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REACTION OF DIPHENYLKETENE WITH OCTACARBONYL DICOBALT UNDER HIGH PRESSURE OF CARBON MONOXIDE —— DEOXYGENATION OF DIPHENYLKETENE

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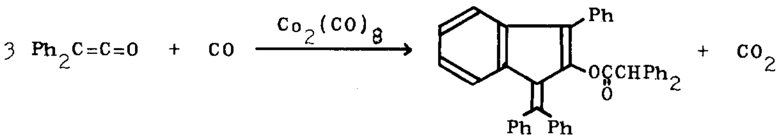
We previously reported[1] that diphenylketene was decarbonylated to give tetraphenylethylene in a high yield when a solution of diphenylketene in aromatic solvents was refluxed in the presence of a catalytic amount of octacarbonyl dicobalt under nitrogen. The formation of tetraphenylethylene could be interpreted through the intermediacy of a diphenylcarbene complex. We now wish to report a novel $Co_2(CO)_8$ catalyzed deoxygenation of diphenylketene under high pressure of carbon monoxide.

Diphenylketene (6.6 g, 34 mmol) and $Co_2(CO)_8$ (1 g, 3 mmol) were placed in an autoclave of 100 ml capacity with 35 ml of toluene and carbon monoxide (45 Kg/cm^2) was charged in. The autoclave was shaken at 120-125°C for 40 hr. After cooling, the gases were discharged and the content was taken out. After removal of the solvent, the residue was chromatographed on alumina. As the main product, orange prisms (1, mp. 160-162°C, after recrystallization from EtOH-benzene) were obtained in a 60 % yield from the elution with n-hexane-benzene (1:4).

Based on the elementary analysis, the molecular weight measurement, and the mass spectrum, 1 was found the molecular formula $C_{42}H_{30}O_2$, in which an oxygen atom was lost from three molecules of diphenylketene. The infrared spectrum of 1 showed very strong absorptions at 1756 and 1122 cm^{-1}, assigned to an ester group. The NMR spectrum indicated a singlet at τ 6.34 due to a methin proton and a high-field aromatic doublet at τ 3.69 and a complex absorption at τ 2.6-3.45 due to twenty nine aromatic protons. The UV spectrum of 1 in dioxane was similar to that of 1-(diphenylmethylene)-3-phenylindene (2).

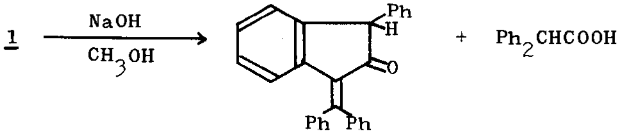
From these evidences it was concluded that 1 was 1-(diphenylmethylene)-2-(diphenylacetoxy)-3-phenylindene.



(1)

1

This structure was further confirmed by the following chemical evidences. Reduction of 1 with $LiAlH_4$ gave 2,2-diphenylethanol in a 74 % yield. Alkaline hydrolysis of 1 afforded diphenylacetic acid, 1-(diphenylmethylene)-3-phenyl-2-indanone (3), and a unknown ketone ($C_{28}H_{20}O$) in 95, 52, and 18 % yields, respectively. Reduction of 3 using $LiAlH_4$ afforded 1-(diphenylmethylene)-3-phenyl-2-indanol (4) in a 65 % yield. 4 was heated at 230-240°C/5 mmHg for 4 hr to give a known compound (2) in a 14 % yield. The structures of 3 and 4 followed their elementary analysis (Table 1) and their spectral data (Table 2).



(2)

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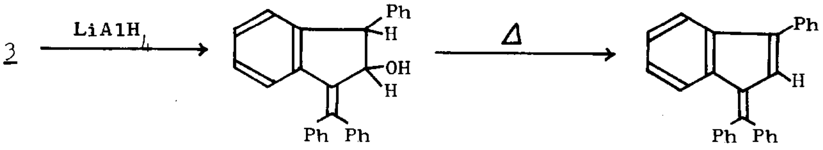


(3)

4 2

A few example of the deoxygenation of diphenylketene have been previously reported. The pyrolysis of an 1:1 adduct of diphenylketene and triethyl phosphite leads[2] to the formation of diphenylacetylene, the deoxygenated product, and triethyl phosphate. A solution of diphenylketene and pentacarbonyl iron in benzene is irradiated[3] to give a diphenylvinylidene coordinated complex, $(Ph_2C=C)Fe_2(CO)_8$, (5), in a small yield.

Table 1. The elementary analysis of 1, 3, and 4

	color	Mp.	Found (Calcd) C %	H %	Mw*
1	orange	160-162°C	89.11(89.02)	5.15(5.34)	566(566)
3	orange	148-151°C	90.19(90.29)	5.44(5.41)	372(372)
4	pale yellow	180-182°C	90.09(89.80)	5.92(5.92)	

* From mass spectra.

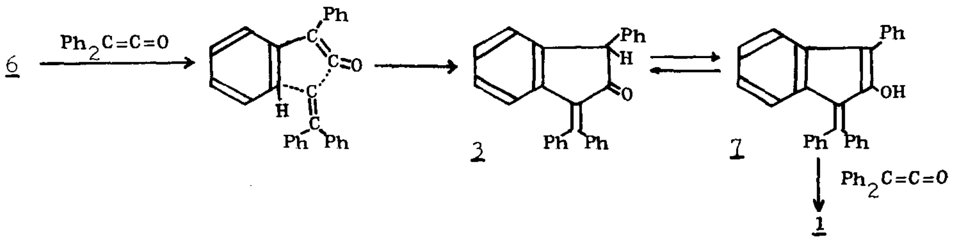
Table 2. The spectral data of 1—4

	I R*1 cm^{-1}	N M R*2 τ	U V*3 λ max $m\mu(\varepsilon \times 10^{-4})$
1	1756(νC=O) 1122(νC-O)	6.34(s), 3.68(d) 2.6-3.45(m)	252(2.66), 300(1.28), 360(1.57)
2			251(2.74), 300(1.28), 351(1.62)
3	1705(νC=O) 1540(νC=C)	5.39(s), 2.5-3.6(m)	218(3.43), 247(1.81), 349(1.18)
4	3525(νOH)	8.42(s), 5.45(d) 5.22(d), 2.4-3.6(m)	

*1 KBr pellet *2 60 Mc., in $CDCl_3$ *3 in dioxane

In our case, also a diphenylvinylidene complex could be thought as a intermediate for the formation of 1. Thus, a diphenylvinylidene complex (6) generated by the reaction of diphenylketene with $Co_2(CO)_8$ undergoes 1,4-addition of another molecule of diphenylketene to form 3. 3 tautomerizes to the enol form (7) and 7 further reacts with diphenylketene to produce the diphenylacetate (1).

$$Ph_2C{=}C{=}O \quad + \quad Co_2(CO)_8 \longrightarrow \underset{6}{(Ph_2C{=}C)Co_n(CO)_m} \quad + \quad CO_2 \qquad (4)$$



(5)

It is of very interest that diphenylketene in the presence of a catalytic ammount of $Co_2(CO)_8$ under high pressure of carbon monoxide was deoxygenated to give diphenylvinylidene in comparison with the formation of diphenylcarbene under nitrogen atmosphere. The mechanism of the deoxygenation of the ketene with $Co_2(CO)_8$ would be interpreted to be similar to that of isocyanate, which was deoxygenated[4] by the metal carbonyls such as $Fe(CO)_5$, $Cr(CO)_6$, and $Mo(CO)_6$ to form carbon dioxide and a isocyanide complex which further reacted with isocyanate to give carbodiimide. In our case, carbon dioxide was detected by bubbling the discharged gases from the autoclave through a solution of barium hydroxide.

Further work on the elucidation of the mechanism involved in this reaction is continuing.

Reperence

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