The Cyanoethylation of Indene and Related Reactions

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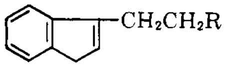
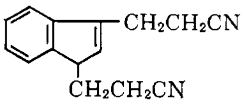
The cyanoethylation of indene was reinvestigated. Improved preparations, physical constants, and unambiguous proofs of structure for the products *via* proton magnetic resonance spectra are described. The related base-catalyzed additions to indene of vinylpyridine and acrylates also were studied. In all cases the mono-, di-, and trisubstitution products were indenes substituted in the 3-, 1,1-, and 1,1,3-positions, respectively. The cyanoethylation products were selectively hydrogenated to give the corresponding (aminopropyl)-indenes rather than the expected substituted indans.

The base-catalyzed addition of acylonitrile to indene was described by Bruson[2] to yield a product mixture which upon distillation gave an unidentified liquid, indenedipropionitrile (II and/or IIIa) in 13.5% yield, plus 1,1,3-indenetripropionitrile (IVa), m.p. 65°, in 35.1% yield. In a more recent paper,[3] the monocyanoethylation of indene in 13.5% yield was described; the liquid product was believed to be 3-indenepropionitrile (Ia), but it was stated that the structure of the product remained uncertain. Indeed, in the past the position of substituents in the alicyclic ring of indene has been frequently problematic since structure proofs were possible only by laborious methods.

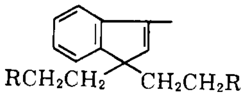
The purpose of this paper is to report supplemental data on the cyanoethylation and related reactions of indene, including the preparation of new indene derivatives, improved preparations of known compounds, and the use of proton magnetic resonance spectroscopy for the structure proof of indenes substituted in the alicyclic ring.



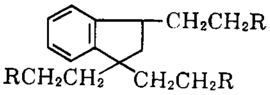
Ia, R = CN
b, R = COOH
c, R = $COOCH_3$
d, R = $COOC_2H_5$
e, R = $COOn\text{-}C_4H_9$
f, R = CH_2NH_2



II



IIIa, R = CN
b, R = COOH
c, R = CH_2NH_2



IVa, R = CN
b, R = COOH
c, R = $COOC_2H_5$
d, R = CH_2NH_2

Cyanoethylation of Indene.—The yield of 3-indenes propionitrile (Ia) was raised to 38% by using an excess of indene and benzyltrimethylammonium chloride plupotassium hydroxide as the catalyst. This product previously was described to be a liquid[3] but we obtained Ia as stout prisms, m.p. 31.0–31.5°. Hydrolysis of this nitrile gave the corresponding carboxylic acid Ib, m.p. 127–128°, whose structure previously had been uncertain (as discussed in ref. 3 with older literature citations). The methyl ester (Ic) of Ib was prepared in the usual manner for further structural identification.

A reinvestigation of the polycyanoethylation of indene showed that the crude reaction product consisted of 20–25% of 1,1-indenedipropionitrile (IIIa) and about 70% of 1,1,3-indenetripropionitrile (IVa). This was inferred from the fact that the distilled dicyanoethylation product (25% yield) underwent almost no further reaction with acrylonitrile; therefore, the major or only indenedipropionitrile formed was IIIa which is incapable of anion formation with base while II, never prepared, would be convertible to indenetripropionitrile. Alkaline hydrolysis of the crude reaction product followed by an extraction–selective reprecipitation process gave a 69% yield of 1,1,3-indenetripropionic acid (IVb) plus a 14% yield of 1,1-indenedipropionic acid (IIIb). The dinitrile (IIIa) had m.p. 40.0–40.5° and the trinitrile (IVa) had m.p. 91.0–91.5° (*vs.* m.p. 65° reported by Bruson[2]). Alkaline hydrolysis of IIIa and IVa gave the corresponding carboxylic acids of m.p. 154–155° (IIIb) and m.p. 167–169° (IVb, Bruson[2] gave m.p. 161–162°), respectively.

Bergmann[4] reviewed the cyanoethylation reaction as a special case of the Michael reaction. He states: "An interesting point emerges from the behavior of compounds such as indene which gives a tris(cyanoethyl) derivative. One has to assume that the primary products rearrange to give a new reactive methylene group." (The primary product is shown to be 1-indenepropionitrile which rearranges to 3-indenepropionitrile, etc.). In a more detailed discussion, other Michael- and aldol-type reactions of indene and fluorene were said to proceed either by a concerted or a two-step mechanism.[5] It is still not possible to decide which mechanism operates here. However, the initial acrylonitrile addition product (anionic) must have the 1-indenepropionitrile structure in either case. The fact that the only monocyanoethylation product isolated is 3-indenepropionitrile then means that it must have been formed by rearrangement; this would be possible only if it were thermodynamically more stable. Perhaps 3-indene propionitrile is stabilized both by conjugation of the 2,3-double bond with the benzene ring and also by hyperconjugation of the methylene group adjacent to the 2,3-double bond with it (similar triad systems are discussed by Ingold[6]). It appears that 1,3-dicyanoethylated indene is not isolated because it is quickly cyanoethylated further. On the other hand, 1,1-dicyanoethylated indene does not have an active hydrogen on the ring and is not capable of rearrangement.

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(1) (a) Koppers Co., Inc.; (b) Carnegie Institute of Technology.

(2) H. A. Bruson, *J. Am. Chem. Soc.*, **64**, 2457 (1942); U. S. Patent 2,280,058 (1942).

(3) F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 3011 (1957).

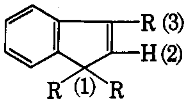
(4) E. D. Bergmann, *Org. Reactions*, **10**, 179 (1959).

(5) M. Avramoff and Y. Sprinzak, *J. Am. Chem. Soc.*, **82**, 4953 (1960).

(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 563 ff.

TABLE I

N.M.R. SPECTRA. CHEMICAL SHIFTS OF INDENE AND DERIVATIVES[a]



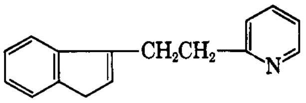
	Substituent(s)		Chemical shift (τ-value)			
Compound	$R^{(1)}$	$R^{(3)}$	$H^{(1)}$	$H^{(2)}$	$H^{(3)}$	Protons on benzene ring and on substituents
Indene[b]	H	H	7.01	3.86	3.34	
Ia	H	CH_2CH_2CN	6.84	3.88		2.86 (benzene ring); 7.5, 7.6 (—CH_2CH_2CN)
Ic	H	$CH_2CH_2COOCH_3$	6.83	3.92		2.81 (benzene ring); 6.44 (—OCH_3); 7.4 (—CH_2CH_2—)
If	H	$CH_2CH_2CH_2NH_2$	6.78	3.91		2.84 (benzene ring); 7.0, 7.4, 7.9 (—$CH_2CH_2CH_2$—); 9.15 (—NH_2)
VI	H	CH_2CH_2-4-pyridyl	6.74	3.88		1.65 (α-H, pyridyl); 2.81 (benzene ring); 2.98 (β-H, pyridyl); 7.1 (—CH_2CH_2—)
IIIa	CH_2CH_2CN	H		3.81	3.18	2.77 (benzene ring); 7.8, 8.3 (—CH_2CH_2CN)
IIIa[c]	CH_2CH_2CN	H		3.71	3.14	
IIIc	$CH_2CH_2CH_2NH_2$	H		3.82	3.35	2.84 (benzene ring); 7.6, 8.3–9.0 (—$CH_2CH_2CH_2$—); 9.16 (—NH_2)
IVa[c]	CH_2CH_2CN	CH_2CH_2CN		3.85		2.70 (benzene ring); 7.16 (—CH_2CH_2CN)
IVc	$CH_2CH_2COOC_2H_5$	$CH_2CH_2COOC_2H_5$		4.16		2.81 (benzene ring); 6.0 (—OCH_2—); 7.3, 7.8, 8.2 (—CH_2CH_2—); 8.8 (—CH_3)
IVd	$CH_2CH_2CH_2NH_2$	$CH_2CH_2CH_2NH_2$		4.13		2.88 (benzene ring); 7.3, 7.6, 8.3–9.0 (—$CH_2CH_2CH_2$—); 9.19 (—NH_2)

[a] Measured as 10% solutions in carbon tetrachloride except where noted otherwise. [b] Ref. 10. Samples of pure indene were run as the neat liquid. [c] Measured as 10% solution in acetone.

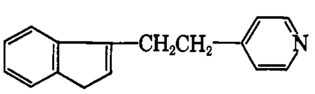
Other Michael-Type Additions to Indene.—Howell and Taylor[3] obtained a 47% yield of ethyl 3-indenepropionate (Id) by the reaction of indene with ethyl acrylate in the presence of sodium methoxide as the catalyst. We obtained a 57% yield of *n*-butyl 3-indenepropionate (Ie) plus a 7.6% yield of di-*n*-butyl indenedipropionate (not identified) by treating excess indene with *n*-butyl acrylate using potassium *t*-butoxide as the catalyst.

Similarly, the reaction of excess indene with 2- and 4-vinylpyridine using potassium *t*-butoxide as the catalyst gave a 47% yield of 3-[2-(2-pyridyl)ethyl]indene (V), b.p. 161–163° (2 mm.), plus an 11% yield of di[2-(2-pyridyl)ethyl]indene; and a 60% yield of 3-[2-(4-pyridyl)ethyl]indene (VI), m.p. 102–103°, plus an 8.4% yield of di[2-(4-pyridyl)ethyl]indene, respectively. The dipyridylethylation products were not further investigated.

In a recent patent[7] these reactions were reported to give a 25% yield of 4-(1-indenylethyl)pyridine, m.p. 96–97°, and a 30% yield of 2-(1-indenylethyl)pyridine, b.p. 145–155° (0.5 mm.), under fairly similar conditions. Structural analyses were not given, making the position of the substituents on the indene nucleus ambiguous. Presumably, the products obtained as described in this patent are identical with those obtained by us.



V



VI

Derivatives of the monoadduct (V) of 2-vinylpyridine to indene were prepared by reaction with bromine to give 2,3-dibromo-3-[2-(2-pyridyl)ethyl]indan and by base-catalyzed reaction with anisaldehyde to give 1-anisylidene-3-[2-(2-pyridyl)ethyl]indene.

Amines from Cyanoethylated Indenes.—There are numerous reports[8] in the literature which show that the catalytic hydrogenation of the alicyclic double bond of indene takes place under relatively mild conditions. It was, therefore, surprising to find that the catalytic hydrogenation of indene cyanoethylation products in the presence of ammonia, using a nickel catalyst and 1000-p.s.i.g. total pressure at 170°, resulted only in the reduction of the nitrile group, leaving the alicyclic double bond intact. In this manner, 3-indenepropylamine (If), 1,1-indenedipropylamine (IIIc), and 1,1,3-indenetripropylamine (IVd) were obtained.

Structure Proof of Products *via* N.m.r. Spectra.—The chemical shifts of indene and the indene derivatives are given in Table I. Certain regularities are apparent: olefinic protons in the 3-position show lines in the neighborhood of $\tau \cong 3.2$–3.3; olefinic protons in the 2-position show lines in the neighborhood of $\tau \cong 3.8$–4.2; and protons at the 1-position show lines in the neighborhood of $\tau \cong 6.8$. It should be noted that the chemical shifts of indene itself, obtained by Elleman and Manatt,[9] are not to be compared too closely with those of the indene derivatives, since the indene sample was run as the neat liquid while the indene derivatives were run as 10% solutions in carbon tetrachloride. It should also be noted that, in general, the chemical shift of the proton in the 2-position shows a progressive upward shift with increasing alkyl group substitution. The 1,1-disubstituted compounds showed an AB quartet for the protons in the 2,3-positions with a coupling constant between the 2,3-protons of about 5.7 c.p.s., in agreement with the coupling constant of 5.58 c.p.s. observed for indene.[9] The coupling between the protons in the 1,2-positions, of the order of 2 c.p.s., was not resolved, presumably because of broadening by the allylic coupling. Other groups of lines, as listed in

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(7) Irwin, Neisler and Co., British Patent 842,996 (1960).

(8) *E.g.*, K. Alder and O. Wolff, *Ann.*, **576**, 182 (1952); W. M. Kutz, J. E. Nickels, J. J. McGovern, and B. B. Corson, *J. Am. Chem. Soc.*, **70**, 4026 (1948); "Chemistry of Carbon Compounds," Vol. IIIB, E. H. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1956, p. 1253.

(9) D. D. Elleman and S. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962).

Table I, were identified with protons on the benzene ring or on substituent groups; only their centers, in the case of unresolved peaks, are given.

The structure proofs for indene derivatives *via* their n.m.r. spectra are unambiguous. In the case of the monosubstituted indenes, substitution at the 3-position is demonstrated by the lines at $\tau \sim 3.9$ (which implies the olefinic proton is at the 2-position), the absence of AB patterns which would arise from olefinic protons at both the 2- and 3-positions, and the presence of lines at $\tau \sim 6.8$ (arising from protons at the 1-position). The disubstituted indenes are substituted at the 1,1-position as shown by the AB coupling pattern from the olefinic protons at the 2,3-positions and the presence of lines at $\tau \sim 3.1$–3.4 (arising from protons at the 3-positions). The trisubstituted indenes are substituted at the 1,1,3-positions, as indicated by lines at $\tau \sim 3.9$–4.2, corresponding to a proton at the 2-position.

Experimental

All melting points are corrected, all boiling points are uncorrected.

3-Indenepropionitrile (Ia).—To a stirred mixture of 348 g. (3.0 moles) of indene, 6.0 g. (0.019 mole) of 60% aqueous benzyltrimethylammonium chloride, 1.5 g. (0.023 mole) of potassium hydroxide, and 2.0 g. of methanol was added 53 g. (1.0 mole) of acrylonitrile dropwise during 5 hr. at 20–27°. The mix was stirred for an additional 0.5 hr. at 25°, then treated with 5.0 ml. of concentrated hydrochloric acid in 100 ml. of water. The organic layer was separated, washed with 100 ml. of 20% aqueous sodium chloride, then distilled through a 4-in. Vigreux column to give 64.0 g. (38% yield) of 3-indenepropionitrile as a pale yellow oil, b.p. 125–130° (3 mm.) [54.3 g. of a higher boiling residue also was produced]. The monocyanoethylation product was diluted with 75 ml. of isopropyl alcohol, cooled to 0°, and filtered to give 62.1 g. of colorless prisms, m.p. 31.0–31.5°.

Anal. Calcd. for $C_{12}H_{11}N$: N, 8.28. Found: N, 8.20.

1,1-Indenedipropionitrile (IIIa) and 1,1,3-Indenetripropionitrile (IVa).—To a stirred mixture of 119 g. (1.0 mole) of 97% indene, 150 ml. of benzene, and a premix of 7.0 g. (0.023 mole) of 60% aqueous benzyltrimethylammonium chloride, 1.7 g. (0.026 mole) of potassium hydroxide, and 2.4 g. of methanol was added 175 g. (3.3 moles) of acrylonitrile dropwise during 4 hr. at 25–27° (the reaction temperature range was maintained by a cold water bath). After stirring for an additional 0.5 hr., the mixture was neutralized by adding a solution of 4.9 ml. of concentrated hydrochloric acid in 100 ml. of 20% aqueous sodium chloride, and filtered. The filtrate was transferred to a separatory funnel, the organic layer was separated and washed acid-free with two 125-ml. portions of 20% sodium chloride solution. The organic product was then flash-distilled to 150° (pot) at 10 mm. to give 261 g. of crude polycyanoethylated indene as a dark oily residue. This crude was distilled through a 4-in. Vigreux column to give 55 g. (24.8% yield) of crude indenedipropionitrile, b.p. 196–202° (1 mm.), a viscous amber oil, and 148 g. (53.8% yield) of 1,1,3-tripropionitrile, b.p. 270–298° (1 mm.), a reddish oil. The latter was crystallized from 300 ml. of 95% ethanol to give 122 g. of pale yellow platelets, m.p. 89–90°; after one recrystallization from benzene-hexane, m.p. 91.0–91.5°.

Anal. Calcd. for $C_{18}H_{17}N_3$ (IVa): N, 15.27. Found: N, 15.0.

To a stirred mixture of 77 g. (0.35 mole) of the above indenedipropionitrile of b.p. 196–202° at 1 mm. (from two runs), 100 ml. of benzene, and a premix of 2.5 g. (0.013 mole) of 60% aqueous benzyltrimethylammonium chloride, 0.61 g. (0.013 mole) of potassium hydroxide, and 0.86 g. of methanol was added 20 g. (0.38 mole) of acrylonitrile dropwise during 1 hr. at 22–29°. After stirring for an additional 0.5 hr., the mixture was neutralized with a solution of 1.8 ml. of concentrated hydrochloric acid in 80 ml. of 20% sodium chloride solution, treated with 4.0 g. of Norit, and filtered. The organic layer was separated, washed free of acid with two 90-ml. portions of 20% sodium chloride solution, and concentrated to 117° (pot) at 5 mm. to give 80 g. of residue. This was distilled through a 4-in. Vigreux column to give 58 g. (79% recovery) of a heart cut of b.p. 186–190° (0.5 mm.) yielding a pale yellow solid, m.p. 39–40°, which after recrystallization from toluene had m.p. 40.0–40.5°.

Anal. Calcd. for $C_{15}H_{14}N_2$ (IIIa): N, 12.66; Found: N, 12.5.

Methyl 3-Indenepropionate (Ic).—A mixture of 64 g. (0.34 mole) of 3-indenepropionic acid (Ib, m.p. 127–128°, obtained by alkaline hydrolysis of the corresponding nitrile), 400 ml. of methanol and 2.5 g. of *p*-toluenesulfonic acid monohydrate was refluxed for 17 hr. The methanol was then evaporated on the steam bath, the residue was taken up in 150 ml. of toluene, and washed successively with 100 ml. of water, 100 ml. of 5% sodium bicarbonate, and two 100-ml. portions of water. The organic layer was dried over Drierite and filtered. The filtrate was stripped of toluene in a Rinco rotating evaporator. The residue was distilled through a 4-in. Vigreux column to give 61.5 g. (90% yield) of methyl 3-indenepropionate (Ic), b.p. 115–121° (1 mm.), a pale yellow oil.

Anal. Calcd. for $C_{13}H_{14}O_2$: sapon. equiv., 205. Found: sapon. equiv., 202.

1,1-Indenedipropionic Acid (IIIb).—A mixture of 22.2 g. (0.1 mole) of 1,1-indenedipropionitrile (m.p. 40.0–40.5°), 9.0 g. (0.22 mole) of sodium hydroxide, and 200 ml. of water was stirred and refluxed for 20 hr., after which no further ammonia was evolved. The clear yellow solution was treated with Norit and filtered hot. The pale yellow filtrate was acidified with dilute hydrochloric acid. The colorless precipitate was filtered off, washed with water, and dried to give 25.4 g. (98% yield) of colorless 1,1-indenedipropionic acid (IIIb), m.p. 155–156°, after recrystallization from 25% aqueous ethanol, m.p. 157–157.5°.

Anal. Calcd. for $C_{15}H_{16}O_4$: neut. equiv., 130.0. Found: neut. equiv., 130.0.

***n*-Butyl 3-Indenepropionate (Ie).**—To a stirred mixture of 232 g. (2.0 moles) of indene and 2.0 g. (0.018 mole) of solid potassium *t*-butoxide was added 128 g. (1.0 mole) of *n*-butyl acrylate dropwise during 1 hr. at 100–120°. The mixture was stirred for an additional hour at 120–150°, then neutralized with 1.5 ml. of glacial acetic acid, filtered, and flash-distilled to 138° (pot) at 2 mm. The residue was distilled through a 4-in. Vigreux column to give 136 g. (57% yield) of *n*-butyl 3-indenepropionate as an almost colorless oil, b.p. 138–150° (2 mm.).

Anal. Calcd. for $C_{16}H_{20}O_2$: sapon. equiv., 244. Found: sapon. equiv., 241.

In addition there was obtained 28.2 g. (7.6% yield) of di-*n*-butylindenedipropionate as a yellow oil, b.p. 210–230° (2 mm.).

Anal. Calcd. for $C_{23}H_{32}O_4$: sapon. equiv., 188. Found: sapon. equiv., 186.

The high boiling residue weighed 24.0 g. and may have represented a 4.8% yield of tri-*n*-butyl indenetripropionate.

Triethyl 1,1,3-Indenetripropionate (IVc).—A mixture of 56 g. (0.17 mole) of 1,1,3-indenetripropionic acid (IVb, m.p. 167–169°, obtained by alkaline hydrolysis of the corresponding trinitrile), 3.0 g. of *p*-toluenesulfonic acid monohydrate, and 350 ml. of absolute ethanol was stirred and refluxed for 6 hr. The excess alcohol was then removed on the steam bath. The residue was taken up in 200 ml. of toluene and washed successively with 100 ml. of 5% sodium carbonate and three 50-ml. portions of water. The organic phase was dried over Drierite, filtered, and concentrated to 150° (pot) at 5 mm. to give 42 g. (59.3% yield) of triethyl 1,1,3-indenetripropionate, a pale yellow oil.

Anal. Calcd. for $C_{24}H_{32}O_6$: sapon. equiv., 139. Found: sapon. equiv., 141.

The low yield was due to losses during the washing step and some foamover during the final devolatilization.

3-[2-(2-Pyridyl)ethyl]indene (V).—To a stirred mixture of 119 g. (1.0 mole) of 97.5% indene, 100 ml. of toluene, and 2.0 g. (0.018 mole) of solid potassium *t*-butoxide was added 110 g. (1.05 moles) of 2-vinylpyridine during 1 hr. at 57–90°. The mixture was stirred for an additional 15 min. at 90–100°, then neutralized with 1.0 ml. of glacial acetic acid, and filtered. The clear filtrate was distilled through a 4-in. Vigreux column to give 103 g. (47% yield) of pale yellow liquid 3-[2-(2-pyridyl)ethyl]indene (V), b.p. 161–163° (2 mm.).

Anal. Calcd. for $C_{16}H_{15}N$ (V): N, 6.33; Found: N, 6.0.

In addition, there was obtained 36.5 g. (11% yield) of a red oil, b.p. 220–250° (2 mm.), with correct analysis for di[2-(2-pyridyl)-ethyl]indene.

Anal. Calcd. for $C_{23}H_{22}N_2$: N, 8.59. Found: N, 8.4.

1-[2-2-Pyridyl)ethyl]-1,2-dibromoindan (VII).—To a stirred solution of 44.2 g. (0.2 mole) of 3-[2-(2-pyridyl)ethyl]indene in 100 ml. of chloroform was added a solution of 32.0 g. (0.2 mole) of bromine in 100 ml. of chloroform during 30 min. at 0–5°. The mixture was stirred for an additional hour, then evaporated to dryness. The brown residue was recrystallized from *n*-butyl alcohol to give 42 g. (55% yield) of light tan crystals, m.p. 204° dec.

Anal. Calcd. for $C_{16}H_{15}Br_2N$ (VII): N, 3.68; Br, 42.0. Found: N, 3.70; Br, 41.2.

1-Anisylidene-3-[2-(2-pyridyl)ethyl]indene (VIII).—Into a mixture of 22.1 g. (0.1 mole) of 3-[2-(2-pyridyl)ethyl]indene, 50 ml. of toluene, and 1.0 g. (0.01 mole) of potassium *t*-butoxide was stirred a solution of 27.2 g. (0.2 mole) of anisaldehyde in 50 ml. of toluene dropwise during 1 hr. at 30–35°. The mixture was then stirred for 2 hr. at 75°, finally neutralized with 1.0 ml. of glacial acetic acid, and filtered. The filtrate was concentrated to 150° (2 mm.) and the brownish residue (48 g.) was recrystallized from 95% ethanol to give 13 g. (38% yield) of a yellow solid, m.p. 88–90°.

Anal. Calcd. for $C_{24}H_{21}NO$ (VIII): N, 4.33. Found: N, 4.10.

3-[2-(4-Pyridyl)ethyl]indene (VI).—To a stirred mixture of 238 g. (2.0 moles) of indene and 2.0 g. (0.018 mole) of potassium *t*-butoxide was added dropwise 110 g. (1.05 moles) of 4-vinylpyridine during 1 hr. at 80–140°. The mixture was stirred for an additional hour at 90–130°, then neutralized with 1.5 ml. of glacial acetic acid, and filtered. The filtrate was concentrated to 162° (pot) at 2 mm. The residue was distilled through a 4-in. Vigreux column to give 133 g. (60% yield) of 3-[2-(4-pyridyl)-ethyl]indene, b.p. 162–165° (2 mm.), a yellow oil which solidified on standing, m.p. 97–101°; after recrystallization from ethyl acetate, large colorless prisms, m.p. 102–103°.

Anal. Calcd. for $C_{16}H_{15}N$: N, 6.33. Found: N, 6.3.

3-Indenepropylamine (If).—A 1-gal. stainless steel, stirring-type autoclave was charged with 338 g. of 3-indenepropionitrile, 500 ml. of benzene, 50 g. of ammonia, 30 g. of nickel-on-kieselguhr catalyst, and a solution of 0.6 g. sodium hydroxide in 30 ml. of 1:1 water–methanol, pressured to 500 p.s.i.g. with hydrogen, and heated to 140° (maximum pressure of 850 p.s.i.g. was reached). The autoclave was repressured with hydrogen to 850 p.s.i.g. whenever the pressure fell to 600 p.s.i.g., until no further pressure drop took place after 2 hr. The autoclave was cooled and vented. The charge was filtered, the cake washed with a little benzene, and the combined filtrates were concentrated to 10° (pot) at 35 mm. The residue was distilled through a 4-in. Vigreux column to give a heart cut of b.p. 146–149° (10 mm.), 273 g. (78% yield) of 3-indenepropylamine, a pale yellow oil.

Anal. Calcd. for $C_{12}H_{15}N$: neut. equiv., 173.0. Found: neut. equiv., 174.1.

1,1-Indenedipropylamine and 1,1,3-Indenetripropylamine.—A 1-gal. stainless steel, stirring-type autoclave was charged with 532 g. of crude polycyanoethylated indene (preparation described before), 500 ml. of benzene, 25 ml. of water, 25 ml. of methanol, 1.0 g. of sodium hydroxide, 142 g. of ammonia, and 50 g. of a stabilized nickel-on-kieselguhr catalyst. The autoclave was pressured to 500 p.s.i.g. with hydrogen and heated to 170°. The autoclave was repressured to 1000-p.s.i.g. total pressure whenever the pressure fell to 600 p.s.i.g. After 2.5 hr. at 172–175° and 1000-p.s.i.g. pressure, no further pressure drop took place. The autoclave was cooled, vented, and discharged. The product was filtered and the filtrate concentrated to 100° (pot) at 9 mm. to give 502 g. of a brown oil. This residue was distilled through a 4-in. Vigreux column to give 55.3 g. of a fraction of b.p. 143–153° (1 mm.) with correct analysis for 1,1-indenedipropylamine.

Anal. Calcd. for $C_{15}H_{22}N_2$: neut. equiv., 115.0. Found: neut. equiv., 116.6.

In addition, there was obtained 253 g. of a fraction of b.p. 220–232° (2 mm.), which corresponded to 1,1,3-indenetripropylamine.

Anal. Calcd. for $C_{18}H_{29}N_3$: neut. equiv. 95.7. Found: neut. equiv., 96.9.

N.m.r. spectra were run at room temperature (22 ± 2°) at 60.00 Mc. on a Varian 4302 DP-60 spectrometer. Line positions were obtained with respect to tetramethylsilane as an internal reference by calibration between side bands of set frequency.[10] Line positions are given in terms of τ-values (chemical shifts in parts per million with respect to tetramethylsilane, tetramethylsilane being set at 10). All samples were run as 10% (by weight) solutions in carbon tetrachloride (except where noted as otherwise in Table I).

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[10] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

Reaction of Indole Derivatives with Thionyl and Sulfuryl Chlorides

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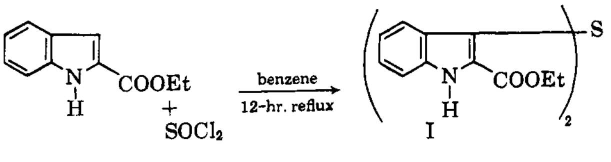
Reaction of 1-methylindole-2-carboxylic acid (II), the corresponding methyl ester V, and of ethyl indole-2-carboxylate with thionyl chloride afforded sulfinyl chlorides III, VI, and XXIII, respectively. Thionyl chloride and N,1-dimethylindole-2-carboxamide (XIX) led to sulfide XX and imide sulfoxide XXI. Sulfinyl chloride VI was converted to several sulfinamides (XI) on treatment with amines. Sulfinamides XI were oxidized with permanganate to sulfonamides XII. Treatment of VI with hydrazine in the cold gave disulfide IV, which was transformed to XXVII on heating with hydrazine. Monosulfide VIII, disulfide IV, and trisulfide X were obtained from the reaction of V with sulfur monochloride. Reaction of 1-methylindole-2-carboxylic acid hydrazide (XXX) with sulfuryl chloride led to the dichloro compound (XXXI), and V with sulfuryl chloride afforded the tetrachloro compound (XXXI) and the hexachloro compound (XXXII).

Kunori[1] has reported recently on the reaction of ethyl indole-2-carboxylate with thionyl chloride and isolation of sulfide I from the reaction mixture. We would like to describe at this time our experiments on the condensation of several indole derivatives with the same reagent.[2]



During an attempted preparation of 1-methylindole-2-carbonyl chloride[3] from the corresponding acid (II)

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[1] M. Kunori, *Nippon Kagaku Zasshi*, **80**, 407 (1959); *Chem. Abstr.*, **55**, 5457 (1961).

[2] This work was complete prior to the appearance of Kunori's paper[1] in *Chemical Abstracts*.

[3] This acid chloride is best prepared from the acid with phosphorus pentachloride in ether according to J. R. Johnson, R. B. Hasbrouck, J. D. Dutcher, and W. F. Bruce, *J. Am. Chem. Soc.*, **67**, 423 (1945).