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THE SYNTHESIS OF 12-FLUORO-7-METHYL- AND 7-FLUORO-BENZ[*a*]ANTHRACENE

A CONTRIBUTION TO THE STUDY OF PHOTOCYCLIZATION

J. Blum, F. Grauer and E. D. Bergmann
Department of Organic Chemistry, Hebrew University, Jerusalem, Israel

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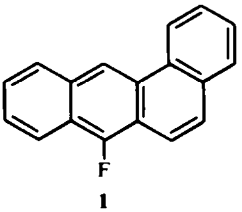
Abstract—In order to study the influence of fluorine substitution at the *meso*-position of benz[*a*]anthracene and at the 12-position of 7-methylbenz[*a*]anthracene on the carcinogenic properties of these hydrocarbons, the title compounds have been prepared by photocyclization of 1-(1-fluoro-2-naphthyl)-2-(*o*-iodophenyl)-ethylene and 1-(4-fluoro-1-methyl-2-naphthyl)-2-(*o*-iodophenyl)ethylene, respectively.

In a previous paper[1] the reasons were outlined for the interest attached to carcinogenic polycyclic hydrocarbons substituted by fluorine in the so-called K region. The introduction of a fluorine atom at the *meso*-position ("L region") of the anthracene moiety of such hydrocarbons is of no less interest, especially as the role of this region in carcinogenesis is not clear. Numerous attempts to prepare compounds such as 7-fluorobenz[*a*]anthracene (**1**) made in our laboratory failed, e.g. the treatment of benz[*a*]anthracene with phenyl- and *p*-tolyl-iododifluoride[2–4] or with N-bromosuccinimide in anhydrous hydrofluoric acid,[4,5] the reaction of 7-bromobenz[*a*]anthracene with heavy metal fluorides, or the conversion of 7-aminobenz[a]anthracene to the fluoro-compound *via* the diazonium fluoborate by methods developed for the syntheses of 9-fluoro- and 9-fluoro-10-phenyl-anthracene.[6,7]

In the present study the synthesis of the title compounds (**1** and **2**) has been achieved by photocyclization of the appropriate fluorinated diarylethylenes.

Though 2-styrylnaphthalene has been shown to photocyclize exclusively to benzo[*c*]phenanthrene,[8,9] the benz[*a*]anthracene skeleton could be expected to be formed when the 1-position of 2-styrylnaphthalene was blocked as in **8**, which could easily be prepared from 2-bromomethyl-1-fluoronaphthalene (**4**) and benzaldehyde by the Wittig–Arbuzov reaction (Experimental). *trans*-1-(1-Fluoro-2-naphthyl)-2-phenylethylene (**8**), however, could not be cyclized but was only photo-isomerized to the *cis*-isomer (**11**), which upon further irradiation gave dimeric and polymeric



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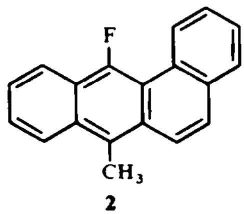

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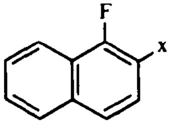
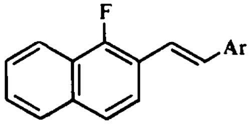
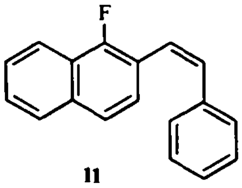
material. Thus compound **8** resembles the closely related 2-styrylquinoline and 1-(3-pyridyl)-2-(2-quinolyl)ethylene.[10] Similarly refractory was the condensation product of **4** and *p*-tolualdehyde, *trans*-1-(1-fluoro-2-naphthyl)-2-(*p*-tolyl)ethylene (**9**).



3: x = $-CH_3$
4: x = $-CH_2Br$
5: x = $-Br$
6: x = $-CN$
7: x = $-CHO$



8: Ar = C_6H_5-
9: Ar = p-$CH_3-C_6H_4-$
10: Ar = o-I$-C_6H_4-$



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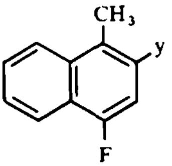
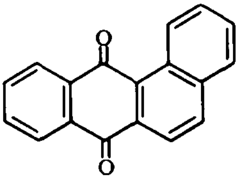


13: y = $-Br$
14: y = $-CN$
15: y = $-COOH$

16: y = $-COOCH_3$
17: y = $-CH_2OH$
18: y = $-CH_2Br$



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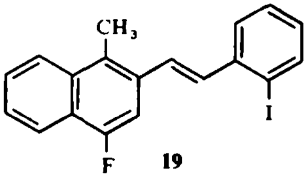

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We only succeeded in the preparation of **1**, when we applied the modification proposed by Kupchan:[11] *trans*-1-(1-fluoro-2-naphthyl)-2-(*o*-iodophenyl)ethylene (**10**) (prepared from **4** and *o*-iodobenzaldehyde) was irradiated with UV light. The structure of **1** was proven by the close resemblance of its electronic spectrum to that of the fluorine-free parent compound (Table 1), and by its smooth oxidation to 7,12-benz[*a*]anthraquinone (**12**).

The preparation of **10** was also attempted by an alternative route, **5** → **6** → **7** → **10**, which was, however, found impractical because of the poor yield in the Stephen reduction of the nitrile **6** to the aldehyde **7**.

The desired compound **1** was formed only when light sources of relatively *low* intensity were applied; a Hanovia 450 *Watt* mercury lamp led to the formation of fluorine-free material. As it is known,[12,13] that mono- and di-fluorostilbenes are converted smoothly to fluorinated phenanthrenes on irradiation with 125 *to* 400 *Watt* mercury lamps, it can be assumed that the intense illumination removed the fluorine atom *after* cyclization has taken place.

The synthesis of 12-fluoro-7-methylbenz[*a*]anthracene (**2**) was achieved

TABLE 1

Compound	Electronic spectra, λ_{max} mμ (log ε)											
Benz[*a*]anthracene[a], [21]	256 (4.58)	268 (4·61)	278 (4·84)	288 (4·92)	300 (4·00)	316 (3·72)	326 (3·81)	341 (3·85)	358 (3·69)	368[a] (3·45)	374 (2·68)	384 (2·90)
1[b]	256·5 (4·15)	269·5 (4·29)	279 (4·51)	289·5 (4·56)	301·5 (3·89)	318·5 (3·96)	328 (3·87)	342 (3·66)	361 (3·30)	368 (3·21)	380 (2·36)	388 (2·54)
7-Methylbenz[*a*]anthracene[c] [22]	258 (4·6)	272 (4·6)	280 (4·9)	293 (5·0)	302 (4·0)	322 (3·6)	335 (3·9)	353 (3·9)	365 (3·7)	370 (3·8)		388 (2·9)
2[c]	264 (4·38)	274 (4·51)	283·5 (4·72)	294 (4·71)		323 (3·72)	343 (3·70)	362 (3·70)	365 (3·70)	376 (3·43)	382 (3·53)	395·5 (3·20)

[a] Heptane as solvent. [b] Chloroform as solvent. [c] Ethanol as solvent.

analogously, it completes in fact Prof. Newman's project of the preparation of all monofluoro derivatives of 7-methylbenz[*a*]anthracene.[14–20]

2-Bromo-4-fluoro-1-methylnaphthalene (**13**) was prepared by two alternative routes, both starting from 1-methylnaphthalene, as described in the Experimental, and converted by cuprous cyanide into the nitrile **14**. The latter compound was hydrolysed, and the ester **16** of the acid **15** so formed, reduced to the alcohol **17**, which was then converted to 2-bromomethyl-4-fluoro-1-methylnaphthalene (**18**). Wittig reaction with *o*-iodobenzaldehyde gave *trans*-1-(4-fluoro-1-methyl-2-naphthyl)-(*o*-iodophenyl)ethylene (**19**), which on irradiation with UV light cyclized to **2**. The spectroscopic properties of this compound (Table 1) indicate clearly the formation of the benz[*a*]anthracene system.

In the course of this study we have tried in vain to condense the Grignard derivative of 2-bromo-4-fluoro-1-methylnaphthalene (**13**) with either phenylacetaldehyde or phenylacetyl chloride. It is rather unexpected that the Grignard reagent is formed in almost quantitative yield, but does not add to the carbonyl groups in these compounds even at 75° (in benzene).

EXPERIMENTAL

2-*Bromomethyl*-1-*fluoronaphthalene* (**4**). A mixture of 69 g of **3**[23], 7·78 g N-bromosuccinimide, 250 ml CCl_4 and 0·5 g benzoyl peroxide was refluxed for 2·5 hr. To the hot soln, 250 ml CCl_4 was added and the succinimide removed by filtration. Upon concentration of the filtrate, 61 g (59%) colourless crystals of **4** separated; m.p. 53–55° from cyclohexane. (Found: C, 55·4; H, 3·5; Br. 33·3. Calc. for $C_{11}H_8BrF$: C, 55·3; H, 3·3; Br, 33·5%).

trans-1-(1-*Fluoro*-2-*naphthyl*)-2-*phenylethylene* (**8**). A stirred mixture of 5 g of **4** and 7 g triethyl phosphite was heated on the steam bath for 2·5 hr. The excess of the reagent was distilled off at 1 mm (oil bath at 120°) and the residue dissolved in 25 ml dry DMF. After the addition of 2·3 g benzaldehyde in 30 ml DMF, a soln of 1·2 g NaOMe in 40 ml of the same solvent was added dropwise with external cooling (internal temp below 40°). The mixture was then heated for 30 min on the steam bath, cooled and poured into cold water. The pale yellow ppt was filtered off and washed with water. Recrystallization from cyclohexane gave 3·7 (71%) of **8** as colourless crystals, m.p. 110–112°. $\lambda_{\max}^{\text{EtOH}}$ (log ε), 226 (4·48); 240 (4·23); 252 (4·15); 274 (4·38); 283 (4·42); 319 (4·51); 335* (4·11); 360 mμ (3·53); $\bar{\nu}_{\max}^{\text{KBr}}$ 962, 970 cm^{-1}; NMR ($CDCl_3$) τ 2·83; 2·96 (*trans*-ethylenic H atoms). (Found: C, 86·8; H, 5·0; F, 7·6. Calc. for $C_{18}H_{13}F$: C, 87·1; H, 5·2; F, 7·7%).

trans-1-(1-*Fluoro*-2-*naphthyl*)-2-(o-*iodophenyl*)*ethylene* (**10**). The same procedure as above was applied to the conversion of 5 g of **4**, 7 g triethyl phosphite, 4·9 g *o*-iodobenzaldehyde[24] and 1·2 g NaOMe into 6·6 g (82%) of **10**; m.p. 97° (from cyclohexane); $\lambda_{\max}^{\text{EtOH}}$ (log ε), 217 (4·57); 252 (4·30); 273 (4·30); 308 (4·30); 345* (4·00); 365 mμ (3·48); $\bar{\nu}_{\max}^{\text{KBr}}$ 958 cm^{-1}; NMR ($CDCl_3$) τ 2·79–3·20 (*trans*-ethylenic H atoms). (Found: C, 57·8; H, 3·0; F, 4·9; I, 33·7. Calc. for $C_{18}H_{12}FI$: C, 57·7; H, 3·2; F, 5·1; I, 34·0%).

trans-1-(1-*Fluoro*-2-*naphthyl*)-2(p-*tolyl*)*ethylene* (**9**). Similarly 5 g of **4**, 7 g triethyl phosphite, 2·5 g *p*-tolualdehyde and 1·2 g NaOMe afforded 3·3 g (60%) of **8** as colourless crystals of m.p. 112–114° (from cyclohexane); $\lambda_{\max}^{\text{EtOH}}$ (log ε), 229 (4·45); 242 (4·26); 253 (4·15); 275 (4·34); 286 (4·38); 323 (4·50); 339 (4·23); 361 mμ (3·56); $\bar{\nu}_{\max}^{\text{KBr}}$ 967, 972 cm^{-1}; NMR ($CDCl_3$) τ 6·63 (CH_3); 2·88, 2·98 (*trans*-ethylenic H atoms). (Found: C, 87·0; H, 5·7; F, 7·2. Calc. for $C_{19}H_{15}F$: C, 87·0; H, 5·7; F, 7·2%.

Attempted photocyclization of **8**. In a 3-necked photolysis tube, equipped with a Teflon magnetic stirrer and a 450-Watt Hanovia UV light source, 405 mg of **8**, 60 mg I_2 and 170 ml purified cyclohexane were irradiated. Within 90 min all the starting material had disappeared; after this period no significant change in the UV spectrum was noticeable (even within 20 hr). The product consisted mainly of **11**; [$\bar{\nu}^{\text{Nujol}}$ 698 cm^{-1}: NMR ($CDCl_3$) multiplets at 5·2 and 5·9 (*cis*-ethylenic H atoms); mol. wt. (mass spectrograph) 248] and of some dimeric material [mol. wt. (mass spectrograph) 496]. No. 7-fluorobenz[*a*]anthracene **1** was formed.

Repetition of the experiment, passing a stream of N_2 or O_2 through the illuminated soln or using a quartz flask or light sources of various intensities did not change the negative result of the experiment. Also compound **9** was completely refractory to photocyclization.

7-Fluorobenz[a]*anthracene* (1). A soln of 400 mg of **10** in 400 ml cyclohexane was placed in a 4·5 × 32 cm quartz tube of a Rayouet photochemical reactor, fitted with 16 75-Watt UV lamps at a distance of 12 cm from the reaction vessel. N_2 was bubbled through the soln. After 5·5 hr the temp of the reaction mixture was 57°. The solvent was removed *in vacuo* and the residue chromatographed on alumina, cyclohexane serving as eluent. The third fraction of the eluate (after 2 mg of high melting material and traces of greasy products) was recrystallized from light petroleum ether at −20° to yield 137·3 mg (52 %) of **1** as colourless shiny needles; m.p. 61°. (Found: C, 87·6; H, 4·8; F, 7·5, MW, 246 (mass spectrograph). Calc. for $C_{18}H_{11}F$: C, 87·8; H, 4·5; F, 7·7%, MW, 246).

The 2,4,7-*trinitrofluorenone complex* was prepared in, and recrystallized from, benzene, red-brown needles, m.p. 210°. (Found: C, 66·1; H, 3·0; F, 3·7. Calc. for $C_{31}H_{16}FN_3O_7$; C, 66·3; H, 2·9; F, 3·4 %).

When a 450-Watt Hanovia lamp was used in the photolysis, only F-free material resulted.

Proof of the structure of **1**. Solid sodium dichromate (65 mg) was added in portions to a soln of 50 mg of **1** in 2·8 ml glacial AcOH. After refluxing for 30 min, water was added and the orange ppt washed with water and recrystallized from AcOH. The yellow crystals obtained in almost quantitative yield had identical analysis, IR spectrum and m.p. with an authentic sample of **12**.

2-Bromo-1-fluoronaphthalene (5). 1-Amino-2-bromonaphthalene (179 g), prepared from 2-naphthylamine[25–27] in an overall yield of 10 % was diazotized with 57·5 g $NaNO_2$, 115 g of conc H_2SO_4 and 1·8 l. water. The excess nitrous acid was carefully destroyed with urea. Addition of 48 % fluoboric acid caused the immediate precipitation of the diazonium fluoborate. The mixture was stirred at 0° and filtered, and the ppt was washed with cold water. EtOH and ether. The dried yellow salt (dec. point 175°) was decomposed in portions by direct heating. The resulting dark liquid was taken up in CH_2Cl_2, washed with alkali and water, dried over K_2CO_3 and distilled to yield 28·5 g (23 %) of **5** as a colourless liquid, b.p. 108° (1·5 mm). (Found: C, 53·7; H, 2·7; F, 8·0. Calc. for $C_{10}H_6BrF$: C, 53·4; H, 2·7; F, 8·4 %).

When the diazonium soln was treated with hexafluorophosphoric acid, the diazonium hexafluorophosphate [m.p. 145° (dec)] was obtained; however, it afforded only a 9 % yield of **5**.

1-Fluoro-2-naphthonitrile (6). A mixture of 57 g of **5** and 34 g cuprous cyanide in 600 ml N-methylpyrrolidone was heated at 200° for 3 hr and poured into cold water, the ppt was filtered off and the organic material extracted with benzene. The washed benzene soln was dried and concentrated and the resulting colourless solid recrystallized from light pet. ether (40–60°), yielding 30 g (69 %) of **6**; m.p. 85·5–86°. (Found: C, 77·5; H, 3·6; N, 8·4. Calc. for $C_{11}H_6FN$: C, 77·2; H, 3·5; N, 8·2 %).

1-Fluoro-2-naphthaldehyde (7). A soln of 5 g $SnCl_2$ in 25 ml dry ether, saturated with HCl, was rapidly added to a soln of 2 g of **6** in 15 ml dry ether. A stream of HCl was passed for 1 hr at 0°; through the stirred mixture; then it was left at room temp for 16 hr during which the liquid separated in two phases. The upper layer was decanted and the viscous lower phase refluxed with 30 ml dil HCl (25 %) for 2 hr. The organic material was taken up in benzene and the soln concentrated and chromatographed on alumina. The oily aldehyde **7** was obtained as traces and was identified by its 2,4-*dinitrophenylhydrazone*; orange needles, m.p. 265° (from EtOH). (Found: C, 57·6; H, 3·1; F, 5·4. Calc. for $C_{17}H_{11}FN_4O_4$: C, 57·6; H, 3·1; F, 5·4 %).

2-Bromo-4-fluoro-1-methylnaphthalene (13). (a) 4-Amino-2-bromo-1-methylnaphthalene (m.p. 117°) was prepared by nitration of 1-methylnaphthalene,[28] followed by bromination[29] and reduction,[27] in an overall yield of only 1·1 %. Nine g of this amine was diazotized with 3 g $NaNO_2$ and 7 g of conc H_2SO_4 in 300 ml water. On addition of an excess of fluoboric acid (48 %), the yellow diazonium fluoborate separated. After filtration, washing and drying, the salt (dec point 130°) was decomposed by direct heating. The residue was worked up in the usual manner and distilled under reduced press. The fluoro compound was obtained as a colourless liquid, b.p. 106° (0·4 mm), which solidified on standing at room temp. After recrystallization from MeOH at −20° 3·2 g (35 %) of **13**, colourless crystals of m.p. 36°, was obtained. (Found: C, 55·5; H, 3·3; Br, 33·2; F, 8·3. Calc. for $C_{11}H_8BrF$: C, 55·3; H, 3·3; Br, 33·5; F, 7·9 %).

(b) Alternatively, 1-amino-4-methylnaphthalene (m.p. 51°) was prepared from 1-methylnaphthalene *via* 1-methyl-4-nitronaphthalene[28] in 16 % yield, or by the sequence of acetylation, oxime formation rearrangement and hydrolysis[30] in an overall yield of 66 %. The amine was converted in 60 % yield to 1-fluoro-4-methylnaphthalene (120°, 25 mm). A mixture of 69 g of the latter compound, 1 g of Fe dust and 150 ml CCl_4 was treated with 69 g Br_2 in 100 ml of the same solvent. The mixture was refluxed with agitation for 2 hr, washed with $NaHSO_3$ aq, dried and fractionated *in vacuo*. The fraction boiling at 108° (0·5 mm) was recrystallized from MeOH, yielding 87 g (85 %) of **13** identical with the material obtained from procedure (a).

4-Fluoro-1-methyl-2-naphthonitrile (14). Similar to the preparation of **6** described above, 16·5 g of **13**

10 g cuprous cyanide and 165 N-methylpyrrolidone afforded 10 g (78%) of the expected nitrile as colourless needles; m.p. 97° from hexane. (Found: C, 77·6; H, 4·5; F, 9·9. Calc. for $C_{12}H_8FN$: C, 77·8; H, 4·3; F, 10·3%).

Attempts to convert **14** into 4-fluoro-1-methyl-2-naphthaldehyde by the Stephen reduction, failed.

4-*Fluoro*-1-*methyl*-2-*naphthoic acid* (**15**). A mixture of 17 g of **14**, 170 ml conc H_2SO_4, 340 ml AcOH and 17 ml water was refluxed for 18 hr. Upon cooling, white crystals of the expected acid separated and were filtered off. After purification by extraction with Na_2CO_3aq, reacidification and recrystallization from EtOH, 17 g (90%) of **15** was obtained; m.p. 230–232°. (Found: C, 70·9; H, 4·2; F, 9·8. Calc. for $C_{12}H_9FO_2$: C, 70·6; H, 4·4; F, 9·3%).

Methyl 4-*fluoro*-1-*methyl*-2-*naphthoate* (**16**) was obtained on treatment of **15** with diazomethane. Recrystallization from cyclohexane afforded colourless needles; m.p. 67–68°. (Found: C, 71·6; H, 4·9; F, 9·0. Calc. for $C_{13}H_{11}FO_2$: C, 71·6; H, 5·0; F, 8·7%).

4-*Fluoro*-1-*methyl*-2-*naphthalenemethanol* (**17**). To a stirred suspension of 1·5 g LAH in 150 ml dry ether, a solution of 7 g of the foregoing ester in 50 ml of ether was added dropwise. After refluxing for 1 hr, the excess reagent was destroyed by addition of EtOAc and the product decomposed with water and HCl. The aqueous layer was extracted with benzene, and the combined organic layers were concentrated. The residue was recrystallized from a mixture of benzene–heptane, giving 5·5 g (91%) of **17** as colourless crystals; m.p. 131–133°. (Found: C, 75·8; H, 6·0; F, 10·1. Calc. for $C_{12}H_{11}FO$: C, 75·8; H, 5·8; F, 10·0%).

2-*Bromomethyl*-4-*fluoro*-1-*methylnaphthalene* (**18**). A soln of 9 g PBr_3 in 5 ml benzene was added dropwise to a warm soln of 5 g of **17** in 40 ml dry benzene at such a rate as to permit gentle refluxing of the reaction mixture. After heating for 2 hr, the excess reagent was decomposed with water, the mixture neutralized with Na_2CO_3 and the organic material taken up in benzene, washed with water, dried, concentrated and recrystallized from light pet ether (40–60°). Thus 5 g (75%) of colourless crystals of **18** was obtained, m.p. 60°. (Found: C, 57·0; H, 3·9; Br, 31·1; F, 7·3. Calc. for $C_{12}H_{10}BrF$: C, 56·9; H, 4·0; Br, 31·6; F, 7·5%).

trans-1-(4-*Fluoro*-1-*methyl*-2-*naphthyl*)-2-(o-*iodophenyl*)*ethylene* (**19**). Similar to the preparation of **8**, 2 g of **18** and 1·8 g triethyl phosphite were heated on the steam bath for 2·5 hr, and the phosphonate thus obtained, dissolved in 10 ml DMF and treated below 40° with 1·8 g *o*-iodobenzaldehyde and with 0·42 g NaOMe, each of them dissolved in 20 ml DMF. After heating for 30 min at 100° and the usual work-up, the yellow product was recrystallized from cyclohexane giving 1·5 g (49%) of **19** as colourless crystals, m.p. 111–113°; λ_{max}^{EtOH} (log ε), 217 (4·56); 230 (4·51); 275 (4·28); 314 (4·23) 356^s mμ (3·70); $\bar{\nu}_{max}^{KBr}$ 955 cm^{-1}; NMR ($CDCl_3$) τ 7·37 ($C\underline{H}_3$); 2·75–3·20 (*trans*-ethylenic H atoms). (Found: C, 58·6; H, 3·8; F, 5·1; I, 33·0. Calc. for $C_{19}H_{14}FI$: C, 58·8; H, 3·6; F, 4·9; I, 32·7%).

12-*Fluoro*-7-*methylbenz*[a]*anthracene* (**2**). Analogous to the photolysis of **8**, 770 mg of **19** in 450 ml cyclohexane gave a brown oily product that was purified by chromatography on alumina and by recrystallization from MeOH. Thus 55 mg (11%) of pure **2**; m.p. 81–83° was obtained. From the mother liquor an additional 27 mg of impure material (m.p. 75–78°) containing 10 mg (2%) of **2** (calculated from the UV spectrum) was recovered. (Found: C, 87·4; H, 5·1; F, 7·0; MW, 260 (mass spectrograph). Calc. for $C_{19}H_{13}F$: C, 87·7; H, 5·0; F, 7·3%; MW, 260). The 2,4,7-*trinitrofluorenone derivative* was obtained in, and recrystallized from, benzene as red-brown needles, m.p. 230°. (Found: C, 66·8; H, 3·2. Calc. for $C_{32}H_{18}FN_3O_7$: C, 66·8; H, 3·1%).

As in the photolysis of **8**, light sources with high intensities led to the formation of fluorine-free material.

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