805. *Reactions of Organic Azides. Part VII.*[1] *Ring Expansion* via *Azides : 1 : 2- and 7 : 8-Benzophenanthridine and 9-Phenylphenanthridine. The Hydrazoic–Sulphuric Acid Reaction with Indene.*

By C. L. Arcus, R. E. Marks, and (in part) M. M. Coombs.

1 : 2-Benzofluoren-9-ol with hydrazoic and trichloroacetic acid yields 9-azido-1 : 2-benzofluorene, which when heated with trifluoroacetic acid forms 1 : 2- and 7 : 8-benzophenanthridine in ratio 2·9 : 1. On being heated alone, the azide yields 1 : 2-benzofluorenone imine (two forms).

9-Phenylfluoren-9-ol has been converted into 9-azido-9-phenylfluorene, which on treatment with sulphuric acid, and also on being heated, forms 9-phenylphenanthridine.

It is inferred from these and other results that pyrolysis of secondary and tertiary 9-azidofluorenes yields respectively fluorenone imines and 9-substituted phenanthridines.

Indene with hydrazoic and sulphuric acid forms a base considered to be a polymer of dihydro-quinoline and/or -*iso*quinoline.

Syntheses of phenanthridines,[2,3,4] phenanthridones,[5] and benzoxazines [1,6] by reactions which involve the formation of an azide and rearrangement of its proton-adduct have been described in earlier papers of this series. In some instances the azide was isolated, but usually it was formed, and underwent rearrangement, in the reaction mixture. Extensions of this method to the formation of mononitrogen heterocycles, particularly those which involve the preparation and the subsequent rearrangement of an azide, are now reported.

1 : 2-Benzofluorenone was largely recovered from attempted Schmidt reactions in sulphuric acid at 0° and trichloroacetic acid at 65—85°; from reaction in sulphuric acid at 40—50°, and in polyphosphoric acid at 65°, small quantities of nitrogen-containing products were isolated by vacuum-sublimation, but ketone was again recovered. The resistance of 1 : 2-benzofluorenone to reaction is probably due to steric hindrance of the carbonyl group by the 1 : 2-benzo-group. It is known [7, 8] that benzoylmesitylene does not readily undergo the Schmidt reaction, and Stephenson [9] has found naphtho(1′ : 2′-2 : 3)fluorenone not to react.

Reduction of the ketone with aluminium *iso*propoxide gave 1 : 2-benzofluoren-9-ol in good yield. It was allowed to react with a solution of hydrazoic acid in chloroform, together with sulphuric acid; sulphur-containing products were obtained, and no basic compound was characterised.

The reaction of the fluorenol with sodium azide and trichloroacetic acid gave a good yield of 9-azido-1 : 2-benzofluorene. The azide, on being heated with trifluoroacetic acid, decomposed and rearranged to benzophenanthridines, which were isolated through their picrates in 33% yield. By chromatography on alumina, the mixture of bases was separated into 1 : 2- and 7 : 8-benzophenanthridine in the ratio 2·9 : 1. The rearrangement of the intermediate protonated azide (I), the mechanism of which has been earlier discussed with respect to other azidofluorenes,[2, 3] therefore leads to a greater extent (as indicated) to the phenanthridinium ion (II) and to a smaller extent to the ion (III). It has been shown,[3, 5] from results of reactions of 2- and 3-substituted fluoren-9-ols with hydrazoic and sulphuric acid, that the relative migratory aptitudes of the two rings in such a fluorenol are directly

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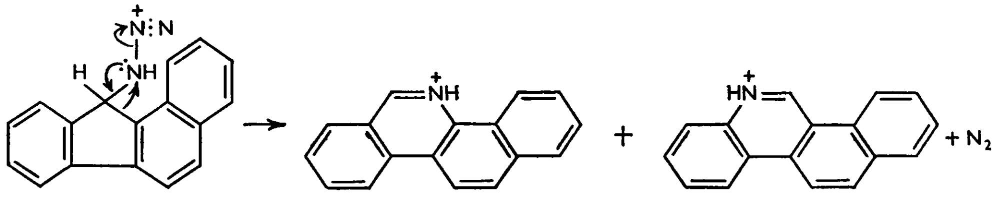
[1] Part VI, Arcus and Marks, *J.*, 1956, 1627.
[2] Arcus and Mesley, *J.*, 1953, 178.
[3] Arcus and Coombs, *J.*, 1954, 4319.
[4] Arcus and Lucken, *J.*, 1955, 1634.
[5] Arcus, Coombs, and Evans, *J.*, 1956, 1498.
[6] Arcus and Coombs, *J.*, 1953, 3698.
[7] Badger, Howard, and Simons, *J.*, 1952, 2849.
[8] Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 431.
[9] Stephenson, *J.*, 1949, 2620.

related to the capacities of the rings for electron-release at their point of attachment to $C_{(9)}$. The comparison in the present instance is substantially between the electron-release of an *o*-2-naphthylphenyl group and a 2-phenyl-1-naphthyl group, and the result of rearrangement indicates the latter to have the greater electron-release. This finding accords with Hey and Lawtons's observation[10] that 2-phenylnaphthalene, on nitration, yields principally 1-nitro-2-phenylnaphthalene, indicating the α-naphthyl position *ortho* to the phenyl group to be the position of greatest electron-release in the molecule.

On being heated alone, 9-azido-1 : 2-benzofluorene decomposed to form 1 : 2-benzofluorenone imine, which was isolated in two forms; their mixture on hydrolysis gave 1 : 2-benzofluorenone in high yield. Taylor and Fletcher[11] have reported that the azomethine compounds derived from the condensation of 2 : 5-dinitrofluorenone with aniline and with *p*-fluoroaniline each exist in two forms. Although the possibility of dimorphism is not excluded, it appears probable that in every case the two forms are the geometric isomers.



(I) (II) (III)

Reaction of 9-phenylfluoren-9-ol with sodium azide and trichloroacetic acid gave a high yield of 9-azido-9-phenylfluorene. This compound, in sulphuric acid, rearranged into 9-phenylphenanthridine, which was also obtained by heating the azide alone. The acid-catalysed rearrangement of the azide is parallelled by those of 9-azidofluorene[2] and -2-methoxyfluorene.[3] The conversion of 9-phenylfluoren-9-ol into 9-phenylphenanthridine, by reaction with hydrazoic and sulphuric acid, has been carried out earlier,[3] and the present results confirm that, as had been inferred, the protonated azide is the essential reaction intermediate.

The uncatalysed decomposition of the azide, with rearrangement to 9-phenylphenanthridine, is similar to conversion of 9-azido-9-α-naphthylfluorene into 9-α-naphthylphenanthridine,[12] and contrasts with the migration of hydrogen, without ring-expansion, leading to the fluorenone imine, which occurs with 9-azido-fluorene[2] and -1 : 2-benzofluorene (above) and is inferred for 9-azido-2-nitrofluorene.[3] The available results therefore show pyrolysis of secondary and tertiary 9-azidofluorenes to yield, respectively, fluorenone imines and 9-substituted phenanthridines.

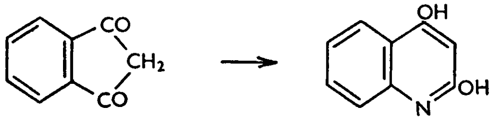
The fluorenes are benzoindenes, whence it appeared that reactions which succeed with this group of compounds might be effective with indenes. Indene, contrary to a statement by Kuhn and Di Domenico[13] that it does not react, except to polymerise, gave on reaction with hydrazoic and sulphuric acid a nitrogen-containing basic oil considered to be a polymer of dihydro-quinoline and/or -*iso*quinoline.

Since the stability of an aromatic compound tends to reduce the possibility of polymerisation or other secondary reactions, attention was directed to indene compounds at such a level of oxidation that ring-expansion yields an aromatic, not a hydroaromatic, product. Benzylideneindene, by analogy with the conversion of 9-benzylidenefluorene into 9-benzylphenanthridine,[3] might be expected to yield 2-benzylquinoline or 1-benzyl*iso*quinoline. However, reaction with hydrazoic acid in the presence of 98% sulphuric acid, sulphuric

[10] Hey and Lawton, *J.*, 1940, 374.
[11] Taylor and Fletcher, *J. Org. Chem.*, 1956, **21**, 523.
[12] Pinck and Hilbert, *J. Amer. Chem. Soc.*, 1937, **59**, 8.
[13] Kuhn and Di Domenico, *ibid.*, 1950, **72**, 5777.

acid monohydrate, and trichloroacetic acid, gave no appreciable quantity of base; with concentrated sulphuric acid a sulphur-containing material was formed; the procedures with monohydrate and trichloroacetic acid yielded a benzylideneindene polymer, a similar material being obtained by reaction with trichloroacetic acid in the absence of azide. Cationic polymerisation is considered to have taken place, a conclusion supported by Whitby and Katz's observation [14] that a hexamer is formed on treatment of benzylideneindene with antimony pentachloride.

The reaction with a second more highly oxidised indene, indane-1 : 3-dione, has been carried out by Fusco and Rossi,[15] who obtained 2 : 4-dihydroxyquinoline. This result has been confirmed; the dihydroxy-compound was characterised by conversion into 2 : 4-dichloroquinoline. Although the product is doubly enolised to yield an aromatic ring, the reaction is surely a normal ketonic Schmidt reaction, the mechanism of which has recently been discussed.[5]



On several occasions in the course of the work recorded in Part III we prepared 9-phenylfluoren-9-ol, for which m. p. 107° is recorded in the literature,[16, 17] but our material always had m. p. 85°.[18, 3] Like the higher-melting material, our fluorenol formed solvated crystals with several organic solvents. That the compound, m. p. 85°, is 9-phenylfluoren-9-ol is demonstrated by the following observations: with phosphorus pentachloride it gave 9-chloro-9-phenylfluorene [18] and on reaction with hydrazoic and sulphuric acid it gave 9-phenylphenanthridine in almost theoretical yield.[3] It seemed likely that the compound is dimorphic. This has been confirmed by the use of a specimen of the fluorenol, m. p. 109—110°, kindly supplied by Dr. G. W. H. Cheeseman. Seeding our molten material with his gave the higher-melting form. The reverse change could not be effected and we regard our form as metastable.

EXPERIMENTAL

M. p.s are corrected. 98% Sulphuric acid was used; sulphuric acid–sodium azide–chloroform reaction mixtures were prepared as described for indane-1 : 3-dione.

Chrysene was converted into chrysenequinone and thence into 1 : 2-benzofluorenone by methods due to Bamberger and Burgdorf.[19]

To a hot solution of aluminium *iso*propoxide (from aluminium, 12·4 g., and propan-2-ol, 170 ml.), was added a solution of 1 : 2-benzofluorenone (30 g.) in benzene (300 ml.) and the whole was heated under reflux for 3½ hr. The solvents were removed at reduced pressure and the product was decomposed with ice-cold dilute hydrochloric acid. To a solution of the product in hot benzene, *n*-heptane was added; on cooling there separated 1 : 2-benzofluoren-9-ol (21·5 g.), m. p. 175·5°, and, after recrystallisation, m. p. 176° (Found: C, 87·3; H, 5·15. Calc. for $C_{17}H_{12}O$: C, 87·9; H, 5·2%). Bamberger and Kranzfeld [20] record m. p. 166—167°. The fluorenol (0·5 g.), heated for 3 hr. on a steam-bath with acetic anhydride (1 ml.) and pyridine (5 ml.), yielded *9-acetoxy-*1 : *2-benzofluorene*, prisms (from ethanol), m. p. 113° (Found: C, 83·1; H, 5·15. $C_{19}H_{14}O_2$ requires C, 83·3; H, 5·15%).

Azido-reactions.—1 : *2-Benzofluorenone.* To a solution of this compound (4·6 g.) in sulphuric acid (20 ml.) at 0°, sodium azide (2·6 g.) was added; after 1½ hr. the solution was poured on ice;

[14] Whitby and Katz, *ibid.*, 1928, **50**, 1160.
[15] Fusco and Rossi, *Gazzetta*, 1951, **81**, 511.
[16] Ullmann and von Wurstemberger, *Ber.*, 1904, **37**, 73.
[17] Williamson, Anderson, and Watts, *J. Amer. Chem. Soc.*, 1943, **65**, 49.
[18] Arcus and Coombs, *J.*, 1954, 3977.
[19] Bamberger and Burgdorf, *Ber.*, 1890, **23**, 2437; 1885, **18**, 1933.
[20] Bamberger and Kranzfeld, *ibid.*, p. 1934.

the fluorenone (3·7 g.) was recovered. The product from a similar procedure at 40—50° was shaken with 2N-sodium hydroxide, washed, dried, and submitted to vacuum-sublimation; the fluorenone first sublimed, followed by a small yield of a nitrogen-containing product, m. p. 220—260°.

The fluorenone (1·6 g.) was recovered from treatment of this ketone (2·3 g.) in trichloroacetic acid (23 g.) with sodium azide (1·3 g.) at 65—85°.

To polyphosphoric acid (83% P_2O_5; 20 g.) at 65° were added the fluorenone (1·15 g.) and then sodium azide (0·65 g.). After 1½ hr. ice was added, and the product was sublimed in a vacuum; the ketone sublimed, followed by a small quantity of a nitrogen-containing product, m. p. 265—280°.

1 : 2-*Benzofluoren*-9-ol. To a stirred mixture of sulphuric acid (8 ml.), sodium azide (2·6 g.), and chloroform (30 ml.), a suspension of the fluorenol (4·6 g.) in chloroform (20 ml.) was added at 25°; the mixture was finally poured on ice, giving a precipitate of a brown amorphous solid (3·8 g.) and, when the acid aqueous solution was made alkaline with ammonia, a product (0·5 g.), m. p. 245—250°; both contained nitrogen and sulphur.

Sodium azide (2·60 g.), chloroform (20 ml.), and trichloroacetic acid (40 g.) were stirred at room temperature for 15 min. At 30°, a suspension of the fluorenol (4·64 g.) in chloroform (20 ml.) was added during 30 min. After being stirred for a further 2 hr., the mixture was poured on ice (200 g.). The chloroform solution was washed with aqueous sodium hydrogen carbonate, and with water, dried (Na_2SO_4), and evaporated; the product crystallised from light petroleum (b. p. 60—80°) and yielded 9-*azido*-1 : 2-*benzofluorene* (3·53 g.), buff needles, m. p. 90—90·5° (Found: C, 79·3; H, 4·25; N, 16·5. $C_{17}H_{11}N_3$ requires C, 79·4; H, 4·3; N, 16·35%).

A solution of this azide (1·0 g.) in chloroform (10 ml.) was stirred at 0° with sulphuric acid (0·5 ml.), and the mixture was poured on ice; an insoluble material (0·6 g.) was formed, and the azide (0·4 g.) was recovered.

A solution of this azide (3·00 g.) in trifluoroacetic acid (30 ml.) was boiled under reflux for 45 min., cooled, and poured on ice (100 g.). The solid product was shaken for 1 hr. with, then filtered from, 2N-sodium hydroxide (75 ml.), and dried. It (2·56 g.; m. p. 107—115°) was warmed with acetone (125 ml.), and to the solution, filtered from a buff residue (<0·1 g.), was added a solution of picric acid (moist, 5·0 g.) in acetone (25 ml.). A yellow solid (1·89 g.) separated; after recrystallisation from dioxan (25 ml.) it (1·49 g.) had m. p. 236—237° (decomp.). The acetone filtrate was concentrated to 25 ml. and ethanol (25 ml.) was added; the precipitate, recrystallised from dioxan, gave material (0·37 g.) of the m. p. above. The mixed picrates so obtained (1·86 g.) were shaken for 30 min. with aqueous sodium hydroxide (10%, 63 ml.), and the whole was extracted with ether. The extract was washed with water, dried (Na_2SO_4), and on evaporation yielded a buff solid (0·86 g.), m. p. 131—132°. In a similar experiment there were obtained 1·95 g. of the mixed picrates and 0·89 g. of the mixed bases.

To a column of alumina (90 × 3 cm., wet with benzene), a solution of the bases (0·40 g.) in benzene (25 ml.) was added, and the column was eluted with the same solvent. In ultraviolet light, two blue-fluorescent bands could be seen. The first was collected in 2·6 l. of eluate, the product from which (*A*) (0·22 g.) had m. p. 132·5—133°. The second band adhered firmly to the column, the top 30 cm. of which were removed and washed with boiling benzene (4 × 100 ml.). The extract, on evaporation, gave product *B* (0·06 g.), m. p. 171·5—172°.

In a second separation of the bases (0·40 g.), *A* (0·26 g., m. p. 134—134·5°) was obtained as before, but the second band was eluted from the column by acetone, evaporation of which gave a buff solid together with oil; ethanol (25 ml.) was added and the whole was warmed and filtered. To the filtrate was added picric acid (0·3 g.) in ethanol (5 ml.); the yellow picrate which separated was filtered off and dried; it (0·18 g.) had m. p. 272·5° (decomp.).

The base *A*, on recrystallisation from ethanol, gave 1 : 2-benzophenanthridine, m. p. 135° (Found: C, 89·0; H, 4·75; N, 5·95. Calc. for $C_{17}H_{11}N$: C, 89·0; H, 4·85; N, 6·1%). The picrate, prepared in ethanol, had m. p. 256° (decomp.) (Found: N, 11·3. Calc. for $C_{23}H_{14}O_7N_4$: N, 12·2%). This compound, after recrystallisation from dioxan, had a slightly lower m. p. and nitrogen-content; it is presumably unstable. On addition of a solution of the base (0·1 g.) in hydrochloric acid (10 ml.) to aqueous platinic chloride (2%; 10 ml.) there separated 1 : 2-*benzophenanthridine chloroplatinate*, a buff solid, m. p. 279—280° (decomp.) [Found: Pt, 21·8. $(C_{17}H_{11}N)_2,H_2PtCl_6$ requires Pt, 22·5%].

The base *B*, on recrystallisation from ethanol, gave 7 : 8-benzophenanthridine, m. p. 182°

(Found: C, 88·5; H, 4·75; N, 5·95%), whose *picrate*, prepared in ethanol and recrystallised from dioxan, formed yellow needles, m. p. 277—278° (decomp.) (Found: N, 11·95%).

For 1 : 2- and 7 : 8-benzophenanthridine Badger and Seidler [21] record m. p. 136° and m. p. 183°. Graebe [22] records m. p. 256° (decomp.) for the picrate of the former.

With respect to the chromatographic separations: from 0·40 g. base there were isolated (i) 0·22, (ii) 0·26 g. of 1 : 2-benzophenanthridine and (i) 0·06, (ii) 0·09 g. (based on yield of picrate) of the 7 : 8-isomer; the ratio of the isomers from the second, and more nearly quantitative, separation is 2·9 : 1.

9-Azido-1 : 2-benzofluorene (1·50 g.) was heated in an oil-bath at 130°. A slow, then a violent, evolution of gas occurred. A methanolic solution of the product was treated with charcoal (0·1 g.), filtered, and concentrated to 15 ml.; two types of orange solid crystallised, and were separable. The paler (0·74 g.) on recrystallisation from methanol yielded 1 : 2-*benzofluorenone imine*, golden needles, m. p. 106·5° (Found: C, 88·9; H, 5·0; N, 6·0. $C_{17}H_{11}N$ requires C, 89·0; H, 4·85; N, 6·1%); the darker solid (0·11 g.), similarly recrystallised, gave the first form together with dark orange prisms which were separated manually; the latter had m. p. 108—108·5°, and constituted the second *form* of the imine (Found: C, 88·8; H, 5·15; N, 5·9%). A mixture (0·20 g.) of the two forms was heated under reflux for 30 min. with 30% sulphuric acid (10 ml.), and the product was filtered off, washed with water, and dried, giving 1 : 2-benzofluorenone (0·18 g.), m. p. and mixed m. p. 134°.

9-*Phenylfluoren*-9-*ol*. The procedure described for the preparation of azidobenzofluorene, but with half quantities of reagents, was applied to 9-phenylfluoren-9-ol (2·56 g., m. p. 109°). The product (2·52 g., m. p. 75—76°) yielded, after three recrystallisation from light petroleum (b. p. 60—80°), 9-*azido*-9-*phenylfluorene*, rectangular prisms, m. p. 78—78·5° (Found: C, 80·1; H, 4·75; N, 14·65. $C_{19}H_{13}N_3$ requires C, 80·5; H, 4·6; N, 14·85%).

A mixture of sulphuric acid (2 ml.) and chloroform (4 ml.) was vigorously stirred at 25° during the dropwise addition of a solution of the above azide (0·80 g.) in chloroform (4 ml.). After being stirred for a further hour at 25°, the mixture was poured on ice. The chloroform solution was washed with 10N-sulphuric acid (2 × 10 ml.); the acidic solution was made alkaline with sodium hydroxide, then extracted with ether; the ethereal solution was dried (Na_2SO_4), and on evaporation gave a product which, after recrystallisation from light petroleum (b. p. 60—80°), yielded 9-phenylphenanthridine (0·63 g.), m. p. 104°.

The azide (0·83 g.) was heated at 160—170° until no more gas was evolved. The resultant oil was dissolved in ethanol (15 ml.), and picric acid (1·0 g.) was added. The yellow precipitate [1·20 g., m. p. 248—250° (decomp.)] gave, after two recrystallisations from acetic acid, 9-phenylphenanthridine picrate, m. p. 251° (decomp.). It (0·68 g.) was treated with 2N-sodium hydroxide, and the whole was extracted with ether; from the extract there was obtained, as above, 9-phenylphenanthridine (0·18 g.), m. p. 104°. Arcus and Coombs [3] record m. p. 106° for the base, and m. p. 251° (decomp.) for the picrate.

Indene. To a stirred mixture of sodium azide (65 g.), chloroform (200 ml.), and sulphuric acid (150 ml.), a solution of indene (69·6 g.) in chloroform (150 ml.) was so added during 2 hr. that the temperature remained at 25—30°. After being stirred for a further ½ hr., the whole was poured on ice. Much brown tar was formed. The acidic aqueous solution was made alkaline with 30% aqueous sodium hydroxide and extracted with ether; the latter yielded a viscous straw-coloured oil (16·2 g.) (Found: N, 12·6. Calc. for C_9H_9N: N, 10·7%). This product (4·50 g.) was heated at 220° ± 10° for 2¼ hr. with 10% palladised charcoal (4·5 g.), hydrogen equivalent to 690 ml. at N.T.P. being evolved (Calc. for aromatisation of dihydroquinoline: 770 ml.). A solution of the dehydrogenated material in 2N-hydrochloric acid was filtered, made alkaline with 2N-sodium hydroxide, and distilled in steam. There remained a substance of m. p. >300°, and the distillate yielded a yellow oil (0·60 g.), b. p. 140—150°/40 mm., n_D^{20} 1·6100, which smelt of quinoline and gave a picrate having m. p. 193—198°. (For quinoline and *iso*quinoline, respectively, the comparable data are: b. p. 132°/40·5 mm., 142°/40 mm.; n_D^{20} 1·6268, 1·6148; picrate, m. p. 203°, 223°.)

Indane-1 : 3-*dione*. Sulphuric acid (15 ml.) was added dropwise to a stirred, ice-cooled, mixture of sodium azide (2·6 g.) and chloroform (15 ml.). After a further 15 min., the ice was replaced by a water-bath at 30° and indane-1 : 3-dione [(i), (ii) 2·92 g.], in solution in chloroform (20 ml.) was added during 1 hr. Stirring was continued for 2 hr., the mixture was then poured

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[21] Badger and Seidler, *J.*, 1954, 2329.
[22] Graebe, *Annalen*, 1904, **335**, 129.

on ice (200 g.), the whole was shaken mechanically for ½ hr., and the insoluble solid product [(i) 1·99 g., m. p. 311° (decomp.), (ii) 2·10 g., m. p. 322° (decomp.)] was collected. Recrystallisation from butan-1-ol gave 2 : 4-dihydroxyquinoline, needles having a purple tinge, m. p. 331° (decomp.). Reaction of the product (0·5 g.) with phosphorus oxychloride (5 ml.), according to Koller,[24] yielded 2 : 4-dichloroquinoline (0·35 g.), m. p. 63—64°, which after decolorisation and recrystallisation from aqueous ethanol formed needles, m. p. 66°; Koller records m. p. 67—68°.

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BATTERSEA POLYTECHNIC, LONDON, S.W.11.

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[23] Thiele, *Ber.*, 1900, **33**, 3398.
[24] Koller, *Ber.*, 1927, **60**, 1110.