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Reactions of 1,1-Diphenylethylene and Its Derivatives with Tris(*p*-bromophenyl)aminium Hexachloroantimonate

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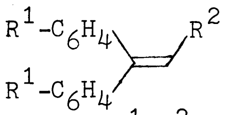
Reaction of 1,1-diphenylethylene(1) with $(p\text{-BrC}_6\text{H}_4)_3\text{N}^{+\cdot}\text{SbCl}_6^-$ produced indan dimer 2 in dried solvents and gave a butadiene derivative 7 and a tetrahydrofuran derivative 8 in wet solvents whereas the dimerization of the derivatives of 1 afforded cyclobutane type dimers and butadiene type dimers.

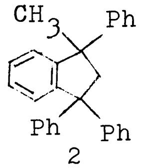
Although the cationic dimerization of 1,1-diphenylethylene(1) has been extensively studied as a model reaction for the polymerization of vinyl monomers, the dimerization of 1 by way of its cation radical has not been well understood. And the cation radical dimerizations of derivatives of 1 are not known. Dimerization of 1 using protic or Lewis acids almost always affords indan type dimer 2 1) whereas the products of cation radical dimerization of 1 varied with the methods for the generation of the cation radical of 1. 2-7)

We, therefore, reinvesitgated the dimerization of 1 using a new method for the generation of the cation radical of 1 by tris(*p*-bromophenyl)aminium hexachloroantimonate, $(p\text{-BrC}_6\text{H}_4)_3\text{N}^{+\cdot}\text{SbCl}_6^-$ (3). 8) We also studied first time the dimerizations of derivatives of 1, namely 1,1-diphenylpropene(4), 1,1-diphenyl-3-methyl-1-butene, 1,1,2-triphenylethylene(5), and 1,1-di-*p*-anisylethylene(6). In the present work, 1(1.82 g, 10 mmol) was dimerized by addition of catalytic amount of 3(0.41 g, 0.5 mmol) in rigorously dried CH_2Cl_2 or CH_3CN(25 ml) under nitrogen atmosphere at room temperature to afford indan 2 in 85% yield.

In the presence of a small amount of water, however, compounds 7 and 8 were produced in 37:63 ratio in 60% yield. The reaction in the presence of water required one equivalent of 3 for the completion. Product 2 obtained in the present work is same as that of the cationic dimerization of 1. We, therefore, examined the possibility of the involvement of the protic acid which might be produced from the initial reaction of 1 and 3. When 1 was treated with 3 in the presence of 2,6-di-*t*-butylpyridine 9) in dried CH_2Cl_2, no reaction occured and 3 decomposed in the prolonged reaction time. In the presence of a small amount of water, however, 2,6-di-*t*-butylpyridine did not affect the dimerization of 1 and compounds 7 and 8 were produced again. Other hexachloroantimonate salts such as benzyltriethylammonium, tetraethylammonium, and triphenylmethyl salts did not initiate the dimerization of 1.



1 $R^1=R^2=H$
4 $R^1=H$, $R^2=CH_3$
5 $R^1=H$, $R^2=Ph$
6 $R^1=$*p*-OCH_3,$R^2=H$



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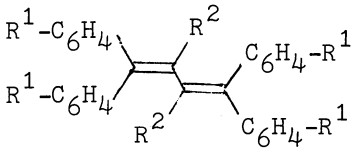
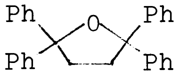


7 $R^1=R^2=H$
9 $R^1=H$, $R^2=CH_3$
11 $R^1=H$, $R^2=Ph$
13 $R^1=$*p*-OCH_3,$R^2=H$



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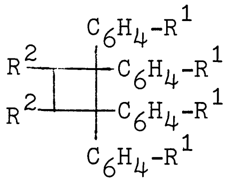

10 $R^1=H$, $R^2=Ph$
12 $R^1=$*p*-OCH_3, $R^2=H$

Compound **4** was not dimerized by **3** in dried solvents but it was transformed into a butadiene type dimer **9**[10] in 85% yield in the presence of water. 1,1-Diphenyl-3-methyl-1-butene, on the other hand, was not dimerized at all either in dried solvents or in wet solvents. Unlike **1** and **4**, the dimerizations of **5** and **6** by **3** gave rise to different type of products such as cyclobutane type dimers. Thus the reaction of **5** with **3** afforded compounds **10** and **11** in 9:1 ratio and compound **6** was dimerized to **12** and **13** in 4:1 ratio in 75% yield. Water or 2,6-di-*t*-butylpyridine did not affect the dimerization of both **5** and **6**.

Indan type product **2** might be resulted from cationic dimerization by of **1** protic acid or Lewis acid generated in the initial steps, while the products **7** and **8** must be produced by the way of the cation radical of **1**. Although it is apparent that the substituents on 1,1-dipnenylethylene and the methods for the generation of the cation radical are critical for the types of the dimers produced in this reaction, the exact reason for the variant products is unclear as yet.

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9) Pyridine, 2,6-lutidine, triethylamine, or solid sodium bicarbonate readily destroyed compound **3**.
10) All new compounds gave satisfactory microanalytical and spectral data.

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