

PHOTODECOMPOSITION OF DIHALOGENOALUMINUM PHENOLATES IN BENZENE.
A NOVEL DEOXYGENATION OF PHENOLS

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



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It is known that phenol reacts with aluminum chloride to form dichloroaluminum phenolate which is relatively stable thermally.¹⁾ Addition of ethylaluminum dichloride (EtAlCl_2) to a benzene solution of a phenol gives a similar phenolate with rapid evolution of ethane.²⁾ Heating this solution at 80° apparently causes no change and the phenol is recovered completely from the reaction mixture after hydrolysis. However, we have found that irradiation of the solution causes the deoxygenation of the phenol to give the corresponding benzene, chlorobenzene and phenylbenzene.

An equimolar mixture of phenol and EtAlCl_2 in absolute benzene (0.27 M) in a quartz tube sealed under an atmosphere of nitrogen was irradiated for 5 hr from a 300 W high-pressure mercury lamp with quartz housing at $\text{ca. } 50^\circ$. Usual work up of the reaction mixture after treatment with water gave chlorobenzene (10 %) and biphenyl (16 %) along with the recovered phenol (83 %). Similarly irradiation of *p*-cresol yielded toluene (6 %), *p*-chlorotoluene (11 %) and *p*-methylbiphenyl (23 %), together with the recovered phenol (80 %).

It is presumed that primary products of photolysis of dichloroaluminum phenolates are chlorobenzenes and that benzenes and biphenyls may be derived from them under the conditions.³⁾ However, the possibility can never be excluded at present that some of the benzenes and biphenyls are formed directly without intermediacy of the chlorobenzenes:

Table 1. Photodecomposition of Dihalogenoaluminum Phenolates in Benzene^a

R in HO- 	EtAlCl ₂ (equiv.)	Irrad. time (hr)	Conv. (%)	Products (%) ^b		
					Cl- 	
R = H	0.5	6	15	—	0	0
H	1.0	5	17	—	10	16
H	1.0	24	15 ^e	—	20	20
H	2	6	23	—	40	29
H	2	23	42	—	42	27
<i>p</i> -Me	0.5	5	23	0	0	0
<i>p</i> -Me	1.0	5	20	6	11	23
<i>p</i> -Me	1.0	23	22 ^e	7	11	20
<i>p</i> -Me	2	5	22	17	6	31
<i>p</i> -Me	2	22	34	14	4	38
<i>p</i> -Me	AlCl ₃ , 1.0	21	35	N.D. ^f	4	7
<i>p</i> -Me ^c	AlCl ₃ , 2	21	27 ^e	N.D. ^f	8	4
<i>p</i> -Me	AlBr ₃ , 1.0	21	65	N.D. ^f	3	17
<i>p</i> -Me ^d	AlBr ₃ , 2	21	12 ^e	N.D. ^f	0	2.4
3,5-(Me) ₂	2	41	60	37	N.D. ^f	28
2,4-(Me) ₂	3.3	63	81	31	N.D. ^f	29

^a A mixture of a phenol (2.7 — 3.4 mmol) and EtAlCl₂ in absolute benzene (10 — 16 ml) was irradiated in a quartz cell at a distance of 3 cm from a 300 W high-pressure mercury lamp with quartz housing at ca.50°.

^b Yields are based on the consumed phenol.

^c In addition, *m*-methylbiphenyl (7 %) and diphenylmethane (7 %) were obtained.

^d In addition, *m*-methylbiphenyl (5 %) and diphenylmethane (6 %) were obtained.

^e Relatively large amount of resinous material was deposited on the cell-wall which might have retarded the reaction.

^f Not determined.

EtAlCl_2 (2 equiv.) gave the biphenyl (52 %) at 75 % conversion. However, such an effect of EtAlCl_2 was not significant in the case of the decomposition of chlorobenzene.

It was found that aluminum chloride and bromide can also be used in place of EtAlCl_2 . But the reaction in these cases was complicated due to the deposition of a tarry material on the reaction vessel, and to the further reaction of the products under the conditions. When an excess of aluminum halide was employed, *p*-cresol gave *m*-methylbiphenyl and diphenylmethane as well as the expected product, *p*-methylbiphenyl. *p*-Methylbiphenyl was found to be thermally rearranged to the *m*-isomer by aluminum bromide or chloride in benzene. Irradiation of a mixture of *p*-methylbiphenyl and aluminum bromide or chloride in benzene gave diphenylmethane in addition to *m*-methylbiphenyl, the latter of which was formed thermally. However, these isomerizations were caused neither thermally nor photochemically by EtAlCl_2 . No reaction occurred when *p*-cresol was irradiated with diethylaluminum chloride or triethylaluminum.

The light below 2800 Å is required for the reaction since no change of the starting material was observed when a Pyrex tube was used in place of the quartz tube.

The reaction may provide a unique tool for one step synthesis of biphenyls, especially of alkylsubstituted ones, from the corresponding phenols. As further examples 3,5- and 2,4-dimethylbiphenyls were prepared from 3,5- and 2,4-dimethylphenols, respectively.

References

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