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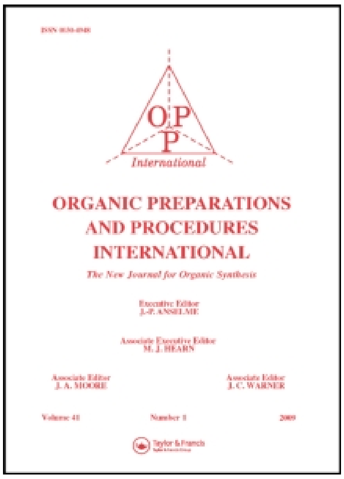

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SYNTHESIS OF 1, 3-DIVINYLAZULENES

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SYNTHESIS OF 1,3-DIVINYLAZULENES

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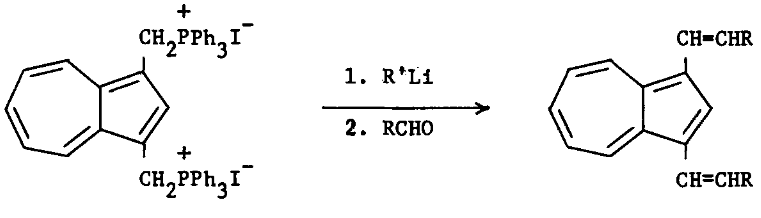
The reaction of aldehydes and, less satisfactorily, ketones with 1-azulylmethyltriphenylphosphonium iodide provided an improved route to 1-vinylazulenes.[1] We now report the extension of this method and an example of another method for the preparation of 1,3-divinylazulenes.

Quaternization of 1,3-bis(dimethylaminomethyl)azulene[2] with methyl iodide and treatment of the azulyl-1,3-bis(methyltrimethylammonium) diiodide with triphenylphosphine gave azulyl-1,3-bis(methyltriphenylphosphonium) diiodide (I). Reaction of the ylid from I with aldehydes afforded the corresponding divinylazulenes (II) in better than 65% yield (Table 1).[5] These procedures can be scaled up to give gram quantities of products.



I

II

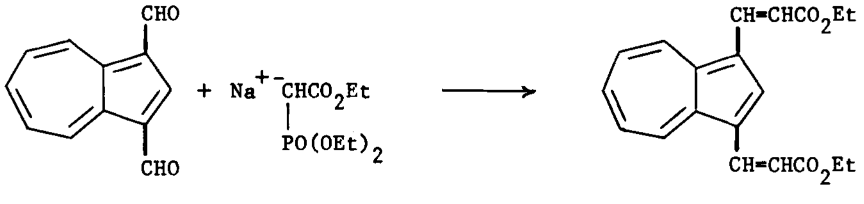
TABLE 1. 1,3-Divinylazulenes (II)

II	R[1]	λmax(nm)[2]	Yield	Anal. Calcd. (found) C	H
a	H	661	65	61.08(60.77)[3]	3.83(3.67)[3]
b	Et	669	15[4]	91.47(91.13)	8.53(8.25)
c	Ph(c,c)	653	29	93.94(93.86)	6.06(6.23)
d	Ph(c,t)	673	57	93.94(93.73)	6.06(6.02)
e	Ph(t,t)	692	12	93.94(93.87)	6.06(6.13)
f	*p*-MeOPh(c,c)	668	21	85.68(85.69)	6.16(6.21)
g	*p*-MeOPh(c,t)	680	36	85.68(85.83)	6.16(6.29)
h	*p*-MeOPh(t,t)	684	20	85.68(85.64)	6.16(6.21)
i	*m*-BrPh(c,c)	650	21	54.62(54.58)[3]	2.97(2.87)[3]
j	*m*-BrPh(c,t)	664	66.4	54.62(54.58)[3]	2.97(2.87)[3]
k	*m*-BrPh(t,t)	668[5]	8.8	63.68(63.52)	3.68(3.71)
l	*m*-IPh(c,c)	652	28	583.9492(583.9487)[6]	
m	*m*-IPh(c,t)	659	56.5	583.9492(583.9478)[6]	
n	*m*-IPh(t,t)	672[c]	6.3	54.57(54.42)	3.14(3.19)

1) c = *cis*, t = *trans*. 2) In *n*-hexane or cyclohexane.
3) As *sym*-trinitro benzene complex. 4) See reference 5.
5) In DMF. 6) Mass spectrum, molecular ion.

The structures of the *cis*, *cis*-, *cis*, *trans*- and *trans*, *trans*-1,3-bis(styryl)azulenes (IIc-e) were assigned on the basis of their visible absorption maxima (653, 673 and 692 nm, respectively) and the nmr shielding of the hydrogen at the 2-position on the ring (δ 7.75, 8.08 and 8.28, respectively). Confirmation was provided by the X-ray analysis of the structure of IIc.[3] The analogous maxima in the visible spectra and chromatographic properties were then used for the structural assignments of IIf-n. No assignments were made for IIb and IV.

The availability of certain other derivatives of this type by a different route was shown by the condensation of 1,3-azulenedicarboxaldehyde (III) with sodium triethyl phosphonoacetate to form diethyl azulene-1,3-diacrylate (IV).



III

IV

EXPERIMENTAL

Melting points are uncorrected. Ultraviolet and visible spectra were recorded with a Cary Model 14 spectrophotometer. Infrared spectra were taken with a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were recorded with Varian Model A-60, T-60 or HA-100 spectrometers. Mass spectra were taken on an AEI MS-9 spectrometer. Elemental analyses were performed by Dr. A. Bernhard, 5251 Elbach uber Engelskirchen, West Germany. All solvents were purified and dried prior to use. Phenyllithium, 1.91M or 2.14M in 30% ether-benzene, was obtained from Alfa Inorganics and butyllithium, 1.6M in hexane, was purchased from Foote Mineral Company. Woelm neutral (activity II) Al_2O_3 was used.

Azulyl-1,3-bis(methyltriphenylphosphonium) Diodide (I).-A solution of 275 mg (0.52 mmol) of azulyl-1,3-bis(methyltrimethylammonium) diiodide[4] (λ_{max} (EtOH) at 537, 567 (sh) and 624 nm (sh)), prepared in 98% yield by the reaction of 1,3-bis(dimethylaminomethyl)azulene[2] with an excess of methyl iodide in ethanol, and 290 mg (1.1 mmol) of triphenylphosphine in 75 ml of absolute ethanol was heated under reflux (N_2 atmosphere) for 23 hr. The volume was then reduced to about 25 ml, 100 ml of water added, and the blue product extracted into dichloromethane. The organic phase was washed twice with water and then dried (Na_2SO_4). Removal of the solvent left a blue solid which was triturated several times with ether to remove residual triphenylphosphine, and the crude product (430 mg, 89%) was recrystallized from absolute ethanol to give 240 mg (50%) of I as blue crystals, mp. 223.5-225 (dec.); λ_{max}(EtOH) visible (ε)

at 575 (490), 610 (435) sh and 680 nm (155) sh, uv (log ε) at 270 (4.32) sh, 278 (4.45) sh, 288 (4.54), 339 (3.74), 348 (3.74) and 366 nm (3.85).

Anal. Calcd for $C_{48}H_{40}P_2I_2$: C, 61.80; H, 4.29. Found: C, 62.18; H, 4.37.

1,3-Divinylazulene (IIa).- To a solution of 0.116 g (0.125 mmol) of I in 5 ml of dimethylformamide (DMF)[6] at -50° (N_2 atmosphere) was added 0.15 ml of 1.6M butyllithium in hexane. After 10 min., 1.0 ml of a saturated dry solution of formaldehyde in DMF was added. The mixture was stirred at -50° for 30 min. and then allowed to warm to 0°. It was poured into 200 ml of cold water containing 20 g of sodium chloride and the whole was extracted five times with 20-ml portions of dichloromethane. The concentrate from the combined, washed (twice with 50 ml of water), dried (sodium sulfate), organic extracts was chromatographed over 50 g of alumina. Petroleum ether eluted 14.3 mg (65%) of IIa, obtained as an amorphous green solid, mp. 60-105° (dec.); uv (hexane) λ_{max} (log ε) 258 (4.09), 292 (4.23), 302 (3.60) and 391 nm (3.60); visible (ε) 413 (log ε 3.48), 610 (189) sh, 661 (234), 702 (190), 734 (178) and 793 nm (83); mass spectrum, M^+ (m/e) 180.0926 (calcd. for $C_{14}H_{12}$: 180.0938). The sym-trinitrobenzene complex crystallized from ethanol, mp. 72-74° (dec.).

1,3-Bis(1'-butenyl)azulene (IIb).-To a stirred solution of 233 mg (0.25 mmol) of I in 5 ml of DMF at -50° under N_2 was added (syringe) 1.9 ml of 0.27M solution of phenyllithium in DMF. After 10 min, 1 ml of 0.5M solution of propanal in DMF was added (syringe). After 30 min, the mixture was allowed to warm to 0° over a period of 1.5 hr. It was kept at this temperature for 1 hr and then worked up as described for IIa. The first eluate fraction yielded 9 mg (15%) of IIb as an unstable green oil; uv (cyclohexane) λ_{max} (log ε) 263 (4.49), 292 (4.62) and 395 nm (4.00); visible (ε) 669 nm (308).

Further elution gave 19 mg of a green oil thought to be *cis*-1-styryl-3-(1'-butenyl)azulene; uv (cyclohexane) λ_{max} (log ε) 236 (4.32), 284 (4.46); visible (ε) 664 nm (269). A third eluate fraction afforded 12 mg (14%) of IIc, identified by spectral comparison with an authentic sample (vide infra). Other minor products were not fully characterized but exhibited spectra indicative of the presence of IId and *trans*-1-styryl-3-(1'-butenyl)azulene.^{5}

1,3-Distyrylazulenes (IIc, IId, IIe).- The procedure and scale described for IIb were used but with benzaldehyde. The crude product was chromatographed on 25 g of alumina. Elution with ether-petroleum ether (1:7) afforded 19 mg of a pure fraction of IIc as a green oil. An intermediate fraction of 8 mg was separated by tlc into 5 mg of IIc (total 24 mg, 29%) and 3 mg of IId. Crystallization of IIc from n-heptane gave green needles, mp 103-106°, uv (cyclohexane) λ_{max} (log ε) 243 (4.39) sh, 300 (4.42) and 332 nm (4.44); visible (ε) 653 nm (292); nmr ($CDCl_3$) δ 7.75 (s, 1, 2-H).

The second band yielded 44 mg (total 47 mg, 57%) of IId as a green oil which crystallized from *n*-heptane as green crystals, mp. 76-77°; uv (cyclohexane) λ_{max} (log ε) 243 (4.50), 248 (4.48), 305 (4.37) and 342 nm (4.50); visible (ε) 673 nm (275); nmr ($CDCl_3$) δ 8.08 (s, 1, 2-H).

The third band gave 10 mg (12%) of IIe as a brown oil which crystallized from _n_-heptane as brown needles, mp. 157-162°; uv (cyclohexane) λ_{max} (log ε) 253 (4.09), 310 (4.24) sh and 352 nm (4.45); visible (ε) 692 nm (207); nmr ($CDCl_3$) δ 8.28 (s, 1, 2-H).

1,3-Bis(p-methoxystyryl)azulenes (IIf, IIg, IIh).- The procedure and scale for IIb were used but with _p_-methoxybenzaldehyde. To the dried organic solution obtained was added 5 g of alumina and the mixture was evaporated to dryness (reduced pressure). The solid residue was place on top of a column of 30 g of alumina and the azulenic products were eluted with chloroform-petroleum ether (3:2) without separation. The residue from the eluate was rechromatographed on a thin column of 20 g of alumina with chloroform-petroleum ether (1:4) as the eluent. The first band afforded 16 mg (16%) of IIf as a green oil; uv (cyclohexane) λ_{max} (log ε) 248 (4.40), 305 (4.52) and 339 nm (4.60); visible (ε) 668 nm (378).

The second band yielded 50 mg of a green oil which was separated by a preparative tlc (silica gel with chloroform-petroleum ether (1:4) eluent) into IIf (5 mg), IIg (27 mg) and IIh (8 mg). The third band gave 25 mg of green oil from which was obtained in the same manner IIg (5 mg) and IIh (12 mg). The total yields were 21 mg (21%) of IIf, 35 mg (36%) of IIg and 20 mg (20%) of IIh. IIg showed λ_{max} (cyclohexane) uv (log ε) 255 (4.30), 307 (4.53), 349 (4.57); visible (ε) 680 nm (335). IIh exhibited λ_{max} (cyclohexane) uv (log ε) 255 (4.29), 308 (4.56), 3.54 (4.53); visible (ε) 684 nm (294).

1,3-Bis(m-bromostyryl)azulenes (IIi, IIj, IIk).- The procedure and scale for IIb were used with _m_-bromobenzaldehyde. Elution of the chromatograph with chloroform-petroleum ether (1:4) gave 25.5 mg (20.8%) of IIi as a green oil; uv (hexane) λ_{max}

(log ε) 289 (4.30), 334 (4.38), 406 (3.98); visible (ε) 650 (246) and 688 nm (196) sh.

The second band afforded 81.3 mg (66.4%) of IIj as a green oil; uv (hexane) λ_{max} (log ε) 297 (4.29), 338 (4.43), 400 (4.15); visible (e) 616 (219) and 654 nm (248).

The third band yielded 10.2 mg (8.8%) of IIk as brown needles (from *n*-hexane) mp. 157-159°; visible (DMF) λ_{max} (ε) 617 (290) sh and 668 nm (310).

1,3-Bis(m-iodostyryl)azulenes (IIl, IIm, IIn).– The procedure and scale for IIi-k were used with *m*-iodobenzaldehyde. IIl was obtained as a dark green oil (50 mg, 28%); uv (hexane) λ_{max} (log ε) 294 (4.18), 340 (4.31), 403 (3.96); visible (ε) 652 nm (696). IIm was isolated as a green oil (100 mg, 56.5%), uv (hexane) λ_{max} (log ε) 224 (4.60), 299 (4.33), 351 (4.55); visible (ε) 620 (243) sh, 659 (282) and 738 nm (186) sh. IIn was obtained as a brown solid, mp. 163-165°; visible (DMF) λ_{max} (ε) 672 nm (442).

Diethyl Azulene-1,3-diacrylate (IV). To slurry of 184 mg (4 mmol) of sodium hydride (50% dispersion in mineral oil) in 10 ml of dry 1,2-dimethoxyethane was added 1 ml (4.5 mmol) of triethyl phosphonoacetate, bp. 99-100° at 1 mm,[7] with stirring. After 45 min, a solution of 92 mg (0.5 mmol) of III, mp. 186-188° (lit.[8] mp. 190°) in 5 ml of 1,2-dimethoxyethane was added over a period of 5 min. The mixture was stirred at 55° for 30 min and then cooled to room temperature. A few drops of ethanol and then 100 ml of water were added and the whole was extracted with ether. The concentrate from the washed (twice with water, once with saturated salt solution), dried (sodium sulfate) ethereal extracts was chromatographed on basic alumina. Dichloromethane eluted 91 mg (56%, 65% net) of IV, obtained as green needles, mp. 145-146°, and then 13 mg of unchanged III. Recrystallization of IV from ethanol and then from cyclohexane raised the mp. to 147-147.5°; uv (cyclohexane) λ_{max} (D) 266 (0.41), 282 (0.43), 292 (0.41), 329 (0.95), 368 (0.30), 386 (0.28), 408 (0.26), 432 (0.20); visible (ε) 585 (390), 605 (420), 628 (480), 660 (350), 692 (335), 742 (94) and 780 nm (83); ir (CCl_4) 1718 and 1623 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.90; H, 6.16.

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