a silica gel column to give **14** (2.4 mg, 67%) together with recovered **10** (4.2 mg).

c) In benzene. A benzene solution (100 ml) of **10** (66 mg) and DCA (57 mg) was irradiated for 3 h under the same conditions. After evaporation of solvents, the residue was chromatographed on a silica gel column to give **15** (22 mg, 12%) together with **13** (11.6 mg, 12%) and **14** (20.2 mg, 20%). **15**: Yellow crystals, mp 167–168 °C (decomp). ^{1}H NMR (CDCl$_3$): δ 3.88 (1H, dd, J = 9.6, 3.5 Hz), 4.22 (1H, dd, J = 9.6, 8.7 Hz), 4.36 (1H, t, J = 9.6 Hz), 4.73 (1H, dd, J = 8.7, 2.4 Hz), 5.72 (1H, ddd, J = 10.4, 3.5, 2.4 Hz), 6.30 (1H, dt, J = 10.4, 2.4 Hz), 7.00 (1H, dd, J = 10.3, 9.2 Hz), 7.18 (1H, dd, J = 7.9, 1.1 Hz), 7.20 (1H, dd, J = 7.9, 1.1 Hz), 7.33–7.40 (3H, m), 7.48–7.53 (2H, m), 7.87 (1H, dd, J = 7.9, 0.9 Hz), 7.92 (1H, dd, J = 7.9, 2.9 Hz), 8.07 (1H, dd, J = 9.2, 0.9 Hz), and 8.48 (1H, br d, J = 9.2 Hz); ^{13}C NMR (CDCl$_3$): δ 47.9, 49.9, 50.9, 51.6, 56.3, 59.9, 119.6, 119.7, 126.2 (2C), 126.5, 128.6, 129.2, 129.4, 129.7, 129.8, 130.0 (2C), 130.5, 131.6, 132.4, 132.6, 132.8 (2C), 133.2, 135.8, 138.5, 143.6, and 176.0; IR (KBr) 3054, 2220, 1624, and 1608 cm^{-1}; MS *m*/*z* (%) (FAB) 735 (12), 733 (44), 731 (62), 729 (42), 727 (11), 491 (16), 489 (17), 464 (12), 462 (12), 414 (76), 413 (100), 412 (76), and 411 (81); HRMS (FAB) Found [M + H]$^+$: 734.8190, 732.8185, 730.8193, 728.8201, and 726.8210. Calcd for C$_{29}$H$_{19}$ON$_2$Br$_4$ [M + H]: 734.8151, 732.8171, 730.8191, 728.8211, and 726.8231.

X-Ray crystallographic analysis of 15. The monoclinic single crystal of **15** crystallized was analyzed as detailed for **12**. The crystallographic data are listed in Table 1.

e) In hexadeuterated benzene. A C$_6$D$_6$ solution (100 ml) of **10** (66 mg) and DCA (57 mg) was irradiated under similar conditions. After solvents were removed, the residue was chromatographed on a silica gel column to give **15-d** (16.6 mg, 9%) together with **13** (4.8 mg, 5%) and **14** (32.2 mg, 32%). **15-d**: Colorless powder, mp 162–164 °C (decomp). ^{1}H NMR (CDCl$_3$): δ 7.01 (1H, dd, J = 10.8, 9.3 Hz), 7.18 (1H, d, J = 8.0 Hz), 7.19 (1H, d, J = 8.0 Hz), 7.33–7.40 (3H, m), 7.48–7.53 (2H, m), 7.86 (1H, dd, J = 8.0, 1.0 Hz), 7.92 (1H, dd, J = 8.0, 1.0 Hz), 8.07 (1H, dd, J = 9.3, 0.7 Hz), and 8.48 (1H, br d, J = 9.3 Hz); MS *m*/*z* (%) (FAB) 739 (1), 737 (2), 735 (1), 414 (1), 413 (2), 412 (1), 411 (1), and 154 (100); MS *m*/*z* (%) (FAB) 741 (15), 739 (54), 737 (79), 735 (52), 733 (13), 414 (77), 413 (100), 412 (75), and 411 (82); HRMS (FAB) Found [M + H]$^+$: 740.8522, 738.8549, 736.8599, 734.8572, and 732.8597. Calcd for C$_{29}$H$_{13}$D$_6$ON$_2$Br$_4$: 740.8528, 738.8548, 736.8568, 734.8588, and 732.8608.

f) In benzene saturated with water. A solution (10 ml) of benzene saturated with water of **10** (6.6 mg) and DCA (5.7 mg) was irradiated for 3 h under the same conditions. After evaporation of solvents, the ^{1}H NMR spectrum of the crude product **16** was measured in CDCl$_3$ [7.06 (1H, ddd, J = 11.0, 9.2, 0.7 Hz), 7.14 (2H, dd, J = 8.1, 1.1 Hz), 7.36 (2H, m), 7.42 (1H, ddd, J = 11.0, 8.8, 0.7 Hz), 7.54 (2H, td, J = 7.7, 1.1 Hz), 8.14 (1H, dd, J = 9.2, 0.7 Hz), 8.21 (2H, dd, J = 7.7, 1.1 Hz), and 8.53 (1H, J = 8.8, 0.7 Hz)]. The crude product **16** was chromatographed on a silica gel column to give **13** (2.9 mg, 30%) and **14** (2.5 mg, 25%).

g) In a 9 : 1 solution of benzene and methanol. A 9 : 1 solution (10 ml) of benzene and methanol of **10** (6.6 mg) and DCA (5.7 mg) was irradiated for 3 h under the same conditions. After evaporation of solvents, the residue was chromatographed on a silica gel column to give **13** (0.7 mg, 7%) together with **17** (0.6 mg, 5%) and **18** (2.1 mg, 24%).

17: Colorless plates, mp 196–198 °C (decomp). ^{1}H NMR (CDCl$_3$): δ 3.05 (3H, s), 7.01 (1H, dd, J = 10.4, 9.4 Hz), 7.26, (2H, d, J = 7.7 Hz), 7.36 (1H, dd, J = 10.4, 8.9 Hz), 7.40 (2H, td, J = 7.7, 1.5 Hz), 7.55 (2H, t, J = 7.7 Hz), 8.06 (2H, dd, J = 7.7, 1.5 Hz), 8.10 (1H, dd, J = 9.4, 1.2 Hz), and 8.45 (1H, d, J = 8.9 Hz); ^{13}C NMR (CDCl$_3$): δ 50.8, 52.1, 75.1, 118.4, 119.8, 125.9 (2C), 129.3 (2C), 129.6 (2C), 130.5, 130.7 (2C), 131.8, 133.2, 133.8, 136.0, 138.7, 143.8 (2C), 145.9 (2C), and 176.0; IR (KBr) 2940, 2200, 1592, and 1075 cm^{-1}; MS *m*/*z* (%) (FAB) 445 (42), 443 (42), 418 (99), 416 (100), 413 (52), 411 (50), and 228 (29); HRMS (FAB) Found [M + H]$^+$: 443.0396 and 445.0375. Calcd for C$_{24}$H$_{16}$O$_2$N$_2$Br: 443.0395 and 445.0375. **18**: Colorless plates, mp 215 °C (sublimed). ^{1}H NMR (CDCl$_3$): δ 7.03 (1H, t, J = 7.7 Hz), 7.58 (4H, m), 7.76 (1H, dd, J = 7.7 Hz), 7.94 (2H, m), 7.99 (1H, dd, J = 7.7, 1.7 Hz), 8.54 (2H, m), and 10.36 (1H, s); ^{13}C NMR (CDCl$_3$): δ 52.0, 78.5, 111.6, 116.3, 122.2 (2C), 123.1, 123.9 (2C), 126.7 (3C), 126.9, 129.0, 130.0 (2C), 130.1, 130.4, 131.4 (2C), 137.5, 152.4, and 188.0; IR 2854, 2250, 1694, 1584, 1230, 970, and 753 cm^{-1}; MS *m*/*z* (%) (FAB) 349 (75), 307 (13), 289 (12), 228 (16), 154 (100), and 136 (83); HRMS (FAB) Found: 349.0979. Calcd for C$_{23}$H$_{13}$O$_2$N$_2$: 349.0977. Found: C, 79.13; H, 3.55; N, 7.97%. Calcd for C$_{23}$H$_{12}$O$_2$N$_2$: C, 79.30; H, 3.47; N, 8.04%.

Fluorescence quenching. Fluorescence spectra and measurement of fluorescence quenching were recorded on a JSC, FP-700 spectrometer. The fluorescence quenching of DCA was measured at various concentrations of **9** and **10** in acetonitrile. The intensities at $E_{ex} = 400$ nm and $E_{em} = 448$ nm were obtained three times for each cell and an average value for each sample was used. The quenching results were analyzed according to the Stern–Volmer equation and are shown in Fig. 5.

Photoreaction of 2-methoxytropone (3) and DCA in acetonitrile

An acetonitrile solution (10 ml) of **3** (20 mg) and DCA (33 mg) was irradiated. ^{1}H NMR spectra of the residue showed only the signals of **3**.

Photoreaction of 2,5-dimethoxytropone (26) and DCA in acetonitrile

A 1 : 1 solution of acetonitrile and dichloromethane (10 ml) of 2,5-dimethoxytropone **26** (30 mg) and DCA (41 mg) was irradiated. ^{1}H NMR spectra of the residue showed only the signals of **26**.

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