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THE SYNTHESES OF INDENO[2,1-a]AZULENE AND INDENO[1,2-a]AZULENE1)

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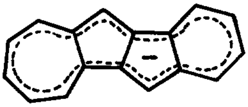
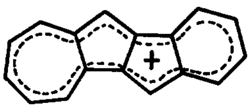
In a series of tetracyclic systems containing the azulene nucleus, the compounds consisting of the azulene nucleus cata-condensed with indene ring, such as indeno[2,1-a]azulene (1) and indeno[1,2-a]azulene (2), are of interest as parent hydrocarbons of fully conjugated system, such as an anion (A) (18π electron system) or a cation (B) (16π electron system) and also as a precursor of azuleno[2,1-a]azulene (C). The compound, 1, has already been synthesized, but its synthetic method and properties have not been described, except that its electronic spectrum has been cited in a literature.2) Recently, Sukh Dev et al.3) have reported on the synthesis of 1 by ring expansion, followed by dehydrogenation, of tetrahydrodibenzopentalene with diazomethane. On the other hand, as reported in the previous paper,4) the present authors have found that the reaction of 2H-cyclohepta[b]furan-2-one (3) with enamines of cycloalkanones yielded 1,2-polymethyleneazulenes in an excellent yield. This communication will describe the one-step syntheses of 1 and 2 by application of this enamine reaction using indanone enamines.


(A)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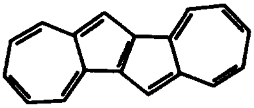
(C)

11H-Indeno[2,1-a]azulene (1) could be synthesized by the reaction of 3

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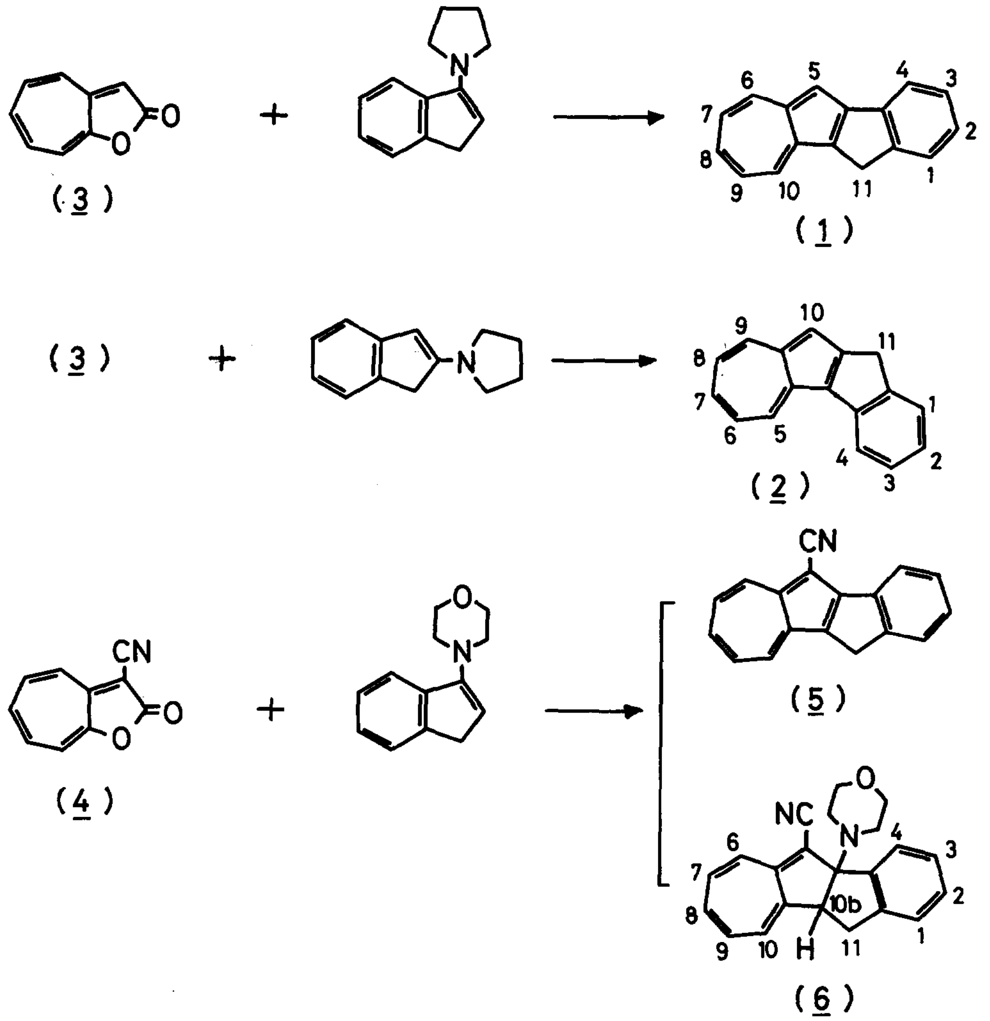


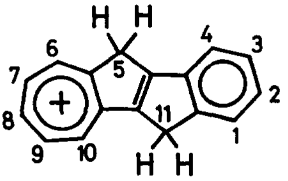
with an α-indanone enamine as follows: When a solution of 3 in anhydrous ethanol was refluxed in the presence of 3 molar equivalents of 1-N-pyrrolidinylindene, the reaction proceeded very easily and blue crystals immediately began to separated out. After refluxing for 60 min., the crystals were collected by filtration to give 1 : blue scales, mp 250-251°C,$^{5)}$ in a 93% yield. The infrared spectral data are agreed with those reported.$^{3)}$ The other spectral data of 1 are shown in Table 1. The nmr spectrum was taken in trifluoroacetic acid as an azulenium ion (1a).

On the other hand, 11H-indeno[1,2-a]azulene (2) was obtained by the reaction of 3 with an β-indanone enamine as follows: A solution of 3 in anhydrous ethanol was refluxed in the presence of 3 molar equivalents of 2-N-pyrrolidinylindene. In this case, however, the reaction proceeded so slowly that the unchanged 3 and the enamine, as well as an azulenic compound, were detected by thin layer chromatography even though the refluxing was continued

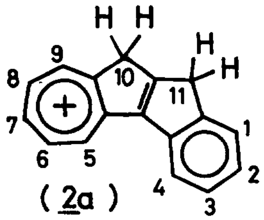
Table 1. The electronic and nmr spectral data of indenoazulenes.

	ES in MeOH, nm (log ε)			NMR, δ ppm
(1)	237(4.15),	301(4.78),	312(4.87)	4.06(2H, t, J=3Hz), -CH$_2$- at C-11
	326(4.31),	342(3.55),	360(3.78)	4.46(2H, t, J=3Hz), -CH$_2$- at C-5[a]
	377(4.03),	395(4.17),	590(2.56)	7.51-8.08(4H, m), H-1,2,3,4
	635(2.53)			8.24-8.82(5H, m), H-6,7,8,9,10
				[in CF$_3$CO$_2$H]
(2)	237(4.34),	287(4.43),	301(4.66)	4.18(2H, s), -CH$_2$- at C-11
	307(4.68),	314(4.67),	320(4.80)	4.53(2H, s), -CH$_2$- at C-10[a]
	342(3,46),	358(3,76),	376(4.04)	7.46-8.19(4H, m), H-1,2,3,4
	396(4.24),	560(2.18),	610(2.30)	8.63-9.65(5H, m), H-5,6,7,8,9
	660(2.16)			[in CF$_3$CO$_2$H]
				3.90(2H, s), -CH$_2$-
				6.66-7.60(7H, m), H-1,2,3,6,7,8,10
				7.81(1H, d, J=7Hz), H-4
				8.10(1H, d, J=10Hz), H-9
				8.50(1H, d, J=10Hz), H-5
				[in CDCl$_3$]
(5)	255(4.07),	268(4.12),	280(4.12)	3.80(2H, s), -CH$_2$-
	324(4.78),	339(4.54),	362(3.99)	7.10-7.17(6H, m), H-1,2,3,7,8,9
	369(3.97),	387(3.97),	405(3.71)	7.87-8.50(3H, m), H-4,6,10
	558(2.92),	586(2.92)		[in CDCl$_3$]

a) This signal was disappeared in deuteriotrifluoroacetic acid and two methylene groups were assigned on the basis of this fact.



(1a)



(2a)

for 140 hr. The azulenic compound was isolated by elution chromatography over an alumina column with benzene to give 2 : greenish blue scales, mp 139-140°C, in a 30% yield. The spectral data of 2 are shown in Table 1. The nmr spectrum of 2 in trifluoroacetic acid was explicable as an azulenium ion (2a).

In a manner similar to that of 3, the reaction of 3-cyano-2H-cyclohepta-[b]furan-2-one (4) with 1-N-pyrrolidinylindene gave 5-cyanoindeno[2,1-a]azulene (5) : greenish blue needles, mp 208-210°C, in a 19% yield, together with an unidentified oily material. On the other hand, the reaction of 4 with 1-morphorinoindene yielded a dihydroazulene-type intermediate (6) : red prisms, mp 181°C, in a 57% yield, as well as 5 in a 20% yield. The structure of 6 was assumed on the basis of the spectral data [IR (KBr) : 2190 cm^{-1} (conjugated CN); NMR ($CDCl_3$) : δ ppm 2.0-2.6(4H, m, $N-CH_2-$), 2.6-4.0(7H, m, $O-CH_2-$, H-10b, H-11), 5.85-6.72(5H, m, H-6,10), 7.03-7.75(4H, m, H-1,4) ; ES (MeOH) : 223 nm (log ε 4.35), 241(4.25), 264(4.08), 272(4.04), 360(4.29), 446(2.90), 480(2.82), 520(2.76)], and confirmed by the fact that 6 yielded 5 in a qauntitative yield on treatment of its benzene solution with a silica gel column. Differing markedly with the enamine of α-indanone, 4 did not react with β-indanone enamines.

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REFERENCES

1) This report corresponds to Part II of the series of the syntheses of azulene derivatives by the reaction of 2H-cyclohepta[b]furan-2-one with enamines. Part I see reference 4.
2) Pl.A. Plattner and E. Heilbronner, Helv. Chim. Acta, 31,804 (1941).
3) R.S.D. Mittal, S.C. Sethi, and Sukh Dev, Tetrahedron, 29,1321 (1973).
4) P.W. Yang, M. Yasunami, and K. Takase, Tetrahedron Letters, 1971,4725.
5) Sukh Dev et al. have reported mp 240-241°C.
6) It was found that the reaction of 3-cyano-2H-cyclohepta[b]furan-2-one (4) with enamines yielded azulenes in a highest yield when morphorino enamines were used : A. Chen, M. Yasunami, and K. Takase should report.