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Cyclopropenones. IV. The Reactions of Diphenylcyclopropenone with Water, Carboxylic Acid, Phenol, and Amide

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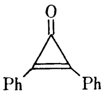
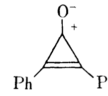
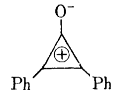
The pyrolysis of diphenylcyclopropenone monohydrate (II) at 150°C afforded α-phenyl-*trans*-cinnamic anhydride (VI). It was proved that the reaction consists of two main steps, the nucleophilic attack of water on I to yield α-phenyl-*trans*-cinnamic acid (IV), and the reaction of I with IV, thus finally yielding VI. The same type of reaction as that of I with IV was also observed when I was heated in phenol to afford phenyl α-phenyl-*trans*-cinnamate (XII). The reaction of I with the weak nucleophilic reagent, α-phenyl-*trans*-cinnamamide (XIV), afforded a monoimino derivative of VI (XVI), which is believed to be produced by the nucleophilic attack of the amide-oxygen of XIV on the carbonyl-carbon of I.

Since the first preparation of diphenylcyclopropenone (I) in 1959 by Breslow and his co-workers[1] and by Vol'pin and his co-workers,[2] independently, many reactions of I have been reported.[3] Because of the strongly polarized nature of the ketone,[4] to which the contribution of the IA and IB structures is considerable, the carbonyl carbon and the double bond of I cause a nucleophilic attack by various reagents. Although the reaction of I with a base such as aqueous sodium hydroxide,[4] hydroxylamine,[4] liquid ammonia,[5,6] aqueous ammonia,[7] primary amine,[6] aziridine,[8] and alkyllithium[9] has been reported, no reaction with acid has yet been done except the case in which I forms hydrobromide in crystalline forms.[2] The salt, however, can be decomposed by heating or by weak bases to give I again.[2]

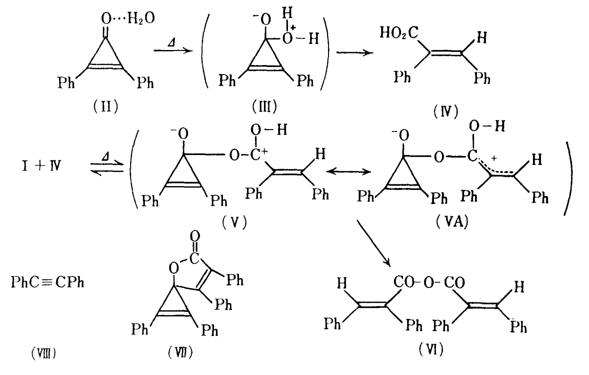

(I)


(IA)


(IB)

We have found that I reacted with such acids as α-phenyl-*trans*-cinnamic acid (IV) and phenol at 150°C to give α-phenyl-*trans*-cinnamic anhydride (VI) and phenyl α-phenyl-*trans*-cinnamate (XII) respectively. We have also found that I reacted with a weak nucleophilic reagent, α-phenyl-*trans*-cinnamamide, and *N*-methylacetamide to afford a monoimino derivative of VI (XVI) and *N*-methyl-α-phenyl-*trans*-cinnamamide (XVII) respectively.

The heating of the monohydrate (II)[10] at 150°C for 32 hr afforded the anhydride VI, the cyclic dimer VII, and tolan (VIII) in 12.6, 14.1, and 23.9% yields respectively. The structure of VI (mp 117—118.5°C) was determined by a comparison of its electronic, infrared, and NMR spectral data with those reported in the literature for the anhydride (mp 113—117°C).[11] The spectral data of VII were identical with those recorded for the cyclic dimer[4] obtained in 40%, together with VIII (20%), by the pyrolysis of I at 145—150°C for 36 hr, to this dimer the structure VII has been assigned[4] provisionally. Since the heating of an equimolar mixture of I and IV at 150°C for 3 hr and 10 hr afforded VI in 25.4 and 55.5% yields respectively, IV must be the intermediate of the pyrolysis of II. The formation of IV from II can be interpreted in terms of the ketonization of the III initially produced by the attack of water on the carbonyl-carbon of I. The reaction of I with IV, of the same fashion as that of I and water, would give V as an intermediate.



Scheme 1

The ketonization and the ring-openning of V afford VI (Scheme 1). The contribution of the cation-delocalized structure (VA) to V, and the reversibility of the process of the formation of V from I and IV, are considerable, judging from the following observations. The heating of an equimolar mixture of I and α-phenyl-*cis*-cinnamic acid (IX) at 150°C for 27 hr afforded VI and the *trans*-acid IV in 35.4 and 31.6% yields respectively, but no recovered IX or *cis*-isomer of VI was detected. Since it is known that[12] the *trans*-acid

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[1] R. Breslow, R. Haynie, and J. Mirra, *J. Amer. Chem. Soc.*, **81**, 247 (1959).

[2] M. E. Vol'pin, Yu. D. Koreshkov, and D. N. Kursanov, *Izv. Akad. Nauk USSR, Otd, Khim. Nauk.*, **3**, 560 (1959).

[3] For a recent review, see A. W. Krebs, *Angew. Chem. Int. Ed. Engl.*, **4**, 10 (1965).

[4] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).

[5] F. Toda, T. Mitote, and K. Akagi, *Chem. Commun.*, **1969**, 228.

[6] F. Toda, T. Mitote, and K. Akagi, This Bulletin, **42**, 1777 (1969).

[7] E. V. Dehmlow, *Ann. Chem.*, **729**, 64 (1969).

[8] E. V. Dehmlow, *Tetrahedron Lett.*, **1967**, 5177.

[9] J. Ciabattoni, P. J. Kocienski, and G. Melloni, *ibid.*, **1969**, 1883.

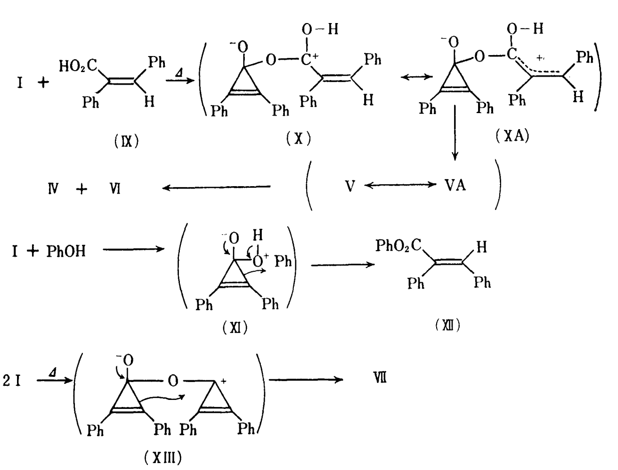
[10] F. Toda and K. Akagi, *ibid.*, **1968**, 3735.

[11] K. G. Krachanov and B. I. Kurtev. *ibid.*, **1965**, 3085.

[12] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Company, Boston (1957), p. 183.

IV is more stable than *cis*-acid IX because of the much greater steric interaction between the phenyl and carboxylic group in IX than that between the two phenyls in IV, and since the heating of IX at 150°C for 34 hr gave recovered IX in almost a quantitative yield, the isomerization of IX into IV probably occurs during the course of the reaction of I and IX.

The above complete isomerization of the geometry around the carbon-carbon double bond both in the product, VI, and in the acid, IV, can be reasonably interpreted by assuming a reversible process and the contribution of the cation-delocalized structure (VA or XA), as has been described above. The intermediate, X, initially produced by the reaction of I and IX can be rearranged to V *via* the cation-delocalized structure, XA, in which a rotation around the carbon-carbon bond of the diphenylethylene part is possible for its increased single-bond nature, as is shown in Scheme 2.

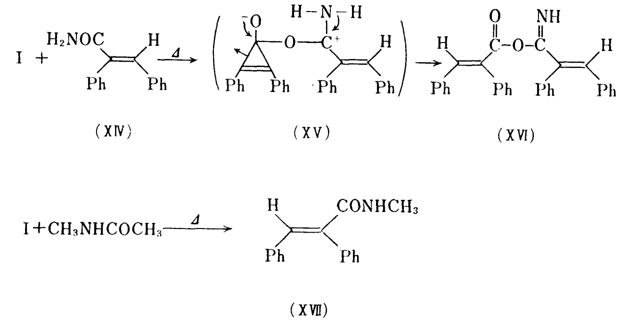


Scheme 2

The reaction of I with another carboxylic acid, such as *trans*-cinnamic acid or benzoic acid, gave no any acid anhydride. However, I reacted with phenol at 150°C for 26 hr to afford the ester XII in a 42% yield. The structure of XII was determined by a comparison of its spectral data with those of an authentic sample prepared according to the previously reported method.[13] The reaction probably proceeds *via* XI, which corresponds to V or X. Therefore, XIII is a possible intermediate of the thermal dimerization of I.

The observation that the oxygen of water, carboxylic acid (IV), and phenol react with I prompted us to investigate the reaction of I with several amides. Our attention was focussed on the question of which it was, the oxygen or the nitrogen of amide, which reacts with I. The heating of a mixture of I and an equimolar amount of the amide XIV at 150°C for 33 hr afforded XVI in a 4.2% yield, together with VIII (17.6%), recovered XIV (45%), and a small amount of an unidentified product, $C_{15}H_{13}ON$. The structure of XVI was determined by means of a study of the spectral data and by a base-catalyzed hydrolysis, which gave IV only. The electronic spectrum of XVI, 225 and 312 nm in ethanol, was comparable to that of VI, 223 and 300 nm in ethanol. The infrared spectrum of XVI in chloroform showed ν_{NH} $\nu_{C=O}$, and $\nu_{C=N}$ and/or $\nu_{C=C}$ at 3380, 1735, and 1615 cm^{-1} respectively, in addition to the strong ester absorption band at 1145 cm^{-1}. Since no absorption band of amide-II appeared in the 1600—1500 cm^{-1} region, and since the $\nu_{C=O}$ appeared at the field of frequencies higher than 1700 cm^{-1}, there is no possibility that XVI is amide or urea. The NMR spectral data, 1.88 (s, =CH, 1H), 2.10 (s, =CH, 1H), 2.86 (m, Ph, 20H), and 8.03 τ (s, =NH, 1H), which disappeared upon shaking with D_2O, also supported the structure of XVI.

The formation of XVI in the reaction of I with XIV shows that the reaction site of XIV is oxygen, not nitrogen, as is shown in Scheme 3. This result is reasonable, since the electron density on the oxygen of amide is higher than that of nitrogen because of the resonance, $-\overset{|}{N}-\overset{|}{C}=O \longleftrightarrow -\overset{|\,+}{N}=\overset{|}{C}-O^-$. This result is also consistent with the fact that the protonation of amide in a solution occurs on its oxygen.[14-16] The *N*-alkyl derivative of XIV, however, did not react with I.



Scheme 3

Nevertheless, the reaction of I with *N*-methylacetamide under the same conditions as those employed for the above reaction showed a widely different mode, and the reaction product was *N*-methyl-α-phenyl-*trans*-cinnamamide (XVII). The structure of XVII was determined by a comparison of its spectral data with those of an authentic sample prepared from IV by the method described in the Experimental section. The product XVII can be derived formally by the attack of the methylamino group produced by the fission of the amide-bond of *N*-methylacetamide on I, in the same fashion as that shown in Schemes 1—3.

Experimental

All the melting points are uncorrected. The electronic spectra were measured on a Hitachi spectrophotometer, model 124. The infrared spectra were recorded on a spectrophotometer, IR-E, of the Japan Spectroscopic Co. The NMR spectra were recorded in deuteriochloroform on a Japan Electron Optics Laboratory H-100 spectrometer, TMS being used as the internal standard.

Materials. Diphenylcyclopropenone (I) was prepared according to the reported procedure;[4] mp 119—120°C (lit,[4] mp 119—121°C). Diphenylcyclopropenone monohydrate (II)

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[13] R. A. Nicolaus, *Ann. Chim. Applicata*, **39**, 542 (1949).

[14] G. Fraenkel, A. Loewenstein, and S. Meiboom, *J. Phys. Chem.*, **65**, 700 (1961).

[15] R. L. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963).

[16] S. J. Kuhn and J. S. McIntyne, *ibid.*, **43**, 997 (1965).

was prepared according to the previously-reported method;[10] mp 87.5°C (lit,[10] mp 87.5°C). α-Phenyl-*trans*-cinnamic acid (IV) and α-phenyl-*cis*-cinnamic acid (IX) were prepared by the reported method.[12]

Pyrolysis of II. In an oil bath, II (2.2 g, 10 mmol) was heated at 150°C for 32 hr. After cooling, the crude product which had solidified was dissolved in ethanol (20 m*l*). An alcohol-insoluble crystalline solid was collected by filtration and recrystallized from ethanol to yield VI as colorless needles; yield, 0.27 g (12.6%); mp 117—118.5°C (lit,[11] mp 113—117°C). λ_{max}^{EtOH}: 223 (13400) and 300 nm (ε, 16000), IR (Nujol): 1715 and 1750 cm^{-1} (C=O), NMR: 2.23 (s, =CH, 2H) and 2.80 τ (m, Ph, 20H). The spectral data were identical with those reported for VI in the literature.[11]

The ethanol mother liquor remaining after the separation of VI was concentrated to dryness, and the residue was recrystallized from cyclohexane to afford VII; yield, 0.29 g (14.1%); mp 180—181°C (lit,[4] mp 181—182°C). The infrared and electronic spectra of VII thus obtained were identical with those of an authentic sample.[4] The evaporation of the solvent of the cyclohexane solution remaining after the removal of VII afforded tolan (yield, 0.45 g (23.9%)) after recrystallization from petroleum ether.

Reaction of I with IV. A mixture of I (0.5 g, 2.5 mmol) and IV (0.56 g, 2.5 mmol) was heated at 150°C for 3 hr. After cooling, the reaction mixture was recrystallized from ethanol to afford VI; yield, 0.28 g (25.4%). When the above mixture was heated at 150°C for 10 hr, 0.61 g (55.5%) of VI was isolated.

Reaction of I with IX. A mixture of I (0.7 g, 3.4 mmol) and IX (0.76 g, 3.4 mmol) was heated at 150°C for 27 hr. After cooling, the reaction mixture which had solidified was fractionated into the following two components by fractional recrystallization from ethanol: VI, 0.53 g (35.4%), and IV, 0.24 g (31.6%).

Reaction of I with Phenol. A mixture of I (2 g, 10 mmol) and phenol (2.8 g, 30 mmol) was heated at 150°C for 26 hr. After cooling, the crude product which had crystallized was recrystallized from cyclohexane to give XII; 1.68 % (42%); mp 138.5—139.5°C (lit,[13] mp 142—143°C). The infrared spectrum of the XII thus obtained in Nujol mull, 1725 (C=O), 1620 (C=C), and 1235, 1200, 1170, and 1155 cm^{-1} (ester), was identical with that of an authentic sample prepared according to the literature.[13]

Reaction of I with XIV. A mixture of I (3.0 g, 15 mmol) and XIV (3.36 g, 15 mmol) was heated at 150°C for 33 hr. After the mixture had cooled, cyclohexane (10 m*l*) was added. The crystals which separated out were collected by filtration and recrystallized from ethanol to afford XVI as colorless needles; 0.27 g (4.2%); mp 199—200°C. λ_{max}^{EtOH}: 225 (13000) and 312 nm (ε, 19500), IR ($CHCl_3$): 3380 (NH), 1736 (C=O), and 1145 cm^{-1} (ester), NMR: 1.88 (s, =CH, 1H), 2.10 (s, =CH, 1H), 2.86 (m, Ph, 20H), and 8.03 τ (s, =NH, 1H).

Found: C, 84.04; H, 5.34; N, 3.74%. Calcd for $C_{30}H_{23}O_2N$: C, 83.89; H, 5.40; N, 3.26%.

The heating of a solution of XVI in acetone-aqueous potassium hydroxide afforded IV.

The cyclohexane solution which remained after the removal of XVI was concentrated to dryness. Then the residue was chromatographed on alumina, using carbon tetrachloride as the solvent. From the fraction eluted with carbon tetrachloride, tolan (0.47 g (17.6%)) was obtained. From the fraction eluted with benzene, an unidentified product, $C_{15}H_{13}ON$, was isolated, 0.1 g; mp 161—163°C. From the fraction eluted with benzene - chloroform (1:1), XIV (1.51 g (45%)) was recovered.

Reaction of I with N-*Methylacetamide.* A mixture of I (1.5 g, 7.5 mmol) and *N*-methylacetamide (1.1 g, 15 mmol) was heated at 150°C for 40 hr. The crude product which solidified upon cooling was chromatographed on alumina, using carbon tetrachloride as the solvent. The fraction eluted with carbon tetrachloride was concentrated by distillation to afford tolan (0.38 g (28%)). From the fraction eluted with chloroform, XVII (0.14 g (7.9%)) was isolated, mp 166—167°C. λ_{max}^{EtOH}: 223 (8500) and 289 nm (ε, 12300), IR (Nujol): 1630 (C=O), 1610 (C=C), and 1540 cm^{-1} (amide-II), NMR: 2.68 (m, Ph, 10H), 3.13 (s, =CH, 1H), 4.06 (s, NH, 1H), and 7.23 τ (d, CH_3, 3H).

Found: C, 80.92; H, 6.30%. Calcd for $C_{16}H_{15}ON$: C, 80.98; H, 6.37%.

The spectral data of XVII were identical with those of an authentic sample (mp 165.5—167°C) prepared by the reaction of methylamine and α-phenyl-*trans*-cinnamoyl chloride derived from IV.

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