

Formation of Fused Azetines by Photolysis and Pyrolysis of Triazinones. *N*-Aminonaphth[2,3-*b*]azet-2(1*H*)-one and *N*-1-Adamantylbenzazet-2-(1*H*)-one

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N-Aminonaphth[2,3-*b*]azet-2(1*H*)-one (4b) has been isolated as a labile crystalline solid from the photolysis of 3-aminonaphtho[2,3-*d*]-*v*-triazin-4(3*H*)-one (3b) in acetonitrile. When heated or when treated with acetic acid, the azetinone is converted into benz[*f*]indazol-3(2*H*)-one (7). Oxidation of (4b) by lead tetra-acetate gives 2-naphthoic acid. Photolysis or pyrolysis of 3-amino-1,2,3-benzotriazin-4(3*H*)-one (1a) gives the indazolinone (6) directly. 3-(1-Adamantyl)-1,2,3-benzotriazin-4(3*H*)-one (1b) is resistant to photochemical cleavage, but at 600° in the vapour phase it undergoes two competing fragmentations. *N*-1-Adamantylbenzazetinone (2b) is formed in the major reaction, and adamantyl isocyanate and biphenylene are produced in the minor reaction.

PHOTOLYSIS of 3-substituted benzotriazinones (1) has been shown to lead to the formation of the azetines (2) in the cases where R = aryl and R = benzoyl.^{1,2} The azetines could not be isolated but their presence in solution was shown by spectroscopic means and by their interception with added nucleophiles. By applying the reaction to the naphthotriazinone (3a), Ege was able to isolate *N*-phenylnaphth[2,3-*b*]azet-2(1*H*)-one (4a) as a labile crystalline solid.³ Thermolysis of benzotriazinone has also been observed to lead to extrusion of nitrogen,

¹ E. M. Burgess and G. Milne, *Tetrahedron Letters*, 1966, 93.

² G. Ege, *Chem. Ber.*, 1968, **101**, 3079; G. Ege and F. Pasedach, *ibid.*, p. 3089.

³ G. Ege and E. Beisiegel, *Angew. Chem. Internat. Edn.*, 1968, **7**, 303.

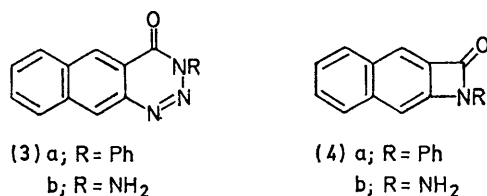
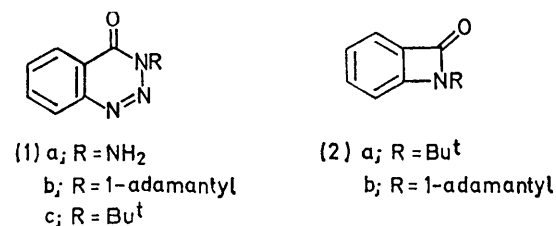
with the formation of a formal dimer of benzazetinone.⁴

The present work was undertaken with the object of isolating other benz- and naphth-azetines by photolysis or pyrolysis of the corresponding triazinones, particularly *N*-amino-azetines which were required for studies of their oxidation. During the course of the work, Olofson and his co-workers reported an elegant synthesis of *N*-alkylbenzazetines which involved the reaction of *N*-alkylanthranilium salts (5) with triethylamine.⁵ By this means *N*-*t*-butylbenzazet-2(1*H*)-one

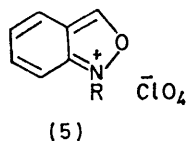
⁴ R. K. Smalley and H. Suschitzky, *Tetrahedron Letters*, 1966, 3465.

⁵ R. A. Olofson, R. K. Vander Meer, and S. Stournas, *J. Amer. Chem. Soc.*, 1971, **93**, 1543.

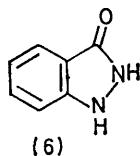
(2a) was isolated as a stable liquid. The present work has produced two more examples of isolable azetinone



derivatives, namely *N*-aminonaphth[2,3-*b*]azet-2(1*H*)-one (4b) and *N*-1-adamantylbenzazet-2(1*H*)-one (2b).



3-Aminobenzotriazinone (1a) and 3-aminonaphthotriazinone (3b) were available from earlier work.⁶ Photolysis of 3-aminobenzotriazinone in acetonitrile (Pyrex filter) resulted in the rapid evolution of nitrogen and the formation of a precipitate, which was shown to be indazolin-3-one (6) by comparison with an authentic

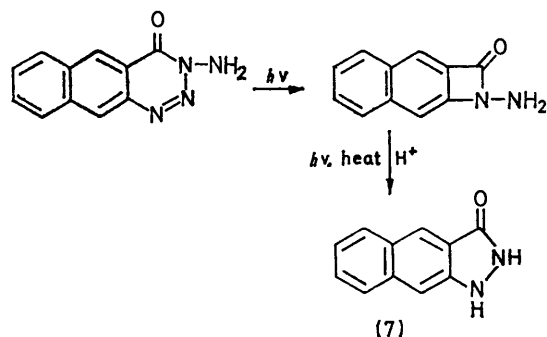


specimen. When the photolysis was stopped before all the nitrogen had been evolved, only the starting material and indazolinone were detected; there was no evidence for the presence of an azetinone.

Similar photolysis of 3-aminonaphthotriazinone (3b) also resulted in the evolution of nitrogen. When nitrogen evolution ceased the solution was evaporated to small bulk; yellow crystals separated and were identified as *N*-aminonaphth[2,3-*b*]azet-2(1*H*)-one (4b) from analytical and spectral data. The crystals decomposed without melting above 220° and lost their yellow lustre on exposure to air. Treatment of the azetinone with acetic acid at room temperature, or by heating, alone or in a solvent, converted it into benz[*f*]indazol-3(2*H*)-one (7); the indazolinone was also formed on attempted deamination of the azetinone with pentyl nitrite or with nitrous acid. Prolonged irradiation of

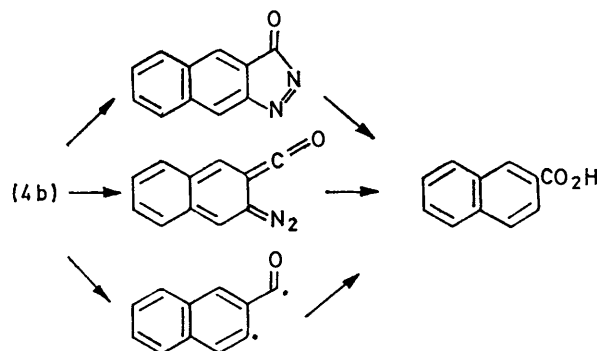
3-aminonaphthotriazinone also gave the indazolinone (7). The reactions are summarised in Scheme 1.

Two reactions of the azetinone were observed which did not cause rearrangement to the indazolinone (7). One was the reaction with methanol, which resulted in ring opening to methyl 3-hydrazino-2-naphthoate (isolated as its isopropylidene derivative). The other was its oxidation by lead tetra-acetate in the presence of dimethyl sulphoxide. In this reaction, a gas was evolved on adding the oxidant, and 2-naphthoic acid was



SCHEME 1

isolated after an aqueous work-up. The amino-azetinone therefore belongs to the group of amino-lactams which undergo fragmentation on oxidation,⁷ and there is no evidence for interception of an intermediate by dimethyl sulphoxide. The possibility that the oxidant catalyses a rearrangement of the azetinone to the indazolinone (7), and that this is then oxidised, was rendered unlikely by the results of investigating the oxidation of the indazolinone independently. Oxidation by lead tetra-acetate was slow and no 2-naphthoic acid was detected in the product mixture. Possible mechanisms for the formation of 2-naphthoic acid from the azetinone are shown in Scheme 2.



SCHEME 2

3-(1-Adamantyl)benzotriazinone was prepared in order to test whether the azetinone synthesis could be extended to the benzo-series if a sufficiently inert blocking substituent were employed. The 1-adamantyl group has been successfully used before to stabilise strained hetero-

⁶ J. Adamson, D. L. Forster, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc. (C)*, 1971, 981.

⁷ D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc. (C)*, 1970, 576.

benzamide (86%), m.p. $>300^\circ$ (from dichloromethane) (Found: C, 68.2; H, 6.9; N, 9.4. $C_{17}H_{20}N_2O_3$ requires C, 68.0; H, 6.7; N, 9.3%); ν_{\max} 3250 and 1650 cm^{-1} .

(b) The nitro-amide (5.0 g) was hydrogenated over Pd-charcoal in ethanol, to give N-(1-adamantyl)-2-aminobenzamide (95%), m.p. 151–152° (from heptane) (Found: C, 75.6; H, 8.2; N, 10.3. $C_{17}H_{22}N_2O$ requires C, 75.5; H, 8.2; N, 10.4%); ν_{\max} 3300, 3250, 1600, 1560, and 720 cm^{-1} .

(c) To the amino-amide (5.0 g) in hydrochloric acid (15 ml) and water (15 ml) at 5° was added sodium nitrite (0.9 g). The mixture was neutralised with sodium carbonate and the precipitate filtered off and recrystallised to give 3-(1-adamantyl)-1,2,3-benzotriazin-4(3H)-one (60%), m.p. 116–117° (from methanol) (Found: C, 72.3; H, 6.8; N, 14.9. $C_{17}H_{19}N_3O$ requires C, 72.6; H, 6.8; N, 14.9%); ν_{\max} 1680, 1620, 1590, and 780 cm^{-1} .

3-*t*-Butyl-1,2,3-benzotriazin-4(3H)-one (1c). (a) 2-Nitrobenzoyl chloride (5.6 g) and *t*-butylamine (6.0 g) in dry ether (100 ml) gave 2-nitro-*N*-*t*-butylbenzamide (60%), m.p. 102° (Found: C, 59.8; H, 6.3; N, 12.8. $C_{11}H_{14}N_2O_3$ requires C, 59.45; H, 6.3; N, 12.6%); ν_{\max} 3250, 1650, 1570, and 1540 cm^{-1} .

(b) The nitroamide (3.0 g) was hydrogenated over 5% palladium-charcoal (0.2 g) to give 2-amino-*N*-*t*-butylbenzamide (95%), m.p. 126–127° (from petroleum) (Found: C, 68.9; H, 8.4; N, 14.5. $C_{11}H_{16}N_2O$ requires C, 68.7; H, 8.4; N, 14.6%); ν_{\max} 3400, 3250, 1640, and 1590 cm^{-1} .

(c) To the amino-amide (2.0 g) in hydrochloric acid (15 ml) and water (15 ml) was added sodium nitrite (0.8 g). After 10 min the mixture was neutralised with ammonia and the precipitate filtered off. Recrystallisation gave 3-*t*-butyl-1,2,3-benzotriazin-4(3H)-one (60%), m.p. 69–70° (from ethanol) (Found: C, 65.3; H, 6.7; N, 20.6. $C_{11}H_{13}N_3O$ requires C, 65.0; H, 6.45; N, 20.7%); ν_{\max} 1700, 1600, 1620, and 780 cm^{-1} .

Photolysis of Aminotriazinones.—(a) 3-Amino-1,2,3-benzotriazin-4(3H)-one. The triazinone (0.550 g) in acetonitrile (100 ml) was irradiated (Hanovia 300 W medium-pressure immersion lamp, Pyrex filter) until gas evolution ceased (3.5 h). A precipitate (0.280 g) was filtered off and identified as indazolin-3-one, m.p. and mixed m.p. 248–250°, ν_{\max} 1649 and 1625 cm^{-1} . A further crop (0.084 g) was obtained by evaporating the filtrate to small bulk (total 0.364 g, 85%).

(b) 3-Aminonaphtho[2,3-*d*]-*v*-triazin-4(3H)-one. (i) The triazinone (0.220 g) in acetonitrile (80 ml) was irradiated until gas evolution ceased (2 h). The mixture was filtered and the filtrate evaporated to dryness below 35°. The residue, a yellow solid, was recrystallised from ether-petroleum (1:1) below 30° to give yellow crystals of 1-aminonaphth[2,3-*b*]azet-2(1H)-one (4b) (0.108 g, 57%), m.p. 220–230° (decomp.) (Found: C, 72.1; H, 4.6; N, 14.6. $C_{11}H_8N_2O$ requires C, 71.7; H, 4.4; N, 15.2%); ν_{\max} (KBr) 3340 and 3260 (NH), 1802 and 1792 (C=O), 1645, 1450, 1050, 945, 839, and 740 cm^{-1} , *m/e* 184, 155, 149, and 127. The solid was stored for several weeks at 0° without change, but darkened within a few hours when exposed to air and light at room temperature. Spontaneously or on mild heating the azetinone gave benz[*f*]indazol-3(2H)-one (7),⁶ m.p. 320° (decomp.), ν_{\max} 3100, 1640, 1582, and 1502 cm^{-1} .

(ii) The triazinone (3b) (0.260 g) in acetonitrile (100 ml) was irradiated for 6 h. Evaporation to small bulk gave yellow crystals of benz[*f*]indazol-3(2H)-one (0.140 g, 62%). Evaporation of the filtrate gave a brown solid, ν_{\max} 3100,

1640, 1582, and 1502 cm^{-1} , the spectrum being identical to that of benz[*f*]indazol-3(2H)-one.

Pyrolysis of Triazinones.—(a) 3-Amino-1,2,3-benzotriazin-4(3H)-one. The triazinone (100 mg) was pyrolysed by sublimation and passage of the vapour through a tube at 500° and 0.05 mmHg to give indazolin-3-one (80%), m.p. 248–250°.

(b) 3-(1-Adamantyl)-1,2,3-benzotriazin-4(3H)-one. (i) Heating at 500° and 0.005 mmHg resulted in recovery of the starting material; adamantyl isocyanate (ν_{\max} 2270 cm^{-1}) was detected as a minor contaminant.

(ii) The triazinone (290 mg) was pyrolysed by sublimation at 150° and 0.05 mmHg, the vapour being passed through a tube (20 × 1 cm) heated to 600°, and condensed on a surface cooled to –78°. The condensate was a yellow solid (210 mg), ν_{\max} (Nujol) 2270 and 1795 cm^{-1} . The solid was dissolved in ether and applied to a chromatography plate (silica, 20 × 20 × 0.1 cm). The plate was developed with petroleum. A yellow band was observed which decomposed during development. A colourless solid (12 mg) was isolated from a band of R_F 0.7; ν_{\max} 2270 cm^{-1} . The solid contained two components which were identified as biphenylene and adamantyl isocyanate by comparison of u.v. and i.r. spectra and g.l.c. retention times with those of authentic specimens.

(iii) The pyrolysis was repeated and the condensate triturated briefly with petroleum (2 ml). The residue was sublimed and the sublimate recrystallised to give *N*-1-adamantylbenzazet-2(1H)-one (30%), m.p. 98–99° (from heptane) (Found: C, 80.4; H, 7.4; N, 5.6. $C_{17}H_{19}NO$ requires C, 80.6; H, 7.6; N, 5.5%); ν_{\max} (KBr) 1790, 1600, and 740 cm^{-1} ; *m/e* 253, 238, 210, 196, 159 (base), and 135.

(c) 3-*t*-Butyl-1,2,3-benzotriazin-4(3H)-one. The triazinone (100 mg) was pyrolysed at 600° and 0.05 mmHg. The pyrolysate, a yellow oil, showed a strong band at ν_{\max} 1800 cm^{-1} . T.l.c. indicated the presence of several components, but decomposition of the yellow component was observed during attempted isolation.

Reactions of 1-Aminonaphth[2,3-*b*]azet-2(1H)-one.—(a) With methanol in the presence of acetone. The azetinone (50 mg) was heated in methanol (2 ml) containing acetone (0.5 ml) at 50° for 2 min. The mixture was applied to a chromatography plate (silica; ether-petroleum, 1:1) and a yellow band was extracted from the plate. Recrystallisation of the solid so obtained gave methyl 3-(isopropylidenehydrazino)-2-naphthoate (20 mg, 29%), m.p. 112° (from ether-petroleum) (Found: C, 70.1; H, 6.4%; *m/e* 256. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.3%; *M*, 256).

(b) Oxidation. The azetinone (47 mg) was dissolved in dimethyl sulphoxide (3 ml) and lead tetra-acetate was added. A gas was evolved immediately. The solution was poured into water and the mixture extracted with ether (20 ml). The ethereal solution was evaporated and the residue purified by sublimation, giving 2-naphthoic acid (5 mg, 11%), m.p. and mixed m.p. 182–184°.

(c) Attempted deamination. The azetinone (30 mg) was dissolved in acetonitrile (5 ml) and pentyl nitrite (0.5 ml) was added. After 12 h the mixture was evaporated to dryness. The residue was benz[*f*]indazol-3(2H)-one (i.r.).

(d) Reaction with acetic acid. To the azetinone (9 mg) acetic acid (1 ml) was added. There was an exothermic reaction, and benz[*f*]indazol-3(2H)-one was formed (i.r.).

Reactions of *N*-1-Adamantylbenzazet-2(1H)-one.—(a) Attempted pyrolysis. The azetinone (50 mg) was heated at 85° and 0.05 mmHg and the vapour passed through a tube

at 600°. The condensate (45 mg), m.p. 92—94°, was the unchanged azetinone (i.r.).

(b) *Hydrolysis in moist ether.* The azetinone (50 mg) was dissolved in ether (10 ml) containing traces of water, and the solution kept at 20° for 36 h. Crystals appeared after 12 h. The crystals were filtered off and identified as 2-(1-adamantylamino)benzoic anhydride (20 mg), m.p. 244—246° (Found: C, 77.9; H, 7.65; N, 5.45%; *m/e* 524. $C_{34}H_{40}N_2O_3$ requires C, 77.8; H, 7.7; N, 5.3%; *M*, 524); ν_{\max} (Nujol) 3320 (NH) and 1720 and 1680 (C=O) cm^{-1} . The anhydride (50 mg) was heated under reflux with potassium hydroxide (100 mg) in aqueous dioxan (5 ml) for 2 h. The solution was neutralised and gave 2-(1-adamantylamino)benzoic acid (35 mg, 68%), m.p. 205—206° (from ether-petroleum)

(Found: C, 74.8; H, 7.9; N, 5.1. $C_{17}H_{21}NO_2$ requires C, 75.25; H, 7.8; N, 5.2%); ν_{\max} (Nujol) 3300 (NH) and 1660 (C=O) cm^{-1} .

(c) *Reaction with methanol.* The azetinone (30 mg) was heated under reflux in methanol (5 ml) for 0.5 h. Evaporation of the solution gave methyl 2-(1-adamantylamino)benzoate (33%), m.p. 110—111° (from petroleum) (Found: C, 75.4; H, 8.2%; *m/e* 285. $C_{18}H_{23}NO_2$ requires C, 75.8; H, 8.1%; *M*, 285); ν_{\max} 3250, 1685, 1620, and 1600 cm^{-1} .

We thank Professor C. W. Rees for discussion, and the British Council for a maintenance award (to N. B.).

[2/2482 Received, 2nd November, 1972]