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REACTIONS OF DIPHENYLCYCLOPROPENONE WITH KETENES IN THE PRESENCE OF NICKEL TETRACARBONYL

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Summary

Reactions of diphenylcyclopropenone with ketenes in the presence of catalytic amounts of nickel tetracarbonyl have been studied. In these reactions, 1 : 1 cycloadducts, cyclopentene-1,2-dione derivatives, were obtained in yields above 80%. The cycloaddition reactions were significantly affected by solvents, and DMF was the most suitable solvent. Iron pentacarbonyl did not act as a catalyst. Reaction mechanisms are discussed.

Introduction

Because of their aromaticity, the stability and reactivity of cyclopropenones are different from those of other three-membered ring compounds.

For cycloaddition reactions with diphenylcyclopropenone, many reactions across the carbon—carbon double bond have been reported [1,2,3], but reports of reaction at the carbon—carbon single bond are rare [4]. The results of studies of cycloaddition reactions of diphenylcyclopropenone with ketenes in the presence of catalytic amounts of nickel tetracarbonyl are reported in this paper. We find that diphenylcyclopropenone undergoes cycloaddition reactions via cleavage of the carbon—carbon single bond with ketenes to give the cyclopentene-1,2-diones (IVa,b) and cyclopentene-1,3-dione (Va).

Diphenylcyclopropenone reacts with diphenylketene at 160°C without a catalyst to produce 2,3,4-triphenyl-1-naphthyldiphenylacetate, but this product arises from the reaction with diphenylacetylene, formed by decarbonylation of diphenylcyclopropenone [5].

Its reaction with nickel tetracarbonyl is thought to give the nickelacyclobutenone complex [6], and the same complex is assumed as a product of the reaction of diphenylacetylene with nickel tetracarbonyl [7]. It is reported that

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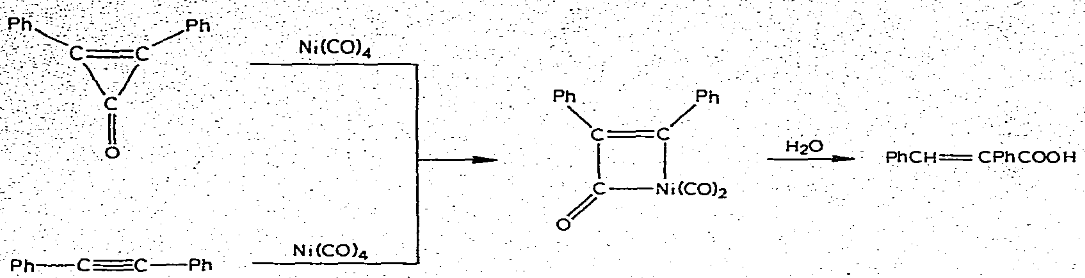
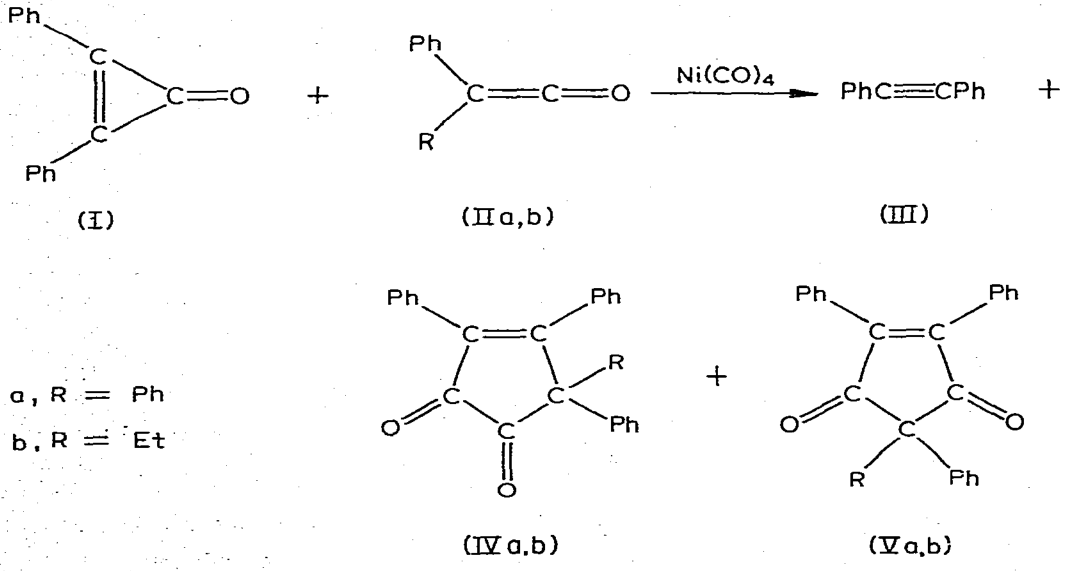


diphenylcyclopropenone reacts with iron carbonyls ($Fe_2(CO)_9$ or $Fe_3(CO)_{12}$) to form stable metal complexes and diphenylacetylene [8].

Results and discussion

In the presence of nickel tetracarbonyl, the reactions of diphenylcyclopropenone with ketenes (IIa,b) at 55—60° C in DMF (*N,N*-dimethylformamide) gave diphenylacetylene (III), the cyclopentene-1,2-diones (IVa,b) and cyclopentene-1,3-dione (Va) (Scheme 1).

SCHEME 1



The identification of the 1,2-dione IVa and the 1,3-dione Va was carried out by ^{13}C NMR spectroscopy. The spectra of these products are shown in Fig. 1. The structure of 3,4,5,5-tetraphenyl-4-cyclopentene-1,2-dione (Va) is symmetric and the spectrum shows its one carbonyl carbon signal and one olefinic carbon signal at 201 and 152 ppm, respectively. The spectrum of 2,3,5,5-tetraphenyl-2-cyclopentene-1,3-dione (IVa) shows two carbonyl carbon signals and two olefinic carbon signals at 239, 169, 150 and 145 ppm, respectively. The 1,2-dione IVa was identified by comparison with an authentic sample [9]. Other data of the products are shown in the experimental section.

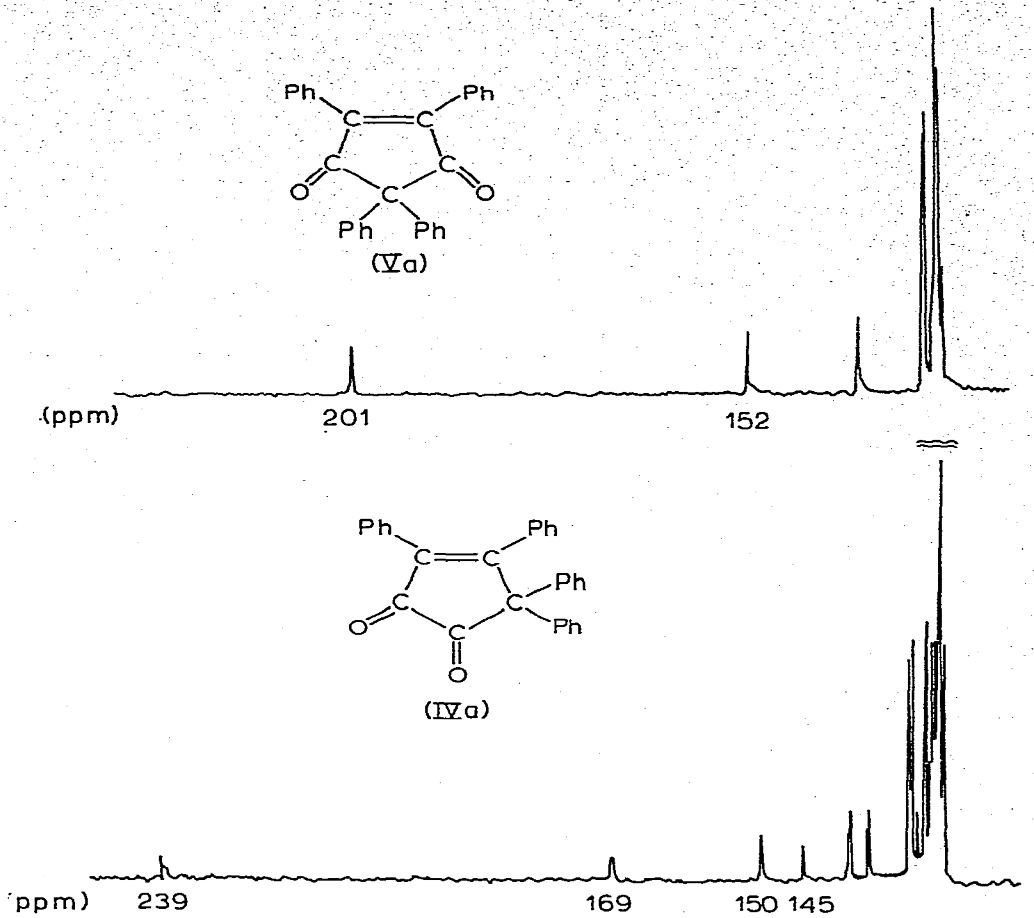


Fig. 1. ^{13}C NMR spectra of the cyclopentene-1,2-dione IVa and the cyclopentene-1,3-dione Va. TMS used as internal standard.

Diphenylacetylene was produced by decarbonylation of diphenylcyclopropenone with nickel tetracarbonyl. This was confirmed in the reaction of diphenylcyclopropenone with nickel tetracarbonyl in anhydrous DMF; diphenylacetylene was isolated in 28% yield. The results of the reactions are summarized in Table 1.

It is clear that this reaction proceeded smoothly with catalytic amounts of nickel tetracarbonyl. Previously, we reported that the same products were obtained in the reaction of diphenylketene with diphenylacetylene in the presence of iron pentacarbonyl, but in this case an equimolar amount of iron pentacarbonyl was necessary and the yield and selectivity were lower [9].

The effect of solvents was significant. DMF was the most appropriate solvent and the 1,2-dione was produced selectively in yields above 80%. The yield and the selectivity of the products were lower in THF (tetrahydrofuran), and the 1,2-dione IVa and the 1,3-dione Va were scarcely produced in benzene. The yield of the 1,2-dione IVa was lower in HMPA (hexamethylphosphoric triamide) which is a strong donor solvent.

TABLE 1

THE REACTIONS OF DIPHENYLCYCLOPROPENONE WITH KETENES (PhRC=C=O)

R	Catalyst (molar ratio)	Solvent	Temp. (°C)	Time (h)	Yield (%)		
					III	IV	V
Ph	$Ni(CO)_4$ (1.0)	DMF	55—60	3	4.8	85.9	[b]
Ph	$Ni(CO)_4$ (0.5)	DMF	55—60	3	4.8	84.5	[b]
Ph	$Ni(CO)_4$ (0.3)	DMF	55—60	3.5	9.2	83.4	[a]
Ph	$Ni(CO)_4$ (0.1)	DMF	55—60	4	9.1	78.8	[a]
Ph	$Ni(CO)_4$ (1.0)	C_6H_6	65—70	5	14.7	7.8	3.1
Ph	$Ni(CO)_4$ (0.1)	C_6H_6	65—70	6	56.0	3.7	[a]
Ph	$Ni(CO)_4$ (1.0)	THF	55—60	4	24.1	11.0	8.5
Ph	$Ni(CO)_4$ (0.3)	HMPA	55—60	3.5	9.4	29.1	[a]
Et	$Ni(CO)_4$ (0.3)	DMF	55—60	3.5	5.8	85.3	[b]
Ph [c]	$Fe(CO)_5$ (0.5)	DMF	80	5	9.4	[a]	[a]
Ph [d]	$Ni(CO)_4$ (0.3)	DMF	r.t.	120	[b]	17.5	[a]

[a] Not detected. [b] Trace amount. [c] Cyclopropenone was recovered in 88% yield. [d] This reaction carried out in a sealed tube.

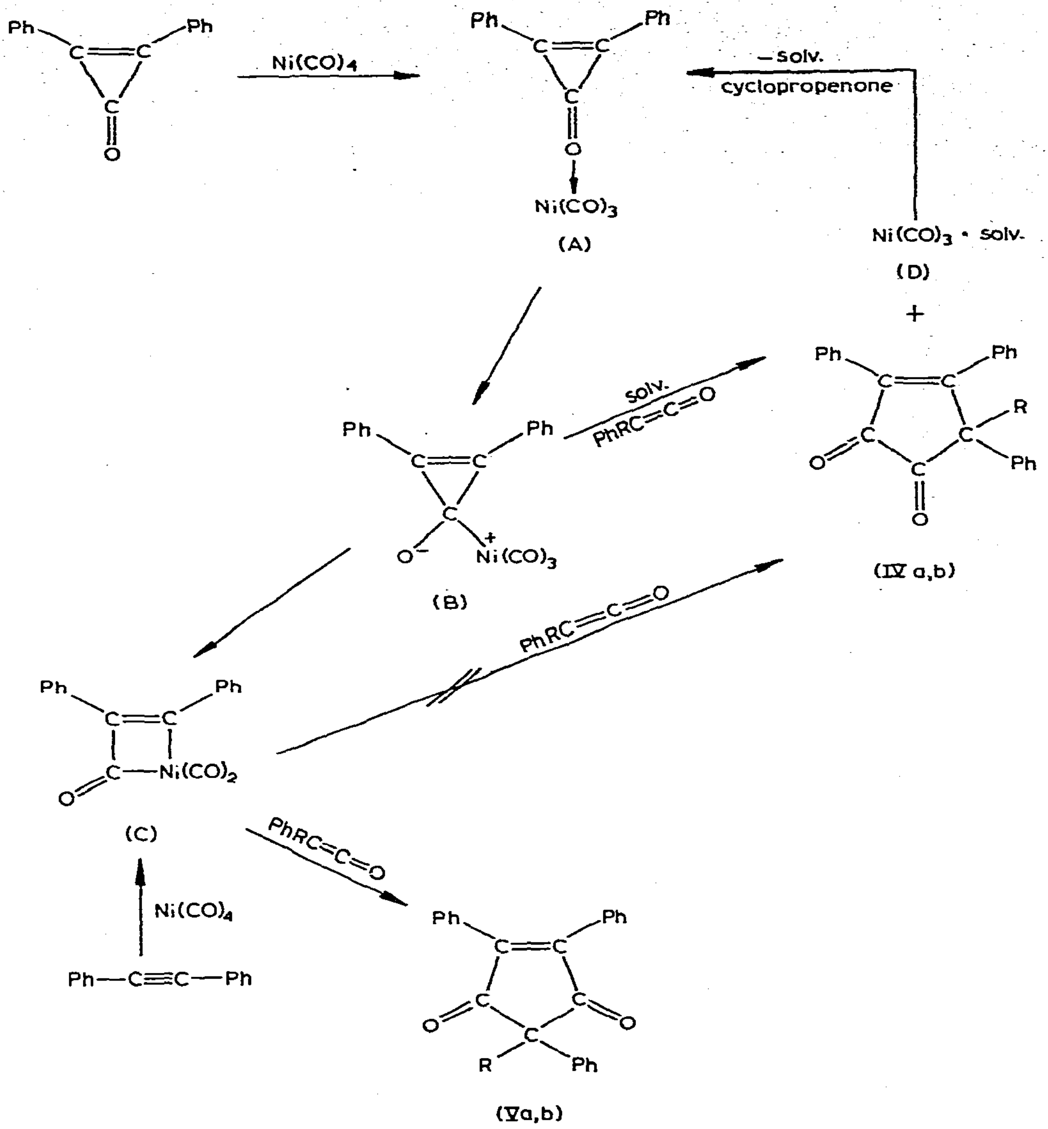
This reaction proceeded even at room temperature, but the rate was slow. Iron pentacarbonyl did not act as a catalyst, and thus diphenylcyclopropenone was recovered quantitatively. A possible mechanism is shown in Scheme 2.

Previously, we reported that the reaction of diphenylacetylene with diphenylketene in the presence of an equimolar amount of nickel tetracarbonyl gave only the 1,3-dione in 12% yield without the formation of the 1,2-dione [9]. In this report, the 1,3-dione Va was believed to be produced via the nickelacyclobutenone complex C. If the reactions of diphenylcyclopropenone proceeded via the nickelacyclobutenone complex, an equimolar amount of nickel tetracarbonyl would be necessary and the cyclopentene-1,3-diones Va,b would be obtained as main products. Bird and coworkers reported that a cyclopropenone was liable to coordinate to metal via oxygen [10].

From these facts, we assume that the reaction proceeds as follows. The oxygen coordinated complex A was formed first, and then it was converted to the intermediate B. One molar equivalent of the ketene reacted with intermediate B to produce the cyclopentene-1,2-diones (IVa,b). On the other hand, complex B changed to the nickelacyclobutenone complex C and the ketene reacted with it to produce the cyclopentene-1,3-diones (Va,b).

The complex B was considered to be stabilized by a polar solvent and DMF was the most effective solvent in this reaction. The 1,2-dione was formed as the major product in a smooth reaction with the ketene. The formation of IV was not selective in THF. In HMPA, however, the yield of 1,2-dione was low, although HMPA was thought to stabilize complex B. To explain the solvent effect, the complex D, $Ni(CO)_3 \cdot$ solv., would have to be considered as an active species from the fact that the reaction using DMF proceeded smoothly with a catalytic amount of nickel tetracarbonyl. A similar species was assumed by Koch and coworkers [11]. The coordinating ability of HMPA was too strong to reform complex B from the active species D with diphenylcyclopropenone. The solvent must have a suitable coordinating property to become effective. DMF was the most

SCHEME 2



suitable solvent. The reaction did not proceed in a non-coordinating solvent (benzene).

Experimental

All melting points were determined on Yanagimoto micro melting point apparatus and are uncorrected.

Infrared spectra were recorded on Nujol mulls of solids with a JASCO IR-E spectrometer. Proton magnetic resonance spectra were taken with a JEOL LNM-3H-60 spectrometer with TMS as the internal standard. Mass spectra were taken with a Hitachi RMU-6E. ^{13}C NMR spectra were taken on a JEOL FT-100 spectrometer with TMS as the internal standard.

All reactions were carried out under a nitrogen atmosphere in a four-necked flask equipped with a magnetic stirrer and a reflux condenser.

Reactions and post-treatments were carried out in a closed system, residual nickel carbonyl was decomposed by addition of iodine, and all glassware was washed with iodine/acetone solutions.

Chromatographic separations were carried out using silica gel columns.

Materials

Nickel tetracarbonyl [12], diphenylketene, ethylphenylketene [13], and diphenylacetylene [14] were prepared by reported methods. Commercial iron pentacarbonyl was used without further purification. Diphenylcyclopropenone was prepared from dibenzylketone [15].

DMF and HMPA were dried over calcium hydride. THF and benzene were dried by refluxing over sodium wire.

Reactions of diphenylcyclopropenone with ketenes

(a) Reaction with diphenylketene in the presence of nickel tetracarbonyl. A mixture of diphenylcyclopropenone (8 mmol) and nickel tetracarbonyl (2.4 mmol) in 30 ml of DMF was stirred for 30 min at room temperature. Diphenylketene (8 mmol) was added to the mixture, and then this mixture was heated at 55—60°C for 3.5 h with stirring. Subsequently, 100 ml of 15% HCl was added and the mixture was extracted with 150 ml of ether. The organic layer was dried over Mg_2SO_4, concentrated in vacuo, and the residue was recrystallized from benzene/hexane to give 2.0 g of 3,4,5,5-tetraphenyl-3-cyclopentene-1,2-dione (IVa): green-yellow needles; m.p. 230—232°C (lit. [9] 231—232°C); IR: 1755 cm^{-1} $\nu(C{=}O)$; mass spectrum m/e 400 $[M^+]$, 372 $[M - CO]^+$, 344 $[M - 2CO]^+$, 194 $[Ph_2C{-}C{=}O]^+$ and 178 $[PhC{\equiv}CPh]^+$; NMR ($CDCl_3$) δ 6.8—7.3 ppm (all aromatic protons). (Found: C, 87.19; H, 4.79. $C_{29}H_{20}O_2$ calcd.: C, 86.97; H, 5.03%.)

The filtrate was chromatographed and eluted with hexane (fraction 1) and hexane/benzene (fractions 2 and 3). From the first fraction, 0.13 g of diphenylacetylene (III) was obtained and recrystallized (hexane/benzene): white needles; m.p. 60—61°C (lit. [14] 60—61°C). No depression of the melting point was observed for the mixture with an authentic sample. From the second fraction, a trace amount of 2,3,5,5-tetraphenyl-2-cyclopentene-1,3-dione (Va) was obtained: yellow needles; m.p. 198—200°C (lit. [9] 196.5—197.5°C); IR: 1730 and 1700 cm^{-1} $\nu(C{=}O)$; mass spectrum m/e 400 $[M^+]$, 372, 344, 194 and 178. (Found: C, 86.81; H, 4.90. $C_{29}H_{20}O_2$ calcd.: C, 86.97; H, 5.03%.) From the third fraction, 0.7 g of the 1,2-dione IVa was obtained (total yield 83.4%).

Other reactions of diphenylcyclopropenone with diphenylacetylene in the presence of nickel tetracarbonyl were carried out in the same manner as above. The results of the reactions are summarized in Table 1.

(b) The reaction with ethylphenylketene in the presence of nickel tetracarbonyl. Ethylphenylketene (9.7 mmol), diphenylcyclopropenone (9.7 mmol) and nickel tetracarbonyl (2.9 mmol) were heated in 35 ml of DMF at 55—60°C for 3.5 h with work-up carried out in a manner similar to that described above. Diphenyl-

acetylene (0.1 g) (III) was obtained (5.8% yield). 5-Ethyl-3,4,5-triphenyl-3-cyclopentene-1,2-dione (IVb) was obtained (2.9 g, 85.3% yield) and recrystallized (benzene/hexane): green-yellow needles; m.p. 196—198°C; IR: 1750 cm^{-1} $\nu(C{=}O)$; mass spectrum *m/e* 352 $[M^+]$, 347 $[M - CH_3]^+$, 324 $[M - CO]^+$, 323 $[M - Et]^+$, 234 $[PhC{-}CPhCOCO]^+$, 206 and 178 $[PhC{=}CPh]^+$; NMR ($CDCl_3$) δ 0.68 ppm (3H, t, $-CH_3$), 2.15 (2H, q, $-CH_2-$), 7.1—7.48 (15H, m, aromatic protons). (Found: C, 85.12; H, 5.95. $C_{25}H_{20}O_2$ calcd.: C, 85.20; H, 5.72%.)

Pure 5-ethyl-2,3,5-triphenyl-2-cyclopentene-1,3-dione (Vb) was not isolated because of its very low yield, but it was identified by means of its IR spectrum (1730 and 1700 cm^{-1} $\nu(C{=}O)$).

(c) The reaction with diphenylketene in the presence of iron pentacarbonyl. Diphenylcyclopropenone (6 mmol), diphenylketene (6 mmol) and iron pentacarbonyl (3 mmol) were allowed to react in 25 ml of DMF at 80°C for 5 h. 30 ml of 15% HCl was added and the mixture was extracted with 200 ml of ether, concentrated and chromatographed. Diphenylacetylene was obtained (0.1 g, 9.4% yield). Diphenylketene was converted to diphenylacetic acid by adding water (1.1 g, 86% yield). Diphenylcyclopropenone was recovered (eluted with ethanol, 1.1.g, 88% yield).

Reaction of diphenylcyclopropenone with nickel tetracarbonyl

Diphenylcyclopropenone (4 mmol) was heated with 2 mmol of nickel tetracarbonyl in 15 ml of anhydrous DMF for 5 h. The reaction mixture was extracted with 100 ml of ether and washed with 100 ml of water. The organic layer was concentrated and chromatographed. Diphenylacetylene was obtained (eluted with hexane, 0.2 g, 25.8% yield).

^{13}C NMR spectral data of the 1,2-dione IVa and the 1,3-dione Va

Va ($CDCl_3$); (TMS, internal standard) 200.762, 151.677, 138.026, 130.018, 128.562, 127.712 and 63.887 ppm.

IVa ($CDCl_3$): (TMS, internal standard) 239.597, 168.898, 149.858, 144.703, 138.757, 136.510, 131.477, 131.112, 130.384, 129.593, 128.807, 128.501, 127.895 and 127.229 ppm.

Acknowledgment

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