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First intramolecular trapping and structural proof of the key intermediate in the formation of indolizine photochromics†

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The reaction of substituted spirocyclopropenes 1 with 1-(3,5-dinitrophenyl)-3,4-dihydroisoquinoline 2 in dry ether solution afforded not only the expected THI 4 by 1,5-electrocyclization but also novel fluorenespiroazanorcaradienes 5 which is the first intramolecularly trapped product of the key intermediate in the formation of indolizine photochromics.

The reaction of the easily accessible spirocyclopropenes **1** with isoquinolines **2** has been shown to be an extremely powerful tool to prepare new photochromic dihydroindolizines (DHI), tetrahydroindolizines (THI) and pyrrolopyrrolizidines.[1–4] A vast number of tailormade molecules having interesting properties for applications such as ophthalmic lenses,[5] molecular switches,[6] dental material[7] and potential application in information recording and data storage and holography[8] has been published. We have shown recently that the reaction of 1-styryl-3,4-dihydroisoquinolines with spirocyclopropenes **1** is controlled by substituents to afford a pericyclic reaction to either THI's **4** or azepine derivatives **6**.[9] This reaction is governed by the substituents in the fluorene part and can form in a periselective way THI's **4** or azepines **6**. These results incited us to introduce strongly electron attracting groups (NO_2) which might stabilize the first intermediate in this reaction or even allow isolation of the product directly derived from this—until now—unproved intermediate. In this paper we describe the isolation of fluorenespiroazanorcaradienes **5** the trapped key intermediate in the indolizine formation and their X-ray structure, and also new THIs **4**.

Analogues of **2** with an unsubstituted 2-phenyl-ring, or with halogen or one nitro-group in the ring led only to ring-closed THIs when reacted with spirocyclopropenes **1** (see Table 1). The reaction of spirocyclopropenes **1** with dinitrosubstituted **2** in diethyl ether at rt after 5 d not only afforded the ring-closed THI **4** but a novel product, the azanorcaradiene **5**. Both products were isolated using column chromatography on silica gel (eluent CH_2Cl_2 and CH_2Cl_2–MeOH), their structures were determined *via* elemental analysis, ^{1}H-NMR, ^{13}C-NMR, IR-spectra and X-ray analysis (see ESI†).The general mechanism for the reaction of **2** with **1** is shown in Scheme 1. The reaction of **1** with **2** can proceed in three possible ways. The carbon atoms 2″ and 6″ in the 5′-phenyl ring of intermediate **A** are positively polarised because of the influence of two strong electron withdrawing nitro-groups in *ortho*- and *para*-positions. In the first case (path **a**), after nucleophilic addition of **2** on the double-bond of **1** starting from the intermediate cyclopropylcarbanion **A** by 1,6-electrocyclization through attack of the negative C2′ on the positive C2″ and finally by rearrangement results in **5** which must be regarded as the product of the intramolecularly trapped intermediate **A**. This is the first direct proof of intermediate **A** postulated in the mechanism of indolizine formation. In the second case (path **b**), the intermediate **A** rearranges to the betaine **3** through a cyclopropylallylanion rearrangment, which yields THI **4** through 1,5-electrocyclization. In the third possible case (path **c**), the betaine **3** may form through 1,7-electrocyclization to produce the 7-membered compound **6′**, a reaction not observed here.

Besides spectral data, the structure of products was confirmed by X-ray analysis for the fluorenespiroazanorcaradiene dye **5b** (Fig. S1†) and tetrahydroindolizine **4f** (Fig. S2†).

The green to green-blue dyes **5** have two absorption bands in the visible. The UV–Vis data and color are shown in Table 2.

The novel azanorcaradienes **5** possess acidochromic or halochromic properties, for example the ethanol solution of **5a** has a green color (459 and 655 nm); the color changed at once from green to deep violet (548 nm) after adding a few drops of aqueous sodium hydroxide. This process is reversible with hydrochloric acid many times without decreasing the absorption intensity. It is suggested that the acidochromism of dye **5** giving the anion **5′** (proton abstracted at 4′a position) is due to dissociation of the **4′**a-H atom and the reversible reprotonation

† Electronic supplementary information (ESI) available: Figs. S1 and S2. See http://www.rsc.org/suppdata/cc/b1/b101044l/

Table 1 The physical data of newly prepared tetrahydroindolizines **4a–g** and betaines **3a–d**

4	R	E	λ_{max}/nm $t_{½}$/s of betaine	Mp/°C	Yield (%)	^{1}H-NMR ($CDCl_3$) δ in ppm 5′-CH_2	6′-CH_2	^{13}C-NMR ($CDCl_3$) δ in ppm 5′-C	6′-C
4a	H	CO_2Me	500, 700 1.57	262–264	47.5	3.58(m, 1H) 3.81(m, 1H)	2.71(dt, 1H) 3.18(m, 1H)	41.00	29.24
4b	H	CO_2Et	500, 700 1.0	253–255	46.2	3.59(m, 1H) 3.84(m, 1H)	2.71(dt, 1H) 3.19(m, 1H)	40.79	29.14
4c	Br	CO_2Me	500, 750 0.579	305–307	50.4	3.58(m, 1H) 3.85(m, 1H)	2.77(dt, 1H) 3.22(m, 1H)	41.02	29.20
4d	Cl	CO_2Et	500, 750 0.418	258–260	48.7	3.58(m, 1H) 3.87(m, 1H)	2.75(dt, 1H) 3.23(m, 1H)	40.83	29.17
4e	H	CO_2iPr	480, 725 0.417	232–234	24.3	3.59(m, 1H) 3.75(m, 1H)	2.65(m, 1H) 3.13(m, 1H)	40.49	29.58
4f	H	CO_2tBu	500, 725 0.213	200–202	21.5	3.54(m, 1H) 3.90(m, 1H)	2.64(m, 1H) 3.21(m, 1H)	40.55	29.14
4g	H	$CO_2C_6H_{11}$	500, 725 0.278	168–170	18.5	3.49(m, 1H) 3.89(m, 1H)	2.61(m, 1H) 3.20(m, 1H)	40.42	29.14

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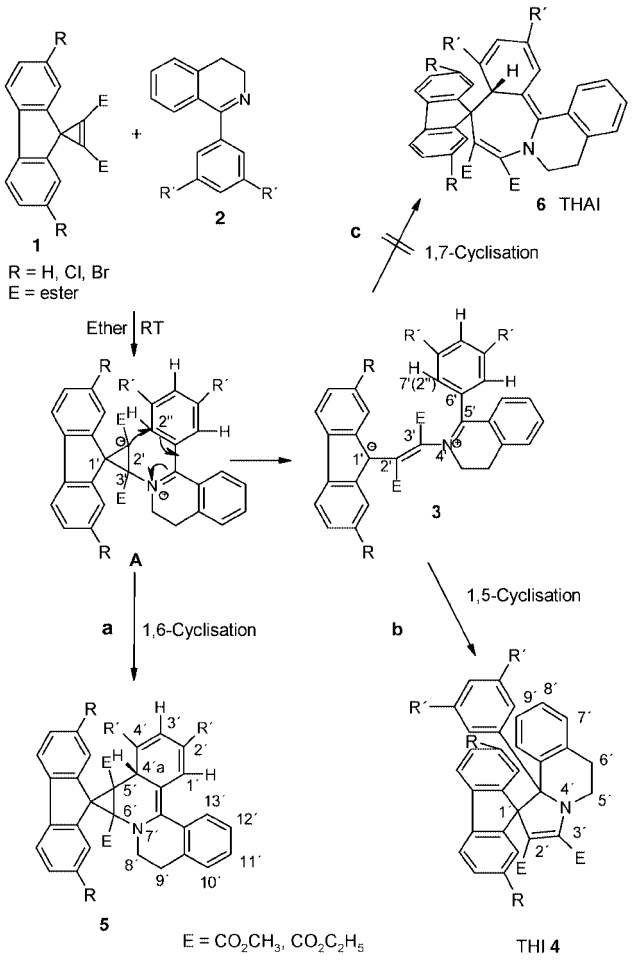
Table 2 Analytical and spectral data of fluorenespiroazanorcaradiene dyes **5a–g**

5	R	E	mp/°C	Yield (%)	^{1}H-NMR ($CDCl_3$) δ in ppm 4′a-H	8′-CH_2	9′-CH_2	^{13}C-NMR ($CDCl_3$) δ in ppm 4′a-C	8′-C	9′-C	λ_{max}/ nm	Color of dye
5a	H	CO_2Me	218-220	33	5.27 (s, 1H)	3.47(d,1H) 3.66(td,1H)	2.77(d,1H) 3.20(td,1H)	35.92	47.13	27.4 3	453 656	Green
5b	H	CO_2Et	212–214	40	5.24(s, 1H)	3.47(d,1H) 3.66(td,1H)	2.77(d,1H) 3.27(td,1H)	35.98	47.16	27.4 1	457 659	Green
5c	Br	CO_2Me	227–229	30	5.04(s, 1H)	3.44(d,1H) 3.61(td,1H)	2.82(d,1H) 3.20(td,1H)	36.10	47.02	27.4 6	446 639	Green–blue
5d	Cl	CO_2Et	213–215	35	5.03(s, 1H)	3.41(td,1H) 3.62(td,1H)	2.81(td,1H) 3.26(td,1H)	36.28	46.95	27.5 8	448 646	Green–blue
5e	H	CO_2Pr^i	215–217	17	5.02(s, 1H)	3.40(m,1H) 3.60(m,1H)	2.71(m,1H) 3.23(m,1H)	35.8	46.92	27.4 5	458 663	Green
5f	H	CO_2Bu^t	181-183	13	5.12(s, 1H)	3.43(m,1H) 3.64(m,1H)	2.84(m,1H) 3.25(m,1H)	35.9	46.87	27.6	454 660	Green
5g	H	$CO_2C_6H_{11}$	171–173	11	5.08(s, 1H)	3.40(m,1H) 3.62(m,1H)	2.81(m,1H) 3.20(m,1H)	36.3	46.81	28.0	453 659	Green



Scheme 1

of the resulting carbanion. This has been proved also by ^{1}H-NMR measurements.

Compound **5a** in CD_3CN shows a singlet for 4′a-H at 5.38 and 1′-H at 8.06 ppm as well as a doublet for 3′-H at 8.27 ppm. The addition of NaOD–D_2O changed the green color to violet, 4′a-H disappeared completely and 3′-H is shifted to 4.74 ppm (s) and 1′-H to 7.59 ppm. The original spectrum appears again after addition of DCl. Thus it is clear that the colored species **5′** is the anion where a proton has been abstracted from the 4′a-position. In summary, the intramolecular trapping of intermediate **A** to afford fluorenespiroazanorcaradienes **5** is the first proof for the mechanism of the cyclopropane anion intermediate postulated[1–4] after nucleophilic attack of **2** to the double bond of **1**. The cyclopropyl anion is intramolecularly trapped to give cyclopropane derivatives **5**. The THI **4** are formed *via* the betaine **3** to its precursor the cyclopropylanion **A**.

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