

from methanol and sublimed in an oil-pump vacuum; m. p. 168–169°. The mixture melting point with a sample of Dr. Fieser's⁸ 2,7-dimethoxyphenanthrene was at 168–169°.

2 - Hydroxy - 3 - acetoacetyl - 9,10 - dihydrophenanthrene.—A solution of 1.0 g. of 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene in 20 cc. of dry ethyl acetate was added to 0.4 g. of powdered sodium, and the mixture was refluxed for thirty minutes on the water-bath. It was then poured onto 15 g. of ice and a pellet of sodium hydroxide was added. The yellow precipitate, the sodium salt of the diketone, was filtered and dissolved in water. On acidification, 0.9 g. of crude diketone was obtained, which was recrystallized from 70% ethanol. The hot solutions were bright yellow, but the solid was nearly colorless; m. p. 131–132°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.28; H, 5.74.

9 - Methyl - 5,6 - dihydronaphtho[1,2 - g]chromone.¹⁷—Ring closure of the above diketone was brought about quantitatively by boiling it for ten to fifteen minutes in glacial acetic acid containing a few drops of concentrated hydrochloric acid. The chromone derivative was precipitated by diluting the reaction mixture with water. It is insoluble in alkali and crystallized from ethanol in white plates of m. p. 198°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.64; H, 5.77.

(17) The orientation, name and numbering of this compound was devised upon the nomenclature principles as given by Patterson, *THIS JOURNAL*, **50**, 3074 (1928). For the numbering of the chromone, the "parent" component, see Decennial Index of *Chemical Abstracts*, 3423, 1917–1926.

When refluxed with 2 *N* sodium hydroxide solution, the chromone derivative went gradually into solution in the course of three hours. From the reaction mixture was obtained 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene in a yield of 15% and 2-hydroxy-9,10-dihydrophenanthrene-3-carboxylic acid in a yield of 60%. The latter compound crystallized from benzene in colorless needles of m. p. 219–220°.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 74.98; H, 5.04. Found: C, 75.17; H, 5.14.

Methylation of the hydroxy acid with dimethyl sulfate gave 2-methoxy-9,10-dihydrophenanthrene-3-carboxylic acid methyl ester, which was identified by melting point and mixture melting point with the compound obtained from 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene (Table III).

Summary

In the Friedel–Crafts reaction and the Fries rearrangement with 2-hydroxy- and 2-acetoxy-9,10-dihydrophenanthrene, respectively, the aliphatic acyl group enters position 3 and position 7. Depending upon the experimental conditions, 2-hydroxy-3-acyl- or 2-hydroxy-7-acyl- and 2-hydroxy-3,7-diacyl-9,10-dihydrophenanthrene are formed in varying amounts.

A structural proof for each of the described acyl derivatives has been established.

UNIVERSITY, VIRGINIA

RECEIVED NOVEMBER 2, 1938

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Diphenylketene and Certain Dienes

BY LEE IRVIN SMITH, COURTLAND L. AGRE,¹ R. M. LEEKLEY AND W. W. PRICHARD^{1a}

The reactions between ketenes and unsaturated hydrocarbons have been studied rather extensively

(1) Abstracted from a thesis by Courtland LaVerne Agre, submitted to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October, 1937.

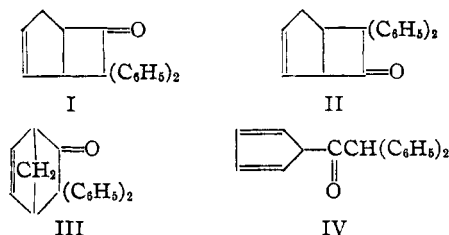
(1a) At the time this paper was submitted, our study of the reactions of the addition product derived from diphenylketene and cyclopentadiene indicated that the structure was best represented by formula II. While the manuscript was in the hands of the Editor, there appeared a paper by Lewis, Ramage, Simonsen and Wainwright [*J. Chem. Soc.*, 1837 (1937)] dealing with the same subject. From their work, the English authors were led to structure I for the adduct, and their conclusion appeared to be well founded inasmuch as they had confirmed, by independent synthesis, the structure of one of their principal degradation products. Accordingly, we have delayed publication of our paper until the completion of a further study. As one of us (C. L. A.) was no longer able to continue the work, this part of the study has been carried out with the aid of Messrs. Leekley and Prichard. Our supplementary study has led us to revise our original conclusion, and we now agree with the English authors that the structure of the adduct is undoubtedly I. Since our method of degrading the adduct differs widely from that used by the English authors, we are now publishing our work and withdrawing from further work in the field except for the investigation of the reaction between diphenylketene and certain acetylenes, such as phenylacetylene, the study of which we have had well under way for some time.—L. I. S.

by Staudinger and his collaborators² who found that many unsaturated hydrocarbons would react with ketenes—notably with diphenylketene—by direct addition, to give substances that were regarded as cyclobutanone derivatives. In the case of cyclopentadiene, a very rapid addition was observed^{2a} and Staudinger considered three structures (I, II, III) for the product, selecting I as best representing the structure of the compound.

However, four structures are possible for this substance (I, II, III, IV) and because of the strain inherent in such structures as I and II, it seemed more likely that the product would possess structure III or IV. Structure III is the result of a diene reaction between the two components, a reaction which has been shown to be

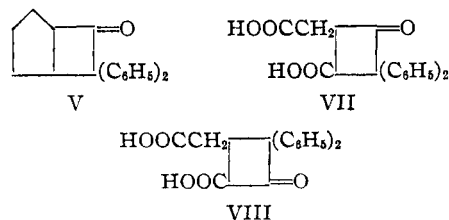
(2) (a) Staudinger and Suter, *Ber.*, **53**, 1092 (1920); (b) Staudinger and Rheimer, *Helv. Chim. Acta*, **7**, 8 (1924); (c) Staudinger and Meyer, *ibid.*, p. 19; (d) Staudinger and Meyer, *Ber.*, **53**, 72 (1920).

quite facile with a wide variety of dienes and unsaturated carbonyl compounds, while structure IV is the result of the addition of cyclopentadiene to the ketene as an active hydrogen compound.



The re-investigation of the structure of the addition product was important and desirable because from compounds of the type I or II, it should be possible to prepare rather complicated cyclobutanone derivatives by oxidation; moreover, bicycloheptene derivatives of this type offer interesting examples for the study of effects of strain in bridged rings. Substances of type III would in a similar way be useful for the preparation of unusual cyclopentane derivatives.

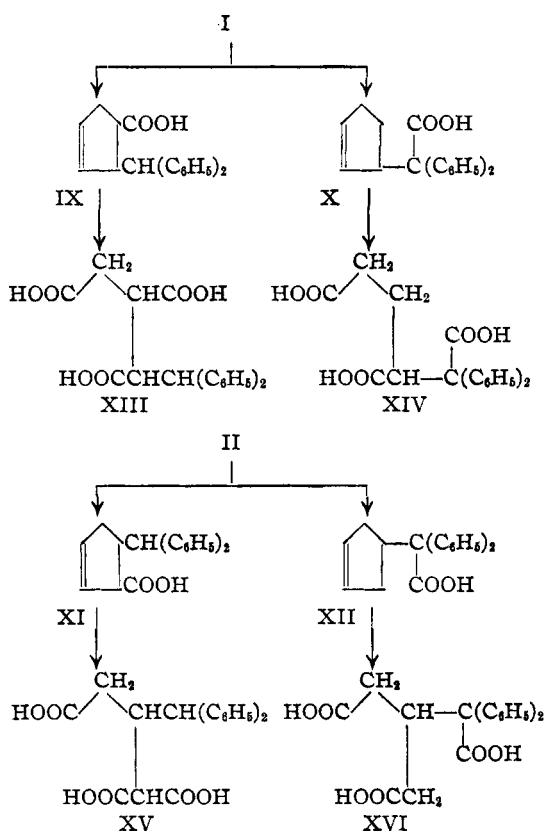
The reaction between diphenylketene and cyclopentadiene in petroleum ether solution was complete after twenty-four hours at room temperature, and the product, $C_{19}H_{16}O$, was formed in 92% yield. The substance did not react with phenylhydrazine, and was quite stable toward potassium permanganate in acetone. The substance reacted with solutions of bromine in chloroform, but only slowly. When the product (I) was reduced, there was formed a product (V) identical with that obtained by adding cyclopentene to diphenylketene. This fact definitely eliminated structure III for the product, and rendered structure IV highly improbable.



To decide between structures I and II, oxidation was first used. Oxidation of I should give the dibasic acid VII, while oxidation of II should produce the acid VIII. Oxidation of the compound by permanganate in acetone was very slow and it was not possible to isolate any pure material from the product. Ozonolysis followed by oxidation with chromic acid gave an impure product

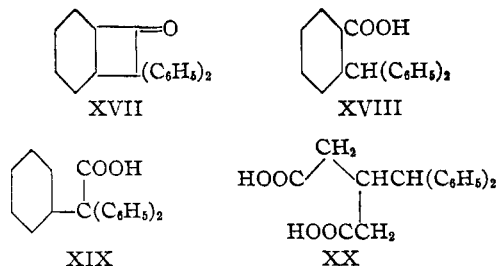
melting at 77–85°, which evolved a gas at about 110° and then solidified; this solid then remelted at about 200°. Attempts to purify these oxidation products were unsuccessful and no pure product could be obtained.

More definite results were obtained by cleavage of the addition product by alkali, followed by oxidation of the cleavage product. Structures I and II, when cleaved by alkali, could each react in two ways, leading to four cyclopentene acids (IX, X, XI, XII). Each of the cyclopentene acids, when oxidized would give a tribasic open chained acid (XIII, XIV, XV, XVI). These relationships are shown in the diagram.



Since none of the cleavage or oxidation products were known in the cyclopentene series, a model experiment was first conducted upon the addition product derived from cyclohexene and diphenyl ketene (XVII). This substance, when cleaved by alkali, gave an acid which could have been either XVIII or XIX. The acid obtained in this manner melted at 151–153°, therefore corresponded to structure XVIII, since acid XIX, previously synthesized by Ziegler,³ melted at 201–202°.

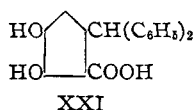
(3) Ziegler, *Ann.*, **437**, 251 (1924).



Assuming that the cleavage of I or II would occur in the same manner as that of XVII, the cleavage product would possess structure IX or XI, and oxidation of the cleavage product should then give an acid XIII or XV. Of these two tribasic acids, XV is a malonic acid derivative and should lose carbon dioxide when heated, leading to a dibasic acid (XX).

When the addition product (I or II) was refluxed with alcoholic potassium hydroxide for three hours, there was obtained a good yield of an acid, melting at 145–147°, which had the composition corresponding to IX or XI. Staudinger^{2b} had reported the melting point of this product, which he regarded as X, to be 125°, and since he had used sodium hydroxide for the cleavage, the addition product was also cleaved using sodium hydroxide. The result was the same—whether sodium or potassium hydroxide was used, the product was a single substance, an acid melting at 145–147°. The formation in this manner of a cleavage product which still contained all of the carbon atoms in the addition product showed that the cleavage had opened a ring and definitely eliminated structure IV for the addition product. It is to be noted that of acids IX, X, XI and XII, only XI is a β,γ -unsaturated acid and so likely to isomerize in the presence of alkali to an α,β -unsaturated acid. The fact that the oxidation product of acid IX or XI was a tribasic acid XIII or (XV) and not a keto dibasic acid, showed that the double bond had not migrated to the α,β -position under the influence of the alkali.

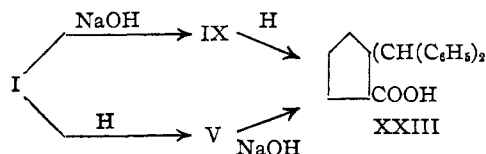
Oxidation of the cleavage product IX or (XI) by alkaline permanganate gave a monobasic acid melting at 201.5°, which was presumably the glycol, XXI, from IX.^{3a} The yield of the glycol



was very poor and most of the product was an oil from which no pure substances were obtained. When the cleavage product was ozonized in acetic acid and the ozonide (without isolation) was oxidized by chromic acid, there resulted a solid tribasic acid XIII or (XV) having the proper composition and neutral equivalent. This acid melted at 208–209.5° with decomposition.

Lewis, *et al.*,^{3a} synthesized the acid XIII, and obtained it in two stereoisomeric forms: the α -acid, m. p. 187–188° (dec.), (methyl ester, m. p. 117–119°), and the β -acid, m. p. 208–209° (dec.), (methyl ester, m. p. 121–122.5°). The data indicated strongly that our acid was identical with the β -form of XIII, but the synthesis of the English authors could not be duplicated and we therefore turned to the synthesis of acid XV, which was based upon the procedure of Newman and Joshel⁴ who had in the meanwhile synthesized acid XX. But the condensation between diphenylacetaldehyde and ethyl malonate was unsuccessful. Hence, while definite proof is lacking, the weight of evidence indicates that our acid is the β form of XIII since the methyl ester melts at 116–117°.

These relationships among the degradation products show that when cyclopentadiene and diphenylketene react, the product is a cyclobutanone derivative formed by 1,2-addition and that the structure of this product is best represented by I. A further check on certain of these relationships among the degradation products was shown by the sequence



that is, the same product was obtained whether cleavage preceded or followed reduction.⁵

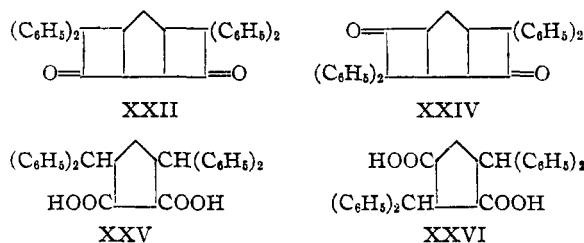
Staudinger and Suter^{2a} state that only one double bond of cyclopentadiene added diphenylketene, but it was found that the addition product I, when heated with diphenylketene at 110° for nine days, gave a crystalline product melting at 250°, which was formed by the addition of two molecules of diphenylketene to one of the diene. That the second molecule of the ketene added in the same manner as the first was shown

(4) Newman and Joshel, *THIS JOURNAL*, **60**, 486 (1938).

(5) Lewis, *et al.*, also obtained an acid which they regarded as XXIII. However, they reported the melting point as 125–127°; our acid XXIII melted at 95–96°.

(3a) Lewis, Ramage, Simonsen and Wainwright reported this glycol to melt at 178–180°; our glycol is possibly a stereoisomer of theirs.

by the fact that the product (XXII or XXIV) when cleaved by alkali, gave a dibasic acid XXV or XXVI containing all of the carbon atoms present in the addition product.



Incidental to the work described in this paper, it was discovered that cyclohexadiene would react with diphenylketene and that the product was formed by 1,2-addition to one of the double bonds. Of the linear dienes, 1,4-diphenylbutadiene did not react at all, while 2,3-dimethylbutadiene reacted readily (with diphenylketene). Ketene itself, however, was found to be inert toward cyclopentadiene under any of the conditions tried. Finally, a most interesting addition product was obtained from phenylacetylene and diphenylketene.⁶

The authors acknowledge with thanks a grant from the Fluid Research Funds of the Graduate School of the University of Minnesota, which enabled them to complete this work.

Experimental Part⁷

Diphenylketene was prepared in 35% yield by oxidation of benzil monohydrazone by mercuric oxide.⁸

Cyclopentadiene was obtained by distilling the dimer twice through a short column. The clear liquid boiled at 42–44°.

Reaction between Cyclopentadiene and Diphenylketene: 6,6-Diphenylbicyclo-[0,2,3]-heptene-3-one-7 (I).—A solution of diphenylketene (8 g.) and cyclopentadiene (8 g.) in petroleum ether (70 cc., washed with concentrated sulfuric acid and distilled; b. p. 60–68°) was placed in a flask, the air was displaced by nitrogen and the reaction mixture was allowed to stand for twenty-four hours at room temperature. The solvent was evaporated and the residual oil solidified when cooled and rubbed. The product was washed several times with small amounts of alcohol and then recrystallized from alcohol. It weighed 9.8 g. (92%) and melted at 88–89°.

(6) In a recent note [*Chemistry & Industry*, 1079 (1937)] Farmer and Farooq have announced that they have obtained addition products from diphenylketene and cyclohexene, cyclopentadiene, cyclohexadiene, dimethylbutadiene and piperylene, but not with tetramethylethylene. They found, as we did, that reduction of the adduct from cyclohexadiene gave the same product as that resulting when the ketene was added to cyclohexene.

(7) Most of the microanalyses by J. W. Opie.

(8) Schroeter, *Ber.*, **42**, 2336 (1909); Staudinger, *ibid.*, **44**, 1619 (1911).

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.69; H, 6.20. Found: C, 87.79; H, 6.40.

The substance gave no reaction with phenylhydrazine in alcohol, was quite stable toward permanganate in acetone, reacted only slowly with bromine in chloroform, and gave no reaction with malonic acid in alcohol in the presence of piperidine.

Reduction: 6,6-Diphenylbicyclo-[0,2,3]-heptanone-7 (V).—To the unsaturated compound (I) in alcohol (20 cc.) was added a palladium-barium sulfate catalyst (0.5 g.) and the reaction mixture was shaken for four hours with hydrogen under a pressure of 37 pounds (2.5 atm.). The catalyst was removed and the alcohol evaporated under reduced pressure. The product, crystallized from alcohol, melted at 91.5–92.5. A mixture of V and I melted at 82–85°.

Anal. Calcd. for $C_{19}H_{18}O$: C, 87.02; H, 6.91. Found: C, 87.35; H, 7.32.

The same compound resulted when cyclopentene (10 g.) and diphenylketene (4.5 g.) were heated for six days at 60° in a sealed tube. The melting point, alone and when mixed with the reduction product, was 90–92°.

Cleavage of I: 2-Benzhydrylcyclopentene-3-carboxylic Acid-1 (IX).—The addition product I (750 mg.) was added to a solution of potassium hydroxide (0.25 g.) in ethanol (10 cc.) and the reaction mixture was refluxed for three hours. The alcohol was evaporated and gradually replaced by water. The cooled solution was extracted thoroughly with ether and the water layer then acidified with dilute sulfuric acid. The solid was removed and crystallized from dilute methanol. It formed white needles which weighed 470 mg. and which melted at 145–147°. Repetition of the experiment using sodium hydroxide in place of potassium hydroxide gave the same product. Staudinger and Rheimer^{2b} reported that an acid, to which they assigned the structure XI, melted at 125°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.02; H, 6.53. Found: C, 82.12; H, 6.68.

Oxidation of IX: 2-Benzhydryl-3,4-dihydroxyl-1-carboxycyclopentane (XXI).—The acid IX (1.8 g.) was dissolved in a solution of sodium carbonate (2 g.) in water (100 cc.). The solution was cooled to 0°, stirred and a solution of potassium permanganate was added slowly until the color persisted for half an hour. The excess permanganate was destroyed by addition of a small amount of formalin and the mixture was filtered. The manganese oxides were extracted well with hot water and the combined filtrates were evaporated to 100 cc. The cooled solution was acidified, extracted with ether, the ether washed with water and dried over sodium sulfate. Evaporation of the ether left a small amount of solid, which was crystallized from dilute acetic acid. The substance formed small white needles which melted at 201.5° (dec.).

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.55; H, 5.85; neut. equiv. (monobasic), 310. Found: C, 73.21; H, 5.63; neut. equiv., 307.

Attempts to acetylate the glycol in the usual manner gave a brown oil which could not be obtained crystalline.

Ozonolysis of IX: 4,4-Diphenylbutane-1,2,3-tricarboxylic acid (XIII).—The cyclic acid IX (1.5 g.) was dissolved in acetic acid (40 cc.) and a stream of ozonized

oxygen (about 4% O_3) was passed slowly through at room temperature until the exit gas liberated iodine from a solution of potassium iodide (one and three-quarters hours). The solution of the ozonide was heated on the steam-bath for twenty-five minutes, then cooled to 0° and to it was added a cold solution of chromic anhydride (1.5 g.) in acetic acid (10 cc.) and water (2 cc.). The temperature was held at 0° for thirty minutes and then the reaction mixture was allowed to stand overnight at room temperature. The solution was evaporated *in vacuo* at 45° to about one-third its volume and then was poured into water (75 cc.). The aqueous solution was extracted six times with ether, and the ether extracts, after washing with water and drying over sodium sulfate, were evaporated. The residue (a greenish oil) was heated at 80° for fifteen minutes under a pressure of 20 mm. in order to remove traces of acetic acid and the glassy solid which remains was finally obtained in crystalline form by rubbing it with ethyl acetate. After crystallization from dilute acetic acid, the product (about 100 mg.) melted at $208-209.5^\circ$ with decomposition.

Anal. Calcd. for $C_{15}H_{18}O_6$: C, 66.66; H, 5.30; neut. equiv. (tribasic), 114. Found: C, 66.49; H, 5.05; neut. equiv., 118.

The methyl ester was prepared using diazomethane. After one crystallization from methanol, the substance melted at $116-117^\circ$. This should be the β -ester, which Lewis, *et al.*, reported to melt at $121-122.5^\circ$.

Anal. Calcd. for $C_{22}H_{24}O_6$: C, 68.75; H, 6.30. Found: C, 68.72; H, 6.52.

Reduction of IX: 2-Benzhydrylcyclopentanecarboxylic Acid (XXIII).—To the cyclopentene acid IX (75 mg.) in dry ether (15 cc.) was added a small amount of platinum catalyst and the mixture was shaken for two and one-half hours with hydrogen under a pressure of 35 pounds (2.3 atm.). The catalyst was removed and the solvent was evaporated. The residue, an oil, partially solidified on standing. The product, crystallized from petroleum ether, melted at $95-96^\circ$. Staudinger^{2b} reported that this acid melted at 85° .

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.43; H, 7.18. Found: C, 81.44; H, 7.21.

The same acid (XXIII) resulted when the bicycloheptanone V (250 mg.) was refluxed with a solution of potassium hydroxide (1 g.) in ethanol (25 cc.) for ten hours. The alcohol was evaporated and the residue taken up in water. The solution was extracted with ether and the aqueous layer was cooled, filtered and the filtrate acidified with dilute sulfuric acid. The oil which formed was taken up in ether, dried over sodium sulfate, and the ether was evaporated. The oily residue crystallized when its solution in petroleum ether was cooled. The product melted somewhat low (90°) and recrystallization did not give a product with a higher melting point. When mixed with a specimen of the acid melting at 95° , the melting point was between the two. A portion of the acid was converted into the anilide via the acid chloride; the anilide melted at $142-143^\circ$. Staudinger^{2b} reported the melting point of the anilide as 139° .

Addition of Diphenylketene to I: the Tricyclic Compound (XXII or XXIV).—The bicyclic compound I (1.53

g., dried twenty-four hours *in vacuo* over calcium chloride) and diphenylketene (1.15 g.) were heated together at 110° for nine days; a solid began to separate after two days. The product, triturated twice with alcohol and once with benzene and dried, weighed 0.7 g. and melted at 230° . When crystallized from alcohol-benzene, the substance was white and melted at $249-250^\circ$.

Anal. Calcd. for $C_{33}H_{26}O_2$: C, 87.20; H, 5.77. Found: C, 87.21; H, 5.74.

Cleavage to Dibasic Acid (XXV or XXVI).—The tricyclic compound XXII or XXIV (0.7 g.) was refluxed for ten hours with a solution of potassium hydroxide (0.75 g.) in alcohol (25 cc.). The alcohol was evaporated and replaced by water and the solution extracted with ether, cooled and filtered. Acidification of the aqueous filtrate produced a white solid which was removed and dissolved in benzene. The benzene solution was filtered and the solvent evaporated from the filtrate. The residue, crystallized twice from dilute acetic acid, was white and melted at $140-145^\circ$.

Anal. Calcd. for $C_{33}H_{30}O_4$: C, 80.8; H, 6.12. Found: C, 80.0; H, 6.42.

Reaction between Cyclohexene and Diphenylketene: 7,7-Diphenylbicyclo-[0,2,4]-octanone-8 (XVII).—Diphenylketene (2.8 g.) and cyclohexene (3.5 g.) were heated at 110° in a sealed tube for three days. The excess hydrocarbon was removed under reduced pressure and the residue was washed three times with petroleum ether and then crystallized from alcohol. The product (about 1 g.) formed white needles which melted at $132-133^\circ$. Staudinger^{2c} reported the melting point as 129° .

Cleavage: 2-Benzhydrylcyclohexanecarboxylic Acid (XVIII).—The bicyclooctanone XVII (1.0 g.) was refluxed for eight hours with a solution of potassium hydroxide (0.3 g.) in ethanol (25 cc.). The alcohol was evaporated and replaced by water. The aqueous solution was extracted with ether, cooled and filtered and the filtrate was acidified. The solid was removed and crystallized three times from dilute acetic acid. It was white and melted at $153-155^\circ$ and further crystallization did not give a product with a higher melting point, although the carbon values found were somewhat low.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.7; H, 7.54; neut. equiv. (monobasic), 294. Found: C, 80.60; H, 7.62; neut. equiv., 287.

Summary

1. When diphenylketene adds to cyclopentadiene, the product is 6,6-diphenylbicyclo-[0,2,3]-heptene-3-one-7, formed by 1,2-addition of the reactants.
2. The bicyclic compound formed in the first reaction will add a second molecule of diphenylketene, also by 1,2-addition.
3. No product formed by a diene synthesis results when diphenylketene reacts with cyclopentadiene or with cyclohexadiene.
4. Ketene itself is inert toward cyclopentadiene.

MINNEAPOLIS, MINN.

RECEIVED NOVEMBER 22, 1937