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Syntheses and Ring Opening Reactions of 2-Alkyl-3,3-dichlorospiro[cyclopropane-1,9'-fluorene] Derivatives

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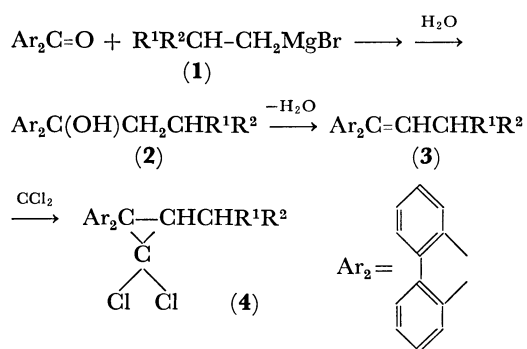
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Synopsis. 2-Alkyl-3,3-dichlorospiro[cyclopropane-1,9'-fluorene] derivatives (**4**) were obtained by the addition of CCl_2 to 9-alkylidene fluorenes. Ring opening reactions of **4** with bases gave enynes, butadienes, or butatrienes.

Most spiro[cyclopropane-1,9'-fluorene] derivatives have been synthesized from the reactions of 9-diazo-fluorene with olefins by heating or by irradiation with UV light.¹⁾ In the present paper, we wish to present a convenient method for the syntheses of similar spiro compounds, in which 2-alkyl-3,3-dichlorospiro[cyclopropane-1,9'-fluorene] derivatives (**4**) are prepared in good yields by the reactions of 9-alkylidene fluorenes (**3**) with dichlorocarbene. Furthermore, we wish to report the ring opening reactions of **4** with some bases.

The olefins **3** were obtained by dehydration of the corresponding 9-alkyl-9-fluorenols (**2**) which were prepared from the reaction of fluorenone with alkyl-magnesium bromides (**1**). The dichlorocarbene was generated from the reaction of chloroform with aqueous sodium hydroxide solution (50%) in the presence of catalytic amounts of benzyltriethylammonium chloride (method A²⁾), or from the reaction of ethyl trichloroacetate with sodium methoxide (method B³⁾).

Syntheses of 4. A group $-\text{CH}_2\text{CHR}^1\text{R}^2$ was chosen as the alkyl group in Grignard reagents **1**, and the syntheses of **2**, **3**, and **4** are shown in Scheme 1. The melting points and yields of the products are summarized in Table 1. All the products had satisfactory



Scheme 1.

elemental analyses (C and H), and the structures of the products were confirmed by their IR and NMR spectra. Compound **4e** was a mixture which was separated into two isomers **4e-1** and **4e-2** by fractional crystallization. The structures of **4e-1** (mp 125—127 °C) and **4e-2** (mp 155—157 °C) were confirmed

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TABLE 1. SYNTHESES OF **2**, **3**, AND **4**

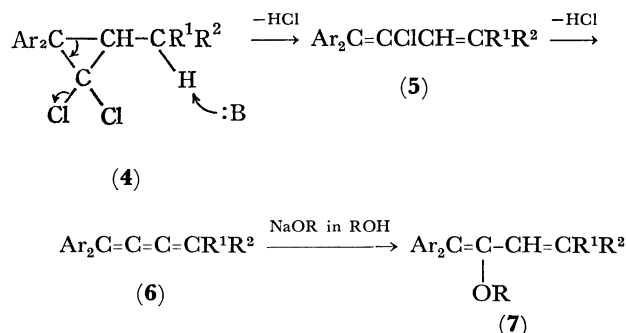
Compd	R ¹	R ²	Mp (°C) (Bp./mmHg)	Yield (%)
2a ⁴⁾	H	H	98—99	77
2b	H	CH ₃	97—100	76
2c	CH ₃	CH ₃	112—115	70
2d ⁵⁾	H	Ph	56—58	42
2e	CH ₃	Ph	89—91	40
3a ⁴⁾	H	H	100—103	72
3b	H	CH ₃	39—42	91
3c	CH ₃	CH ₃	(136—138/0.07)	61
3d ⁵⁾	H	Ph	88—90	89
3e	CH ₃	Ph	74—76	88
3f ⁶⁾	Ph	Ph	103—106	44
4a ^{a)}	H	H	110—112	72
4b ^{a)}	H	CH ₃	71—72	73
4c ^{b)}	CH ₃	CH ₃	81—83	57
4d ^{b)}	H	Ph	116—118	88
4e ^{b)}	CH ₃	Ph	{125—127 155—157}	82
4f ^{a)}	Ph	Ph	169—170	83

a) CCl_2 was generated by the method A.²⁾ b) CCl_2 was generated by the method B.³⁾

as *threo* and *erythro* isomers, respectively, from their NMR spectra.⁷⁾

Ring Opening Reactions of 4 with Bases. The ring opening reactions of **4a**, **4b**, and **4c** with sodium alkoxides in alcohols or with pyridine gave unidentified polymeric powders or tars in each case. However, the products of the reactions of **4d**, **4e**, and **4f** with bases were derivatives of enynes, butadienes, and butatrienes conjugated with the fluorene moiety. The structures of these derivatives were confirmed by elemental analysis and spectral data. The experimental results are summarized in Table 2.

When pyridine was used as a base, compounds of type **5** were isolated. The reaction of **5f** with sodium



Scheme 2.

TABLE 2. RING OPENING REACTIONS OF **4d**, **4e**, AND **4f** WITH BASES

4	Base used	Reaction condition	Product			Yield (%)
			Structure	Mp (°C)	Color	
4d	Pyridine	Δ 48 hr	$\text{Ar}_2\text{C}=\text{CClCH}=\text{CHPh}$ (5d)	133—135	Yellow	43
	NaOMe in DMSO	rt 4 hr	$\text{Ar}_2\text{C}=\text{CHC}\equiv\text{CPh}$ (8d)	88—90	Yellow	35
	NaOEt in EtOH	Δ 24 hr	$\text{Ar}_2\text{C}=\text{C}(\text{OEt})\text{CH}=\text{CHPh}$ (7d)	64—67	Yellow	13
4e	Pyridine	Δ 145 hr	$\text{Ar}_2\text{C}=\text{CClCH}=\text{CMePh}$ (5e)	91—105	Yellow	24
	NaOEt in EtOH	Δ 28 hr	$\text{Ar}_2\text{C}=\text{C}(\text{OEt})\text{CH}=\text{CMePh}$ (7e)	147—149	Yellow	18
4f	Pyridine	Δ 96 hr	$\text{Ar}_2\text{C}=\text{CClCH}=\text{CPh}_2$ (5f)	162—164	Yellow	60
	NaOMe in DMSO	rt 40 min	$\text{Ar}_2\text{C}=\text{C}=\text{C}=\text{CPh}_2^{8)}$ (6f)	223—224	Orange	90
	NaOMe in DMSO	40 °C 2 hr	$\text{Ar}_2\text{C}=\text{C}(\text{OMe})\text{CH}=\text{CPh}_2$ (7f)	177—178	Yellow	33

methoxide in MeOH led to **6f**,⁸⁾ which was easily converted into **7f** by sodium methoxide in DMSO. Therefore, the following mechanism would account for the formation of products **5**, **6**, and **7** from **4** in the presence of bases.

Experimental

*Syntheses of 4 by Method A.*²⁾ A typical procedure was as follows. Compound **2a** (5.3 g, 0.028 mol) in CHCl_3 (12 ml) was added to a mixture of 50% aq. NaOH (20 ml) and $\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3 \cdot \text{Cl}$ (0.4 g). The mixture was stirred for 4 hr at 40 °C, and then poured into water (100 ml). The organic layer was separated and the aqueous phase was extracted with ether. The combined organic extracts were washed with water and dried over MgSO_4 . The dry ether solution was concentrated in a rotary evaporator. Recrystallization of the residue from ethyl alcohol gave **4a**: 5.0 g (72%); mp 110—112 °C.

*Ring Opening of 4 by Bases.*³⁾ A typical procedure was as follows. Compound **4d** (0.5 g, 0.0014 mol) was reacted with commercial sodium methoxide (0.17 g, 0.003 mol) in DMSO (70 ml) for 4 hr at room temperature. The resulting mixture was poured into water and then extracted with ether. The ether solution was washed with water and dried over MgSO_4 . Concentration of the dry ether solution gave **8d**: 0.11 g (35%); mp 88—90 °C (from petroleum benzene-benzene (1 : 1 v/v)).

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7) The NMR data of **4e** are as follows: **4e-1**; δ (CDCl_3) 1.65 (d, $J=8$ Hz, 3, CH_3), 2.76 (d, $J=11$ Hz, 1, $-\text{CH}-$), 3.55 (two q, $J=11$ Hz, and $J=8$ Hz, 1, $-\text{CH}-\text{CH}_3$), 6.82 (s, 5, $-\text{Ph}$), 7.0—7.7 (m, 8, fluorene nucleus), **4e-2**; δ (CDCl_3) 1.0 (d, $J=6.5$ Hz, 3, CH_3), 2.76 (d, $J=11$ Hz, 1, $-\text{CH}-$), 3.55 (two q, $J=11$ Hz, and $J=6.5$ Hz, 1, $-\text{CH}-\text{CH}_3$), 7.0—7.82 (m, 13, aromatic ring protons). It appeared that both the phenyl protons in the stable conformation of the *threo* form and the methyl protons in the stable conformation of the *erythro* form are located above the fluorene ring. Therefore, these protons above the fluorene ring should be shifted to higher field. From the above NMR data, it may be seen that **4e-1** is the *threo* isomer and **4e-2** is the *erythro* isomer.

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