January, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (1), 273—275 (1977) 273

The Temperature and Solvent Effects on the AlCl$_3$-catalyzed Cyclization of 3,3′-Diphenyl-2,2′-biindenyl-1,1′-dione

Fumio Toda and Yozo Todo

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790

(Received August 30, 1976)

Upon the AlCl$_3$-catalyzed cyclization of the title biindenone (**1**) into benz[*c*]indeno[2,1-*a*]fluorene-13,14-dione (**2**) and 3,3′: 3,3′-di(*o*-phenylene)-2,2′-biindenylidene-1,1′-dione (**3**), the **2**: **3** ratio increased when the reaction temperature was raised and decreased when the polarity of the solvent was increased.

During the course of our study of the AlCl$_3$-catalyzed cyclization of the title biindenone (**1**) into benz[*c*]-indeno[2,1-*a*]fluorene-13,14-dione (**2**) and 3,3′:3,3′-di-(*o*-phenylene)-2,2′-biindenylidene-1,1′-dione (**3**), we found that the **2**: **3** ratio is remarkably affected by the reaction temperature and the polarity of the solvent.

Results

The yields of the products under various reaction conditions are summarized in Table 1. Of the products, **2**—**6**, **2**[1] and **6**[2] are known compounds. The spectral and analytical data of **3**, 3,3′-(*o*-phenylene)-3,3′-diphenyl-2,2′-biindenylidene-1,1′-dione (**4a**), and its halo derivatives (**4b**—**c** and **5b**—**c**) are summarized in Table 2.

Table 1. Reaction conditions and yields of products[a)]

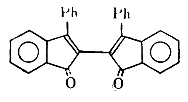
Reaction conditions			Yields (%) of products				
Solvent	Dielectric constant	Reaction temperature (°C)	**2**	**3**	**4**	**5**	**6**
C_6H_6	2.3	20	38		37 (**4a**)		
		80	74				
CS_2	2.6	20	22	6			28
		46	49				28
C_6H_5Br	5.4	20	20	8	19 (**4b**)	12 (**5b**)	
		80	49	14	15		
C_6H_5Cl	5.6	20	12	8	24 (**4c**)	22 (**5c**)	
		80	30	16	16		
CH_2Cl_2	8.9	20		70			
		40	89				
$C_6H_5NO_2$	34.8	20		60			
		80		60			

a) The yields are based on the product of the reaction which was carried out for 3 h; within this period all the reactions were completed.

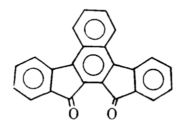
Table 2. Melting points, and spectral and analytical data of **3**, **4**, and **5**[a)]

Compound	Mp (°C)	ν_{max}^{Nujol} (cm^{-1})	$\lambda_{max}^{CHCl_3}$ nm ($\varepsilon\times10^{-2}$)	*m/e* (rel intensity)	Found (Calcd) (%) C	H
3	292	1710 (C=O) 1640 (C=C)	296(375), 308(70), 409(91), 464(16)	408 (M$^+$, 100), 380 (M$^+$—CO, 30), 332 (M$^+$—C_6H_4, 85), 176 ($C_{14}H_8^+$, 30)	87.95 (88.22	3.87 3.95)
4a	>310	1710 (C=O) 1645 (C=C)	298(196)	486(M$^+$, 100), 409 (M$^+$—Ph, 33), 381 (409—CO, 40), 332 (409—Ph, 10)	88.63 (88.86	4.36 4.56)
4b	276—277	1720 (C=O) 1640 (C=C) 820 (1,4-C_6H_4)	296(191)	564 (M$^+$, 100), 566 ((M+2)$^+$, 98), 485 (M$^+$—Br, 50), 409 (M$^+$—C_6H_4Br, 20), 381 (409—CO, 40),	76.24 (76.46	3.55 3.74)
4c	295—296	1720 (C=O) 1640 (C=C) 820 (1,4-C_6H_4)	298(176)	520 (M$^+$, 100), 522 ((M+2)$^+$, 33), 485 (M$^+$—Cl, 45), 409 (M$^+$—C_6H_4Cl, 20)	82.79 (82.99	3.82 4.06)
5b	>310	1720 (C=O) 1640 (C=C)	297(194)	564 (M$^+$, 100), 566 ((M+2)$^+$, 98), 485 (M$^+$—Br, 50), 409 (M$^+$—C_6H_4Br, 20), 381 (409—CO, 20)	76.31 (76.46	3.66 3.74)
5c	>310	1720 (C=O) 1640 (C=C)	294(182)	520 (M$^+$, 100), 522((M+2)$^+$, 33) 485 (M$^+$—Cl, 45), 409 (M$^+$—C_6H_4Cl, 20)	82.71 (82.99	3.97 4.06)

a) All the melting points are uncorrected. The mass spectra were measured with an ionization energy of 75 eV. The NMR spectra showed aromatic protons only.



1



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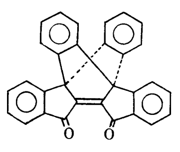

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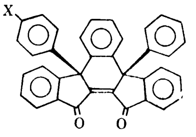
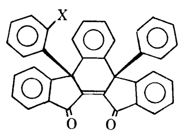


4

a : X=H
b : X=Br
c : X=Cl



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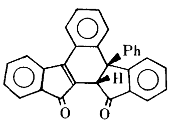

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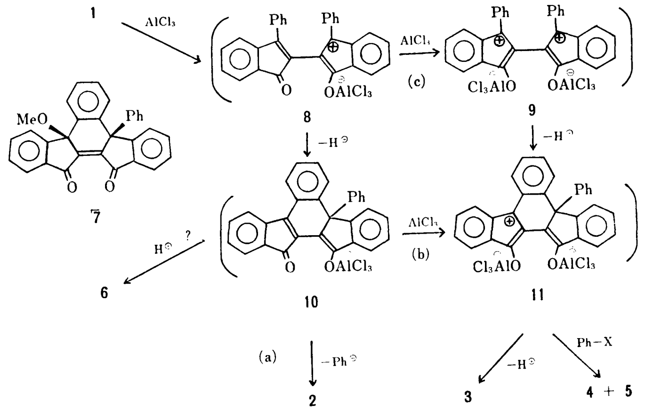

The structures of **4** and **5** were characterized by comparing their spectral data with those of **7**.[2] The structure of **3** was mainly characterized by means of the mass spectrum, which showed the fragmentation of the benzyne from the molecular ion and the formation of an anthracene cation radical (Table 2). The UV spectral bands of **3** in the remarkably longer-wave length region are presumably due to its internal strain. Of the halogen-substituted products (**4b**—**c** and **5b**—**c**), **4b** and **4c** were identified as 4-halo derivatives on the basis of their IR bands of 1,4-disubstituted benzene (820 cm^{-1}). Therefore, **5b** and **5c** are probably 2-halo derivatives.

Discussion

Temperature Effect. In the cases of all the reactions except in nitrobenzene with an extremely high dielectric constant, the **2**: **3** ratio increased when the reaction temperature was raised. This was remarkable in dichloromethane, the products at 20 and 40 °C being **3** and **2** respectively. Of course, no thermal conversion of **3** into **2** under the conditions described in Table 1 was observed. The temperature effect can be interpreted as follows: there are two competing reaction pathways, leading to **2** and **3** respectively. One of them proceeds through the elimination of the benzenide anion and $AlCl_3$ from **10**, which was formed by an intramolecular cyclization of the $AlCl_3$-coordinated intermediate (**8**), giving **2** (Path (a)). Another one proceeds through the further coordination of $AlCl_3$ to **10** (Path (b)); cyclization followed by the ketonization of the resulting intermediate (**11**) finally affords **3**. Such a dehydrogenating ketonization of vinyl alcohol has long been known to occur under the influence of $AlCl_3$.[3] At higher temperatures, Path (a) would be much more accelerated than would Path (b). Because of the increase in the steric and then the electrostatic repulsions at higher temperatures, **11** is less favored and Path (b) is relatively retarded. A similar interpretation has recently been reported with regard to the $AlCl_3$-catalyzed dimerization of indenone in boiling dichloromethane (40 °C) and ethylene chloride (83 °C), which afford endo and exo head-to-tail dimers respectively.[4]

The formation of **4** and **5** can be interpreted in terms of arylation on **11**. At 80 °C, the yields of **4** and **5** decreased. Again, this is due to the retardation of Path (b) for the reason presented above. In addition, the approach of the 2-position of halobenzene to the cationic center of **11** is fully inhibited at 80 °C because of the large steric repulsion.

The additional pathway which proceeds *via* **9** (Path (c)) could also be applied to the interpretation of the formation of **3**—**5**. However, this would be unreasonable, because the cyclization of **9** to **11** should overcome large electrostatic and steric repulsions in a transition state. The pathway of the formation of **6** is not clear. Although the ketonization of **10** can give **6**, this consideration disagrees with the finding that the yield of **6** is not affected by the reaction temperature. If **6** is derived directly from **10**, the yield of **6** should decrease at higher temperatures, because the yield of **2** increases when the temperature is raised.

Solvent Effect. Both the **2**: **3** ratio and the ratio of **2** to the total of **3**, **4**, and **5** at 20 °C decreased as the polarity of the solvent increases. This is remarkable in the cases of the reactions in dichloromethane and nitrobenzene; in both cases **3** was the sole isolable product. Especially, nitrobenzene of an extremely high dielectric constant strongly controlled the reaction causing it to proceed through Path (b) even at 80 °C and to produce **3** only. In a polar solvent, **11** would be stabilized by solvation, and thus Path (b) would be enhanced. If **9** is formed in this reaction, **9** would also be stabilized by the polar solvent. Nevertheless, there still remains the question of why **6** was formed only in the reaction in carbon disulfide.

Experimental

Preparation of 1. A mixture of 2,3-bis(diphenylmethylene)succinyl chloride[5] (10 g), benzene (50 ml), ether (50 ml), and $AlCl_3$ (5 g) was stirred at room temperature for 3 h. The reaction mixture was decomposed with water, and then extracted with benzene. The benzene solution was washed with water and dried over anhyd Na_2SO_4. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to afford **1** as red prisms; 7 g (82%): mp 214 °C (lit,[6] mp 213—214 °C).

General Procedure of the $AlCl_3$-catalyzed Cyclization of 1. A mixture of **1** (0.5 g), the solvent (50 ml), and $AlCl_3$ (2 g) was stirred for 3 h. The reaction mixture was decomposed with water and then extracted with benzene. During the extraction, **2** was crystallized out as orange needles; it was then recrystallized from AcOEt to afford a pure sample of **2**; mp

306—308 °C (lit,[1]) mp 309—310 °C). The benzene solution was washed with water and dried over anhyd Na_2SO_4. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to afford **3** or **4**. In the cases of the reaction in halobenzene, **3**, **4**, and **5** were separated by fractional recrystallization from AcOEt. In the cases of the reaction in carbon disulfide, **3** and **6** were separated mechanically.

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