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Synthesis of 3-Ethoxycarbonyl-1,2,3,4,5,10-hexahydroindeno[1,2-*d*]azepine

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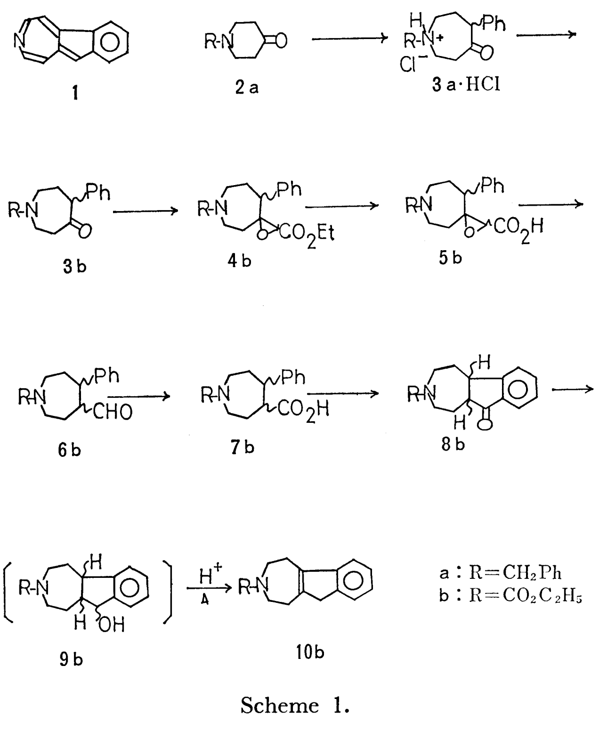
3-Ethoxycarbonyl-1,2,3,4,5,10-hexahydroindeno[1,2-*d*]azepine (**10b**) was synthesized from 1-benzylpiperidin-4-one and 1-benzyl-4-[*o*-(hydroxymethyl)phenyl]hexahydroazepin-4-ol. Compound **10b** is of particular interest as an intermediate for the preparation of the hitherto unknown indeno[1,2-*d*]azepine. It was found that 1-ethoxycarbonyl-4-[*o*-(hydroxymethyl)phenyl]hexahydroazepin-4-ol and 1-ethoxycarbonyl-4-[*o*-(hydroxymethyl)-phenyl]piperidin-4-ol (**16b**) give 1-ethoxycarbonylspiro[azepin-4,1′(3*H*′)-isobenzofuran] and 1-ethoxycarbonyl-spiro[3*H*-isobenzofuran-1,4′-piperidine] (**17b**), respectively. Treatment of **16b** with 88% formic acid gave **17b** and 2-ethoxycarbonyl-2,3,4,9-tetrahydro-1*H*-indeno[2,1-*c*]pyridine.

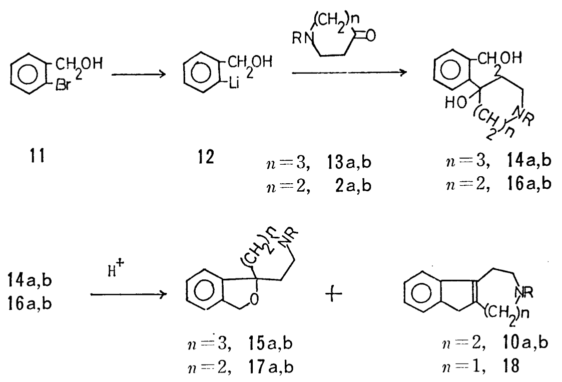
Although several benzazazulenes have been extensively studied in recent years,[1–6] indeno[1,2-*d*]azepine (**1**, 7-azabenz[*a*]azulene) does not seem to have been reported. As the only example of this ring system, 1,2,3,4,5,5a,10,10a-octahydroindeno[1,2-*d*]azepine was reported by Boyakchan *et al.*[6] We wish to report two independent methods A and B for the preparation of the title compound **10a** which might be converted into compound **1** by dehydrogenation.

Method A is characterized by use of **3a**·HCl, the structure of which was determined by X-ray analysis.[7] The structure of the final product **10a** was established as 3-ethoxycarbonyl-1,2,3,4,5,10-hexahydroindeno[1,2-*d*]azepine. The method required 8 steps from **2a**, the overall yield being only 4% on the basis of **2a**. It thus became necessary to develop another facile method for obtaining **10b**.

Recently, Parham *et al.* found that 1-[*o*-(hydroxymethyl)phenyl]cycloheptan-1-ol gives the corresponding 5,6,7,8,9,10-hexahydrobenz[*a*]azulene.[8] We investigated the possibility of preparing **10b** from **14a** according to method B, and attempted application of this method to the preparation of indenopyridine (**18b**, Scheme 2).



Scheme 1.



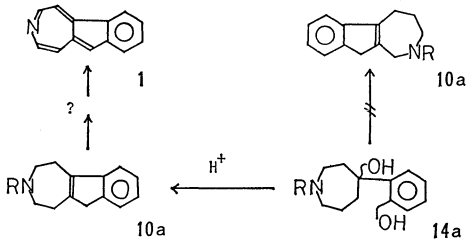
Scheme 2.

Results and Discussion

*Method A. Synthesis of 3-Ethoxycarbonyl-1,2,3,4,5,10-hexahydroindeno[1,2-*d*]azepine (10b) from 1-Benzylpiperidin-4-one (2a).* 1-Benzyl-5-phenylhexahydroazepin-4-one (**3a**) was obtained by ring expansion of **2a** with ethyl *N*-nitrosobenzylcarbamate in 21% yield. Treatment of **3a**·HCl with ethyl chloroformate gave 1-ethoxycarbonyl-5-phenylhexahydroazepin-4-one (**3b**) quantitatively. Condensation of **3b** with ethyl chloroacetate in the presence of potassium *t*-butoxide by Darzen's method,[10] followed by hydrolysis with KOH in methanol gave the corresponding glycidic acid (**5b**) in 55% yield. When the reaction was stopped in the first step, the corresponding glycidic ester (**4b**) was isolated in 96% yield. Decarboxylation of **5a** at 150—155 °C without a solvent gave 1-ethoxycarbonyl-4-formyl-5-phenylhexahydroazepine (**6b**) in 64% yield. Oxidation of **6a** with silver oxide generated *in situ* gave 1-ethoxycarbonyl-4-phenylhexahydroazepin-5-carboxylic acid (**7b**) in 49% yield. Cyclization of **7b** by the Friedel-Crafts reaction (PCl$_5$, SnCl$_4$) resulted in the formation of 3-ethoxycarbonyl-1,2,3,4,5,5a,10,10a-octahydroindeno-[1,2-*d*]azepin-10-one (**8b**) in 83% yield. Further transformation of **8b** by hydrogenation (LiAlH$_4$, MeOH), followed by heating with a trace of hydrochloric acid without a solvent at 215 °C gave the indeno-[1,2-*d*]azepine (**10b**, title compound) in 86% yield; the structure of **10b** was deduced by the NMR and IR data and analytical result. The final step from **8b** to **10b** can be explained by acid catalyzed indene formation *via* a transient intermediate **9b** under the above conditions. Indenoazepines, such as **8b** and

10b, are of particular interest as an intermediate in the preparation of the hitherto unknown indeno[1,2-*d*]azepine (**1**).

*Method B. Synthesis of **10b** from 1-Benzyl-4-[o-(hydroxymethyl)phenyl]hexahydroazepin-4-ol (**14a**).* 1-Benzyl- and 1-ethoxycarbonyl-4-[*o*-(hydroxymethyl)-phenyl]hexahydroazepin-4-ol (**14a** and **14b**), and 1-benzyl- and 1-ethoxycarbonyl-4-[*o*-(hydroxymethyl)-phenyl]piperidin-4-ol (**16a** and **16b**) were prepared in a similar way to that employed by Parham and Egberg,[11] as follows. The lithium derivative (**12**) of *o*-bromobenzyl alcohol (**11**) was allowed to react with 1-benzyl- or 1-ethoxycarbonylhexahydroazepin-4-one (**13a** or **13b**), and 1-benzyl- or 1-ethoxycarbonylpiperidin-4-one (**2a** or **2b**) at −40 °C. The usual work-up gave **14a, 14b**, **16a**, and **16b** in 80, 48, 56, and 31%,[8b)] respectively.



Scheme 3.

The reaction of **14a** in the presence of boron trifluoride etherate in refluxing benzene for 10 h gave indenoazepine (**10a** or **10a′**, Scheme 3) in 10% yield accompanied by 1-benzylspiro[azepine-4,1′(3*H*′)-isobenzofuran] (**15a**) in 42% yield. The structure of this indene has two possibilities, since there are two ways to form the indene ring *via* the elimination of water from **14a** as shown in Scheme 3. For the confirmation of the structure, the indene (**10a** or **10a′**) was treated with ethyl chloroformate in refluxing benzene. The expected 1-ethoxycarbonyl-1,2,3,4,5,10-hexahydroindeno[1,2-*d*]azepine (**10b**, title compound) was obtained in 83% yield. **10b** was identified by comparison with the NMR and IR data of the authentic sample obtained by method A. Method B from **14a** requires much shorter steps than method A from **2a**.

On the other hand, the reaction of **14b** and **16b** gave only 1-ethoxycarbonylspiro[azepine-4,1′(3*H*′)-isobenzofuran](**15b**) and **17b** in 89 and 49% yields, respectively, under the same conditions as in the case of **14a**. However, the reaction of **16b** in 88% formic acid at 100 °C for 90 min gave 1′-ethoxycarbonylspiro[isobenzofuran-1(3*H*), 4′-piperidine] (**17b**) and the other expected 2-ethoxycarbonyl-2,3,4,9-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (**18b**) in 23 and 30% yields, respectively. **16a** which gave only the corresponding spiro compound (**17a**)[8b)] afforded no corresponding indene (**18a**) even in the formic acid at 100 °C.

Experimental

The structures of all the new compounds were confirmed by NMR, IR, and analytical data. All melting points and boiling points are uncorrected. IR (Nujol) spectra were determined on a JASCO IRA-1 grating infrared spectrometer. NMR ($CDCl_3$/TMS, Hitachi-Perkin Elmer R-20) spectra were obtained at 60 MHz. The chemical shifts are represented in terms of δ values. Column chromatography and TLC were performed using Wakogel C-200 and Kieselgel 60F 254, respectively. **2a**, **2b**, **13a**, and **13b** were prepared by the method developed by one of us (S. M).[9)]

*HCl Salt of 1-Benzyl-5-phenylhexahydroazepin-4-one (**3a**·HCl).* Ethyl *N*-nitrosobenzyl carbamate (19.8 g, 0.095 mol) was added over a period of 1.5 h to a stirred mixture of freshly distilled 1-benzyl-1-azacyclohexan-4-one (**2a**, 15.5 g, 0.082 mol), finely powdered potassium carbonate (14.5 g) and absolute methanol (8 ml), the reaction temperature being maintained at 25 °C by means of an ice–water bath. The dark red reaction mixture was then allowed to stand at room temperature until the evolution of nitrogen gas ceased (48 h). Ether (50 ml) and water (30 ml) were added to the mixture. After shaking, the two layers were separated. The ethereal solution was washed with saturated aqueous NaCl solution. A white solid appearing in the aqueous layer was collected, washed with a small amount of water and dried in a desiccator (soild KOH). The solid was recrystallized from ethanol to give colorless prisms (**3a**·HCl, 4.5 g, 21%): mp 225 °C (dec); IR 2540, 1710, 760, 740, 700 cm^{-1}; NMR (CCl_4, free **3a**, mp 72 °C) 1.80—3.30 (9H, m), 3.61 (2H, s, -$\underline{CH_2}$Ph), 7.20 (5H, m, aromatic H), 7.28 (5H, m, aromatic H). Found: C, 71.96; H, 6.74; N, 4.62%. Calcd for $C_{19}H_{21}NO \cdot HCl$: C, 72.25; H, 7.02; N, 4.44%.

*1-Ethoxycarbonyl-5-phenylhexahydroazepin-4-one (**3b**).* A mixture of **3a**·HCl (21.76 g, 0.078 mol) and ethyl chloroformate (19.0 g, 0.172 mol) was stirred for 4 h at 140 °C (bath temp). After being cooled to room temperature, excess formate was removed by a rotary evaporator at 50 °C. Benzyl chloride was then distilled at 70—80 °C/20 Torr (9.6 g). Distillation of the residue gave a colorless viscous oil (**3b**, 19.3 g, 95%, bp 171 °C/0.15 Torr): IR (neat) 1700 cm^{-1}(broad); NMR 1.24 (3H, t, J=7Hz), 2.00 (2H, m), 2.70 (2H, m), 2.90—3.65 (2H, m), 3.70—4.40 (3H, m), 4.15 (2H, q, J=7 Hz), 7.28 (5H, m, aromatic H). Found: C, 68.87; H, 7.48; N, 5.16%. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36%.

*1-Ethoxycarbonyl-5-phenyl-1,2,3,5,6,7-hexahydrospiro[azepine-4(4H),2′-oxirane]-3′-carboxylic Acid (**5b**).* A flask flame-dried at reduced pressure was charged with freshly distilled ethyl chloroacetate (3.07 g, 2.65 mmol) and **3b** (6.98 g, 2.50 mmol). A solution of potassium *t*-butyrate in *t*-butyl alcohol (50 ml, 2.6 mmol) was added from a dropping funnel over a period of *ca.* 30 min to the flask with stirring, the temperature of the reaction mixture being maintained at 10—15 °C on an ice bath. The mixture was stirred for 1—1.5 h at *ca.* 10 °C. Most of the *t*-butyl alcohol was removed by distillation. The oily residue was taken up in ether. The ether solution was washed with water, then with saturated aqueous sodium chloride solution, and was finally dried over anhydrous sodium sulfate. The residue obtained on evaporation of the ether was distilled to give colorless glycidic ester (**4b**, 8.8 g, 96.2%, 195—200 °C/0.2 Torr), ethyl 1-ethoxycarbonyl-5-phenyl-1,2,3,5,6,7-hexahydrospiro[4*H*-azepine-4,2′-oxirane]-3′-carboxylate. IR (neat) 1760 (sh), 1700, 1220, 770, 705 cm^{-1}. No analytical sample could be prepared, since it was partially decomposed during the course of vacuum distillation.

Crude **4b** (8.8 g, 2.5 mmol) was dissolved in a solution of potassium hydroxide (2.65 g, 6.1 mmol) in absolute ethanol (29 ml), and the resulting solution was kept at room temperature under nitrogen atmosphere for 40 min. The mixture was then warmed on a water bath (60 °C) for 7 h, the solvent being evaporated under reduced pressure. The residue was dissolved in 50 ml of water and extracted with benzene (50 ml). The water layer was acidified with aqueous 10% sulfuric acid, and extracted twice with ether (50 ml portions). After the separation, the ether layer was dried over $MgSO_4$, the solvent being distilled off. A dark-red crude product (**5b**, 6.1 g, 75%) was obtained and crystallized from benzene to give pure **5b** (4.1 g, 56.8%, dec 153 °C): IR 1730, 1630 cm^{-1}; NMR 1.25 (3H, t, J=7 Hz), 1.51—2.28 (4H, m), 2.99—3.95 (5H, m), 4.17 (2H, q, J=7Hz), 7.24(5H, m), 8.45 (1H, bs, COOH). Found: (dried for 3 h at 130 °C): C, 64.20; H, 6.93; N, 4.38%. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39%.

1-Ethoxycarbonyl-4-formyl-5-phenylhexahydroazepine (6b). **5b** (2.8 g, 1.0 mmol) was heated on an oil bath (at 150—155 °C) under nitrogen for 4 h. Ether (20 ml) was added. Drying and evaporation of the ether solution gave tan oil. The oil was mixed with 10% sulfuric acid (10 ml) and dioxane (14 ml). The solution was heated under reflux for 14 h. The solution was evaporated under reduced pressure, and the usual work-up gave a reddish residue. The residue was distilled to give **6b** (1.76 g, 64%, 180—183 °C/0 .1 Torr): IR(neat) 1710, 1690 cm^{-1}; NMR 1.24 (3H, t, J=7Hz), 1.59—2.35 (4H, m), 2.59—3.08 (4H, m), 4.14 (2H, q, J=7 Hz), 7.18 (5H, m), 10.29 (1H, s, $\mathrm{C\underline{H}O}$). Found: C, 69.96; H, 7.86; N, 5.13%. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09%.

1-Ethoxycarbonyl-4-phenylhexahydroazepine-5-carboxylic Acid (7b). To a solution of **6b** (2.8 g, 1.1 mmol) and sodium hydroxide (0.79 g, 1.75 mmol) in a mixed solvent (50 ml, ethanol: water=3 : 2) cooled on an ice bath was added a solution of silver nitrate in water (20 ml) in small portions with stirring. The oxidation was complete in *ca.* 5 min after the last addition. The black silver suspension was removed by filtration and washed with several portions of hot water. The cold combined filtrate and washing were acidified with concd hydrochloric acid, a white powder being precipitated out. Recrystallization of this powder from water gave **7b** (2.6 g, 82%, mp 146—147 °C): IR 1720, 1640, 705, 690 cm^{-1}; NMR 1.24 (3H, t, J=7 Hz), 1.60—2.30(4H, b), 2.50—3.10 (2H, b), 3.20—3.90 (4H, b), 4.14 (2H, q, J=7 Hz), 7.18 (5H, s), 10.30 (1H, s, $\mathrm{COO\underline{H}}$). Found: C, 65.99; H, 6.88; N, 4.54%. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81%.

7-Ethoxycarbonyl-4a,5,6,7,8,9,9a,10-octahydro-7-azabenz[a]azulen-10-one (8b). To a suspension of **7b** (1.5 g, 0.55 mmol) in 30 ml of benzene (dried over sodium) was added powdered phosphorus pentachloride (1.14 g, 0.55 mmol) in portions with swirling and cooling on an ice-water bath. After evolution of hydrogen chloride had ceased by the vigorous reaction at 80 °C, all the volatile substances were distilled under reduced pressure at 100 °C. Aluminum chloride (0.5 g, 0.4 mmol) was added to a stirred solution of the residual oily acid chloride in 30 ml of dry benzene at room temperature over a period of 1.5 h. The mixture was then heated at 80 °C for 1.5 h. After being cooled to room temperature, the mixture was poured onto ice and hydrochloric acid, and ether (10 ml) was added for the separation of the layers. The ether layer was concentrated and the product was purified by distillation (**8b**, 1.14 g, 82.6%, bp 180—195 °C/0.1 Torr); IR (neat) 1720, 1680, 770 cm^{-1}; NMR 1.26 (3h, t, J=7Hz), 1.50—3.35 (6H, b), 3.35—3.89 (4H, b), 4.17 (2H, q, J=7 Hz), 7.18—7.91 (4H, m). (the oxime of **8b**, mp 181 °C): Found: C, 66.49; H, 6.99; N, 9.71%. Calcd for $C_{16}H_{20}N_2O_3$: C, 66.65; H, 6.99; N, 9.71%.

3-Ethoxycarbonyl-1,2,3,4,5,10-hexahydroindeno[1,2-d]azepine (10b). A three-necked flask was charged with 1% aqueous sodium hydroxide (4 ml) and sodium borohydride (0.39 g, 1 mmol) and the system was purged with nitrogen. A solution of the indanone (**8b**, 4.8 g, 1.8 mmol) in methanol (70 ml) was added dropwise over a period of 10—20 min. After addition was complete, the mixture was carefully reheated to reflux for 2 h. The mixture was then cooled on an ice bath, and a sufficient amount of 3 M aqueous hydrochloric acid (50 ml) was carefully added dropwise to decompose excess sodium borohydride. The acidified solution was worked up immediately by extraction with benzene. The benzene extract was washed with saturated aqueous sodium hydrogencarbonate. The benzene solution was dried over anhydrous sodium sulfate, the benzene being removed. The residue was distilled and pressure reduced to give the indene **10b** (4.1 g, 85.4%, bp 215—216 °C/0.23 Torr): IR (neat) 1690, 1600, 760, 720 cm^{-1}; NMR (CCl_4) 1.25(3H, t, J=7Hz, $-CH_3$), 2.50—2.90(4H, b, aliphatic CH_2), 3.25 (2H, s, CH_2 in indene system), 3.45—3.81 (4H, b, aliphatic CH_2N), 4.15 (2H, q, J=7 Hz, $\underline{CH_2}CH_3$), 7.02—7.22 (4H, m, aromatic H). Found: C, 74.21; H, 7.51; N, 5.64%. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44%.

Reaction of o*-Bromobenzyl Alcohol (11). Typical Procedure. 1-Benzyl-4-[*o*-(hydroxymethyl)phenyl]hexahydroazepin-4-ol (14a).* Butyllithium (12.2 ml, 3.2 mmol, 2.45 M in hexane) was added to a cold (−40 °C) mixture of **11** (1.3 g, 1.6 mmol) in THF (15 ml) and hexane (10 ml). The mixture was stirred for 5 min at −40 °C and 1-benzylhexahydroazepin-4-one (**13a**, 1.7 g, 0.8 mmol) was added at a rate such that the temperature was maintained at −40 °C for 30 min. The mixture was poured into a large volume of saturated aq NH_4Cl, and extracted with ether. The extract was washed with water, and dried (Na_2SO_4). Removal of the solvent gave a practically pure product. Product **14a** was purified by column chromatography on silica gel eluting with petroleum ether–ethyl acetate (1 : 1): yield 1.83 g (80%); IR (neat) 3360 (OH, hydrogen bonding), and 720 cm^{-1}; NMR (DMSO-d_6) 1.60—2.90 (10 H, two broad peaks, aliphatic CH_2), 3.51 (2H, s, benzylic CH_2N), 4.72 (2H, s, benzylic CH_2O), 4.55—5.32 (2H, bs, alcohol OH), 7.00—7.62 (9H, m, aromatic H). Found: C, 76.83; H, 8.07; N, 4.88%. Calcd for $C_{20}H_{23}NO_2$: C, 77.13; H, 8.09; N, 4.50%.

*1-Ethoxycarbonyl-4-[*o*-(hydroxymethyl)phenyl]hexahydroazepin-4-ol (14b).* The reaction was carried out as described for **14a**. The crude product was purified by preparative TLC (using 50% ethyl acetate in benzene as eluent): **14b**, 47.6%; IR (neat) 3400, 750 cm^{-1}; NMR 1.18 (3H, t, J=7 Hz), 1.50—2.60 (6H, b), 3.00—3.70 (4H, b), 4.06 (2H, q, J=7Hz), 4.30—5.00 (2H, bs, OH), 4.80 (2H, s), 7.10—7.20 (4H, m, aromatic H). Found: C, 65.60; H, 7.82; N, 4.89%. Calcd for $C_{16}H_{23}NO_4$; C, 65.51; H, 7.90; N, 4.78%.

*1-Benzyl-4-[*o*-(hydroxymethyl)phenyl]piperidin-4-ol (16a)* was prepared by the method described in the literature.[8b)]

*1-Ethoxycarbonyl-4-[*o*-(hydroxymethyl)phenyl]piperidin-4-ol (16b).* The crude product, obtained in a similar way to that used for **14a**, was crystallized from ethyl acetate to give **16a**: 31.3% yield, mp 113—114 °C; IR 3400, 1670, 750 cm^{-1}; NMR 1.22(3H, t, J=7 Hz), 1.55—3.68 (8H, two broad peaks), 3.95 (2H, s), 4.40 (2H, q), 4.20—5.01 (2H, bs, OH), 7.18—7.28 (4H, m). Found: C, 64.20; H, 7.82; N, 4.91%. Calcd for $C_{15}H_{21}NO_4$: C, 64.49; H, 7.58; N, 5.01%.

Reaction of 14a, 14b, 16a, and 16b with Boron Trifluoride Etherate. 1-Benzylspiro[azepine-4,1′(3*H*′)-isobenzofuran] (**15a**) and 1-benzyl-1,2,3,4,5,10-1*H*-indeno[1,2-*d*]azepine (**10a**). Boron trifluoride etherate (2.0 g, 1.4 mmol) was added to the benzene (50 ml) solution of **14a** (1.96 g, 0.66 mmol). The reaction mixture was heated to reflux for 2 h. The reaction mixture was poured into a large amount of ice water. The layers were separated and the benzene layer was washed with saturated aqueous sodium hydrogencarbonate followed by water, and dried over MgSO$_4$. The solvent was removed to yield an oil. The oil was chromatographed on silica gel by elution with a mixed solvent (10% ethyl acetate in benzene). From fraction Nos. 17—27, a pale yellow oil (160 mg) was collected . The oil was distilled under reduced pressure to give **10a**: 10% yield, 140—150 °C/0.14 Torr; IR (neat) 1600, 750, 720, 690 cm^{-1}; NMR 2.15—3.10 (8H, two broad peaks), 3.12—3.35 (2H, bs, CH$_2$ in indene system), 3.76 (2H, s, benzylic CH$_2$N), 7.00—7.30 (4H, m, aromatic H), 7.32 (5H, m, aromatic H). When **10a** was treated with ethyl chloroformate in refluxing benzene, the less labile oil **10b** was obtained in 83% yield. **10b** was identified by comparison with the sample obtained from **2a** by method A.

*1-Ethoxycarbonylspiro[azepine-4,1'(3H')-isobenzofuran] (**15b**).* The reaction of **14b** was carried out as described for **10a**. The product was purified by preparative TLC (20% ethyl acetate in benzene as eluent). **15b** (R_f=0.38): 89% yield; IR 1690, 1040, 755 cm^{-1}; NMR 1.22(3H, t, J=7 Hz), 1.60—2.50 (6H, b), 2.80—3.90 (4H, b), 4.10 (2H, q, J=7 Hz), 4.98 (2H, s), 6.90—7.30 (4H, m). Found: C, 69.35; H, 7.92; N, 5.03%. Calcd for C$_{16}$H$_{21}$NO$_3$: C, 69.79; H, 7.69; N, 5.09%.

*1-Ethoxycarbonylspiro[isobenzofuran-1(3H),4'-piperidine] (**17b**).* The reaction of **16b** was carried out as described for **10a**. The product was purified by preparative TLC (50% chloroform in benzene as eluent). **17b** (R_f=0.4): 43% yield; IR 1700, 1035, 750 cm^{-1}; NMR (CCl$_4$) 1.24 (3H, t, J=7 Hz), 1.50—1.90 (4H, b), 2.70—4.30 (4H, two broad peaks), 4.10 (2H, q, J=7 Hz), 5.01 (2H, s), 7.00—7.30 (4H, m). Found: C, 69.42; H, 6.63; N, 5.41%. Calcd for C$_{15}$H$_{17}$NO$_3$: C, 69.48; H, 6.61; N, 5.40%. The reaction of **16a** was carried out as described for **10a**. When the labile product (**17a**) was treated with ethyl chloroformate in refluxing benzene, **17b** was obtained in 65% yield based on **16a**.

*2-Ethoxycarbonyl-2,3,4,9-tetrahydro-1H-indeno[2,1-c]pyridine (**18b**).* **16b** (0.3 g, 0.11 mmol) was added to 2 ml of 88% formic acid and heated at the reflux temperature for 1.5 h. The reaction mixture was added with stirring to a large amount of ice water and resulting mixture was extracted with benzene. After the usual work-up, the solvent of the extract was removed to give a yellow oil (0.23 g). The crude oil was subjected to preparative TLC on silica gel with 20% ethyl acetate in benzene as eluent. From the first band (R_f=0.55), **18b** was collected: 80 mg, 30% yield; IR (neat) 1695. 1605, 760 cm^{-1}; NMR(CCl$_4$) 1.26 (3H, t, J=7 Hz), 2.50—3.00 (2H, bt, J=*ca.* 5Hz), 3.24 (2H, bs), 3.40—3.80 (2H, bt, J=*ca.* 5 Hz), 4.24 (2H, q, J=7 Hz), 7.00—7.40 (4H, m). Found: C, 73.92; H, 7.04; N, 5.76%. Calcd for C$_{15}$H$_{17}$NO$_2$: C, 74.05; H, 7.04; N, 5.76%. From the second band, **17b** (R_f=0.38) was collected in 23% yield.

When a solution of **16a** in formic acid was refluxed for 1.5 h, only **17a** was obtained. Treatment of **17a** with ethyl chloroformate in refluxing benzene gave **17b** in 90% yield based on **16a**.

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