Anal. Calcd. for $C_{10}H_{12}N_2O_3S_2$: N, 10.30 Found: N, 10.50.

When mixed with 3-sulfanilyl-5-methyl-2-thiazolidone,[16] m. p. 190.5–191°, the mixture melted at 190–190.5°.

B. By Hydrolysis of 3-Sulfanilyl-5-methyl-2-imino-thiazolidine.—One gram (0.0037 mole) of 3-sulfanilyl-5-methyl-2-iminothiazolidine was suspended in a solution of 20 cc. of water and 0.7 cc. of concentrated sulfuric acid and heated on a steam-bath for three hours. When cold, the crystalline precipitate was collected, washed with water and dried. The presence of ammonia in the filtrate was shown by a positive reaction with Nessler reagent. The crude product was crystallized from 60 cc. of alcohol; yield, 0.5 g. (49.6%), m. p. 190.5–191.5°.

Anal. Calcd. for $C_{10}H_{12}N_2O_3S_2$: N, 10.30. Found: N, 10.35.

The above compound, when mixed with 3-sulfanilyl-5-methyl-2-thiazolidone[16] and the product obtained by reduction of 3-(*p*-nitrobenzenesulfonyl)-5-methyl-2-thiazolidone, melted at 190–190.5°.

Summary

The preparation and some properties of a series of mono-N^4-acylsulfanilylthiazolines and their hydrolysis products, sulfanilylthiazolidones, have been described. These sulfanilylthiazolidones have been proved to be of the general type
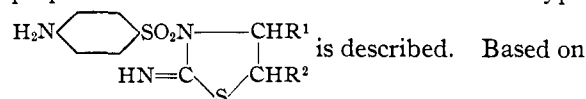
(16) From hydrolysis of 3-(N^4-acetylsulfanilyl)-5-methyl-2-imino-thiazolidine.
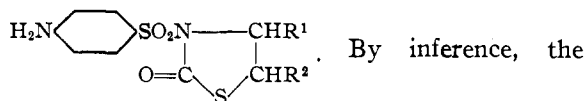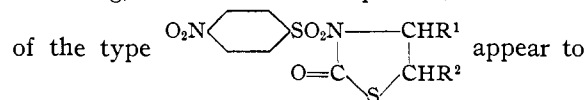

By inference, the mono-N^4-acylsulfanilyl and mono-*p*-nitrobenzenesulfonyl derivatives of the corresponding 2-amino-Δ^2-thiazolines have the structures,

and
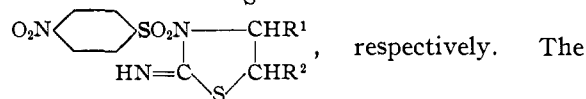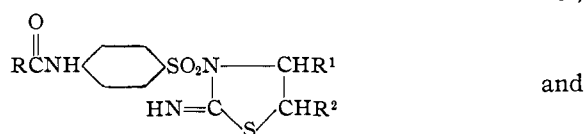
respectively. The preparation of several derivatives of the type

is described. Based on the limited biological data available at the time of writing, in this series of compounds, derivatives of the type

appear to be the most efficacious against experimental β-hemolytic streptococcal infections.

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

The Action of Aliphatic Diazo Compounds upon α,β-Unsaturated Ketones. II.[1] *cis-* and *trans-*Dibenzoylethylene

BY LEE IRVIN SMITH AND KENNETH L. HOWARD[2]

An aliphatic diazo compound, such as diazomethane, will react with simple α,β-unsaturated esters to give, as the first product, a Δ^1-pyrazoline in which the nitrogen atom is always linked to the α-carbon atom of the carbonyl compound. These Δ^1-pyrazolines rearrange under the influence of certain reagents (such as halogen acids), to give Δ^2-pyrazolines; whenever possible, the product of this rearrangement will contain a carbon to nitrogen double bond which is conjugated with the carbonyl group. When pyrolyzed, the usual decomposition of the pyrazolines involves loss of nitrogen with formation of a homolog, usually the β-alkyl derivative of the original unsaturated carbonyl compound, a cyclo-

propane or a mixture of the two; but frequently the pyrolysis also involves merely a dehydrogenation, and gives rise to the pyrazole.[3]

In general, in the reaction with aliphatic diazo compounds, the α,β-unsaturated ketones parallel the esters; thus from the reaction between benzalacetophenone and diazomethane, both pyrazolines were obtained; on pyrolysis, the pyrazolines gave the alkylated ethylene and the pyrazole, but not the cyclopropane.[1] Even when a quinone is used as the unsaturated carbonyl compound, the products conform, in so far as it is possible, with these same types. Thus Fieser and Peters[4] obtained the Δ^1-pyrazoline and from it by oxidation, the pyrazole, when 1,4-naphthoquinone

(1) First paper, Smith and Pings, *J. Org. Chem.*, **2**, 23 (1937).

(2) Abstracted from a thesis by K. L. Howard, presented to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. Degree, July, 1942.
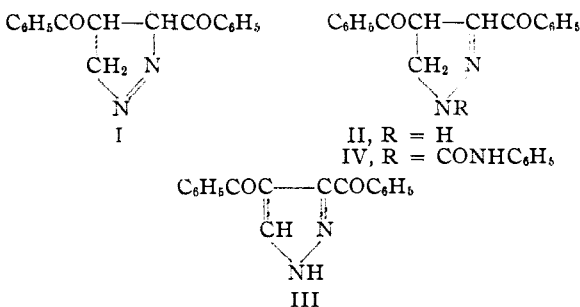
(3) von Auwers, *Ann.*, **470**, 284 (1929); **496**, 27, 252 (1902); *Ber.*, **66**, 1198 (1933); von Pechmann, *ibid.*, **33**, 3590, 3594, 3597 (1900).

(4) Fieser and Peters, THIS JOURNAL, **53**, 4080 (1931).

reacted with diazomethane, and when the same quinone reacted with diphenyldiazomethane, a Δ^1-pyrazolinehydroquinone likewise resulted, and this, on pyrolysis, gave the Δ^1-pyrazolinequinone, the cyclopropane and the "alkylated ethylene."

Although aliphatic diazo compounds have been added to quinones and to the esters of a number of unsaturated, conjugated, dibasic acids such as maleic, fumaric, citraconic and mesaconic,[5] no studies of the reaction between open chained, conjugated 1,4-diketones and aliphatic diazo compounds have apparently been reported. This paper reports the results of a study of the reactions between cis- and trans-dibenzoylethylene and three aliphatic diazo compounds—diazomethane, phenyldiazomethane and diphenyldiazomethane. Of these three diazo compounds, the first and last gave crystalline products with the diketone, but phenyldiazomethane gave only intractable oils.

An ethereal solution of diazomethane reacted rapidly with a chloroform solution of trans-dibenzoylethylene. Within an hour the reaction was complete, and a nearly quantitative yield of Δ^1-3,4-dibenzoylpyrazoline (I), m. p. 108°, was obtained. When this pyrazoline was heated

$$C_6H_5COCH\text{—}CHCOC_6H_5$$
$$CH_2\quad N$$
$$N$$
$$I$$

$$C_6H_5COCH\text{—}CHCOC_6H_5$$
$$CH_2\quad N$$
$$NR$$
$$II,\ R = H$$
$$IV,\ R = CONHC_6H_5$$

$$C_6H_5COC\text{——}CCOC_6H_5$$
$$CH\quad N$$
$$NH$$
$$III$$

above its melting point, or when it was repeatedly crystallized from 60% ethanol, it was converted into the Δ^2-isomer (II), m. p. 129–129.5°. The Δ^2-pyrazoline was stable in air, and could be stored for several months without decomposition. When oxidized by permanganate or by bromine, the Δ^2-pyrazoline was converted into the pyrazole (III), m. p. 170°. The Δ^2-pyrazoline reacted with phenyl isocyanate to form the urea derivative IV, and it was thus differentiated from the Δ^1-pyrazoline I, which did not undergo this reaction.[6] But no carbonyl derivatives could be obtained from II; it failed to react with hydroxylamine, 2,4-dinitrophenylhydrazine or semicarbazide.

(5) (a) von Pechmann, Ber., 27, 1890 (1894); 33, 3590 (1900); (b) Küster, ibid., 35, 2948 (1902); (c) Rydon, J. Chem. Soc., 829 (1936).

(6) v. Auwers and König, Ann., 496, 41 (1932).

When pyrolyzed, the Δ^2-pyrazoline II gave largely dark tars, from which only a small amount of solid material, m. p. 170°, could be obtained. When the pyrolysis was carried out at a lower temperature under reduced pressure, tars were likewise obtained, but these were much lighter in color and from them it was possible to isolate a much larger amount of the solid melting at 170°. This material proved to be the pyrazole III. It is likely that the tars were derived, at least partly, from the "alkylated ethylene" to be expected as a result of the pyrolysis of II, for it has been shown[7] that this compound, 1,2-dibenzoyl-1-propene, must be handled rapidly to avoid contamination with a green oil. No cyclopropane derivative could be isolated from the pyrolysis product of II.
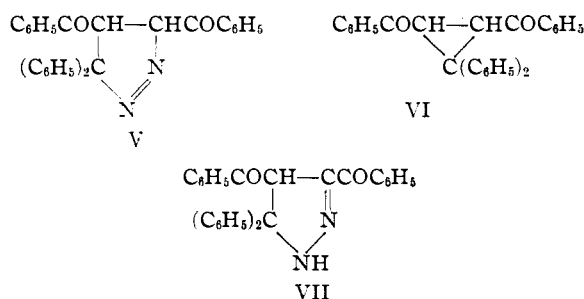
Attempts were made to reduce the pyrazole III in order to arrive at open chained compounds[4] but none of the methods tried led to any useful products. Reduction of III with sodium hydrosulfite, or with sodium and alcohol, led to products of high melting point or else to oils; catalytic reduction under low pressures had no effect, and if high pressures were used, much ammonia was formed. A Clemmensen reduction of III likewise gave only amorphous products and tars.

Addition of ethereal diazomethane to a chloroform solution of cis-dibenzoylethylene produced an orange-red solution, a color which was never observed in the reactions of the trans-isomer. However, crystals of the Δ^2-pyrazoline II soon deposited, and after half an hour the reaction was complete. The yield of II was 80%, and the remainder of the product was a reddish oil. This is to be contrasted with the yield of practically 100% of I from the trans-diketone, and the absence of any oily materials in the reaction product.

When a solution of diphenyldiazomethane in petroleum ether was added to a chloroform solution of trans-dibenzoylethylene, reaction occurred on standing overnight, and two products resulted. One of these was the Δ^1-pyrazoline V, m. p. 157°, and the other was the cyclopropane VI, m. p. 178–179°. These two products accounted for 67% of the starting materials; the rest of the product was a gummy material from which no pure compounds could be isolated. The direct formation of the cyclopropane in a reaction of this sort is new; the literature so far contains no report on the addition of an aliphatic diazo com-

(7) Fuson, Fleming and Johnson, THIS JOURNAL, 60, 1995 (1938).

pound to an α,β-unsaturated compound in which the primary product is accompanied by one of its pyrolysis products.

$$\underset{\substack{\diagdown\diagup\\N\\V}}{\overset{\substack{C_6H_5COCH\text{---}CHCOC_6H_5\\(C_6H_5)_2C\qquad N}}{}}\qquad\underset{VI}{\overset{\substack{C_6H_5COCH\text{---}CHCOC_6H_5\\\diagdown\diagup\\C(C_6H_5)_2}}{}}$$

$$\underset{\substack{\diagdown\diagup\\NH\\VII}}{\overset{\substack{C_6H_5COCH\text{---}CCOC_6H_5\\(C_6H_5)_2C\qquad N}}{}}$$
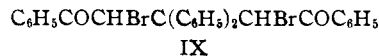
Oxidation of the pyrazoline V by bromine led to a complicated mixture of products, but action of potassium permanganate upon V gave the cyclopropane VI. Pyrolysis of the pyrazoline V at 175° under reduced pressure gave the cyclopropane VI in 68% yield, accompanied by small amounts of two other solids. One of these melted at 156–158° and could not be investigated because of lack of material; the other melted at 173–173.5°, was yellow, and gave analytical values corresponding well with formula VII, the Δ^2-pyrazoline. The pyrazoline V did not react with phenyl isocyanate, and prolonged heating with this reagent converted V into the cyclopropane VI. No carbonyl derivatives could be prepared from V.

cis-Dibenzoylethylene reacted very slowly with diphenyldiazomethane; the characteristic orange-red color of the diazo compound did not disappear until the eighth day. Removal of the solvents left a residue of an orange-yellow oil which was completely soluble in methanol. From this solution a small amount of the pyrazoline V was isolated, and from the mother liquors, a trace of a colorless compound, melting at 151–152°, was obtained. The bulk of the product was a gummy resin.

While there could be little doubt as to the structure of VI, it was decided to synthesize it by an independent method to confirm the structure and to provide larger amounts of material for a study of this interesting cyclopropane derivative. Diphenacyldiphenylmethane (VIII), prepared from benzophenone and acetophenone by a modification of the method of Peres de Carvalho,[8] was

$$\underset{VIII}{(C_6H_5)_2C(CH_2COC_6H_5)_2}$$
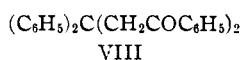
(8) Peres de Carvalho, *Ann. chim. phys.*, [11] **4**, 459 (1935).

$$\underset{IX}{C_6H_5COCHBrC(C_6H_5)_2CHBrCOC_6H_5}$$

converted into the dibromo derivative IX,[9] and the latter, by action of potassium iodide in boiling alcohol,[10] was converted into the cyclopropane VI, m. p. and mixed m. p. 179°. In contrast to the 1-phenyl-2,3-dibenzoylcyclopropane of Kohler and Jones,[10] the diphenyldibenzoylcyclopropane VI could not be reduced to a solid product. Action of zinc dust in acetic acid produced an oil which failed to crystallize even after standing for six months; action of zinc in a mixture of methanol and acetic acid was without effect; and catalytic reduction over Raney nickel produced a gummy material. No furan derivative was obtained from VI by action of hydrobromic acid in acetic acid,[10] nor was any bimolecular product obtained from VI by action of sulfuric acid in boiling acetic acid.[11] The cyclopropane VI was indifferent toward boiling alkaline permanganate and was recovered unchanged after four hours, and it was unaffected by prolonged action of sodiomalonic ester.[12]

Kohler and Jones[10] obtained the higher melting form of 1-phenyl-2,3-dibenzoylcyclopropane in their synthesis, and they assumed that this was the *trans*-form. It would be of interest to establish with certainty the configuration of the diphenylcyclopropane VI because of the great ease with which VI is formed from *trans*-dibenzoylethylene and the great difficulty with which it is formed from the *cis*-diketone. Although VI could not be converted into a 2,4-dinitrophenylhydrazone or an oxime, an attempt was made to prepare a derivative by action of 1-menthyl N-aminocarbamate[13] in the hope that, if VI were actually the *trans*-form, it could be resolved. Action of the reagent had no effect, and VI was recovered unchanged, even after prolonged (thirteen days) treatment.

Addition of phenyldiazomethane to *trans*-dibenzoylethylene was unsuccessful. The reaction product was a yellow, gummy material from which only unchanged diketone could be isolated. It was hoped that this reaction would lead to a pyrazoline which could be pyrolyzed to give either the phenyldibenzoylcyclopropane of Kohler and Jones,[10] or a stereoisomer of their cyclopropane.

(9) Ref. 8, p. 467.
(10) Kohler and Jones, THIS JOURNAL, **41**, 1254 (1919).
(11) Allen and Boyer, *Can. J. Research*, **9**, 159 (1933).
(12) Kohler and Smith, THIS JOURNAL, **44**, 633 (1922).
(13) Woodward, Kohman and Harris, *ibid.*, **63**, 122 (1941).

Experimental Part[14]

Δ¹-3,4-Dibenzoylpyrazoline (I).—A solution of diazomethane (2.7 g., 0.065 mole, prepared from 10.3 g. of nitrosomethylurea[15]) in ether (100 cc.) was cooled to −10° and poured into a cold (−10°) solution of *trans*-dibenzoylethylene[16] (15.7 g., 0.065 mole) in chloroform (100 cc.). Reaction was immediate; within five minutes the product began to deposit. The mixture was allowed to stand at −10° for thirty minutes, and then the solid was removed and dried in a vacuum desiccator. The material weighed 18.0 g. (99.6%) and melted at 108°; when mixed with the starting material (m. p. 109–109.5°), it melted at 103°. It was not possible to purify this material; recrystallization caused a considerable amount of it to change into the Δ²-isomer. In a duplicate experiment, in which the same amounts of materials were used, but in which *cis*-dibenzoylethylene[17] (m. p. 133–134°), was substituted for the *trans*-isomer, there resulted 14.3 g. (79.5%) of material which melted at 129.5–130°. This was the Δ²-pyrazoline, m. p. and mixed m. p. 129–129.5°. Evaporation of the filtrate from this material left a reddish oil, from which no solid material could be obtained.

Δ²-3,4-Dibenzoylpyrazoline (II).—The pyrazoline I (2.0 g.) was crystallized four times from a mixture of ethanol (20 cc.) and water (11 cc.). The white crystals softened at 123° and melted at 129–129.5°. The pyrazoline I (2.0 g., m. p. 108°) was heated for twenty minutes in an oil-bath at 115–120°. The product, when crystallized twice from 75% aqueous ethanol (25 cc.), melted at 129–129.5°. Similar results were obtained when the pyrazoline I was recrystallized from a mixture of ether and petroleum ether.

Anal. Calcd. for $C_{17}H_{14}O_2N_2$: C, 73.39; H, 5.04. Found: C, 73.23; H, 5.17.

Δ²-1-Carbanilido-3,4-dibenzoylpyrazoline (IV).—A mixture of the pyrazoline II (1.78 g.) and phenyl isocyanate (1.19 g.) was heated in a pressure bottle on the water-bath for two hours. Excess phenyl isocyanate was destroyed by addition of methanol (25 cc.), and the solid product (2.25 g., 89%, m. p. 154–155°) was removed. The urea was a very insoluble substance; a small amount (0.75 g.) was recrystallized three times from methanol (500 cc.). The material then melted at 156–156.5°.

Anal. Calcd. for $C_{24}H_{19}O_3N_3$: C, 72.54; H, 4.79. Found: C, 72.80; H, 5.00.

No other derivatives of II could be prepared. Action of hydroxylamine, 85% hydrazine, 2,4-dinitrophenylhydrazine, or semicarbazide under usual or forcing conditions produced red, tarry oils or high melting, amorphous products. Action of nitrous acid produced only a yellow glass and no solid nitroso compounds. Reduction by sodium hydrosulfite produced a small amount of an orange solid which melted with decomposition at 210–214°; action of sodium and alcohol produced an oil; hydrogenation over Adams catalyst was without effect, and hydrogenations in ethyl acetate over Raney nickel at 80° and under 1800 lb.

produced no definite materials and was accompanied by formation of large amounts of ammonia or a volatile amine. Clemmensen reduction of II produced a brown tar.

3,4-Dibenzoylpyrazole (III).—A solution of bromine (4.8 g., 0.03 mole) in chloroform (15 cc.) was added to a cold (0°) solution of the pyrazoline II (8.34 g., 0.03 mole) in chloroform (50 cc.) at such a rate that the temperature did not exceed 12°. An orange precipitate formed during the reaction. After the addition was complete, the solvent was evaporated at room temperature in a current of dry air. Much hydrogen bromide was evolved, and the color of the solid changed to yellow. The residue was washed with water, then dissolved in ethanol (60 cc.) and the solution was filtered and set aside to crystallize. The crude product (5.77 g., 69.3%) melted at 166–167°; after two recrystallizations from methanol, it melted at 169°.

Anal. Calcd. for $C_{17}H_{12}O_2N_2$: C, 73.91; H, 4.35. Found: C, 73.90; H, 4.40.

Oxidation of the pyrazoline (4.8 g.) by permanganate (2.70 g.) in boiling acetone (50 cc.) for two and one-half hours led to an impure product from which there was isolated, after many recrystallizations, 1.11 g. (25%) of the pyrazole melting at 169–170°. Use of larger amounts of permanganate led to extensive cleavage of the pyrazole with production of benzoic acid.

Pyrolysis of the pyrazoline II (7.0 g.) in the presence of polished platinum at 138–141° under 20–24 mm. for seven and one-half hours gave a glass which, after many crystallizations from benzene, petroleum ether and alcohol, yielded 0.09 g. of an infusible substance, 0.81 g. of recovered II, 1.15 g. of the pyrazole III, and a heavy viscous oil from which no solid material could be obtained. Variations in the time, temperature and pressure produced little change in the results of the pyrolysis except that short periods of time resulted in recovery of much more starting material (four hours, 25%), and higher pressures led to much less solid material (0–5% at atmospheric pressure).

No derivatives of the pyrazole could be obtained. A Clemmensen reduction produced only gummy yellow materials which gave fluorescent solutions in most solvents but from which no solid material could be isolated.

1,1-Diphenyl-2,3-dibenzoylcyclopropane (VI) and Δ¹-3,3-Diphenyl-4,5-dibenzoylpyrazoline (V).—A solution of diphenyldiazomethane[18] (8.67 g., 0.044 mole) in petroleum ether (15 cc., b. p. 28–38°) was added to a solution of *trans*-dibenzoylethylene (9.44 g. 0.040 mole) in chloroform (28 cc.). After the mixture had stood for fifteen minutes, the color faded and a gas was evolved. The mixture was then allowed to stand overnight. The solvents were removed at room temperature under reduced pressure, and the yellow residue was triturated with cold ethyl acetate (30 cc.) and the mixture was placed in the refrigerator for three hours. The white solid (VI) was removed and washed with two 5-cc. portions of ethyl acetate (combined filtrate and washings designated as A below). It weighed 3.24 g. (20.3%) and melted at 178–179°. Recrystallization of this material from a mixture of ethyl acetate (25 cc.) and petroleum ether (10 cc., b. p. 28–38°) gave 3.05 g. of VI which melted at 179°.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.57; H, 5.47; mol.

(14) Microanalyses by E. E. Renfrew, C. H. Stratton and Stanley Rolfson.

(15) Arndt, Loewe and Avan. *Ber.*, **73**, 606 (1940); Arndt, *Organic Syntheses*, **15**, 3, 48 (1935).

(16) Lutz, *Organic Syntheses*, **20**, 29 (1940).

(17) Conant and Lutz, THIS JOURNAL, **45**, 1304 (1923).

(18) Staudinger, Anthes and Pfenninger, *Ber.*, **49**, 1932 (1916).

wt., 404. Found: C, 86.85; H, 5.62; mol. wt. (Rast), 394.

Solution A was diluted with petroleum ether (15 cc., b. p. 60–68°) and placed in the refrigerator overnight. The precipitate was removed and washed with a 1:1 mixture (10 cc.) of ethyl acetate and petroleum ether (b. p. 60–68°); the filtrate and washings were combined, diluted with petroleum ether (90 cc., b. p. 60–68°) and placed in the refrigerator overnight. The solid product was removed and washed with 10 cc. of the ethyl acetate–petroleum ether mixture. The combined solids (V) weighed 8.93 g. (47.3%), softened at 139°, and melted at 151–152°. The pyrazoline was dissolved in ethyl acetate (24 cc.), the solution was filtered and the filtrate was diluted with petroleum ether (40 cc., b. p. 28–38°) and placed in the refrigerator overnight. The pyrazoline V thus obtained weighed 8.12 g. A small sample was purified for analysis by recrystallization from alcohol. This softened at 147° and melted at 157°.

Anal. Calcd. for $C_{29}H_{22}O_2N_2$: C, 80.94; H, 5.12. Found: C, 81.22; H, 5.29.

The combined amounts of VI and V represented a yield of 67.5%. The combined filtrates and washings were evaporated and the residue was pyrolyzed at 175° under 20 mm. The resulting dark brown glass weighed 4.5 g. It was completely soluble in ethyl acetate (20 cc.) but when the solution was diluted with petroleum ether a black tar resulted.

A solution of diphenyldiazomethane (0.012 mole) in petroleum ether (14 cc., b. p. 28–38°) was added to a solution of *cis-*dibenzoylethylene (2.55 g., 0.0106 mole) in chloroform (90 cc.). The red color of the diazo compound did not disappear until the eighth day. The solvents, when removed under reduced pressure at room temperature, left a yellow-orange residue which was completely soluble in methanol (50 cc.). The solution was concentrated to a volume of 25 cc. and allowed to stand overnight. The solid (0.59 g.) was removed and recrystallized from a mixture of ethyl acetate (10 cc.) and petroleum ether (25 cc., b. p. 28–38°). It then melted at 157–159°, alone or when mixed with a specimen of the pyrazoline V prepared from *trans-*dibenzoylethylene. The methanol filtrate was evaporated under reduced pressure on the steam-bath. The residue (4.5 g.) was a resinous, orange material from which only insignificant amounts of amorphous product could be obtained.

Action of bromine (0.4 g.) in chloroform (5 cc.) upon V (1 g.) in chloroform (10 cc.) was very slow at 0°. On standing in the refrigerator overnight, the solution acquired a green color, but the product obtained by evaporation of the solvent was an orange glass from which only a very small amount of unidentified solid could be obtained. Action of chloranil in boiling xylene likewise failed to convert V into definite products; a small amount of unchanged V was the only material isolated.

A solution of V (1.0 g.) and potassium permanganate (3.0 g.) in acetone (35 cc.) was allowed to stand at room temperature for two days. Excess permanganate was destroyed by addition of a few drops of formalin, the mixture was filtered and the manganese dioxide was washed with three 10-cc. portions of acetone. The combined filtrates and washings were concentrated to a volume of 40

cc., and an equal volume of water was added slowly to the boiling solution. On cooling, the solution deposited a yellow solid (0.45 g.), m. p., 173–177°. This was impure cyclopropane VI. The filtrate was slowly diluted to a volume of 130 cc. with water and the solid was removed. The combined solids, after several crystallizations from petroleum ether (b. p. 60–68°), weighed 0.65 g. and melted at 179–179.5°, alone or when mixed with VI.

The pyrazoline V was largely unchanged when it was heated for three minutes at 160°; it failed to react with phenyl isocyanate before or after heating, and it formed no carbonyl derivatives with hydroxylamine, semicarbazide, or 2,4-dinitrophenylhydrazine. In all but the last of these reactions, either the pyrazoline or a mixture of it with the cyclopropane was recovered.

Pyrolysis of V (4.0 g.) for eight hours at 175° under 20–21 mm. gave a pale amber colored glass. This was triturated with warm ethyl acetate (10 cc.), transferred to a flask with another 10-cc. portion of the solvent, and the mixture was kept overnight in the refrigerator. The white solid (2.11 g.) was removed and washed with a 1:1 mixture (6 cc.) of ethyl acetate and petroleum ether (b. p. 40–70°). The washings and the main filtrate were combined, diluted with petroleum ether (25 cc.) and again kept in the refrigerator overnight. The solid was removed, washed with the solvent mixture, and the filtrate and washings, when concentrated to a volume of 7 cc., diluted with petroleum ether (20 cc.) and kept cold overnight, deposited more solid. The combined solids (2.68 g., 68.8%), after crystallization from ethyl acetate (19 cc.), weighed 2.14 g. and melted at 179–179.5°, alone or when mixed with the cyclopropane VI. The filtrates and washings were combined and allowed to evaporate spontaneously. The residue (0.65 g.), which melted at 150–159°, was separated by repeated partial extraction with methanol (4–6 cc. portions) into two fractions, one of which melted at 156–158° and whose analysis indicated that it was impure cyclopropane VI; the other melted at 173–173.5° and was an isomer of V, probably the Δ^2-3,4-dibenzoyl-5,5-diphenyl pyrazoline VII.

Anal. Calcd. for $C_{29}H_{22}O_2N_2$: C, 80.94; H, 5.12. Found: C, 81.36; H, 5.62.

Pyrolysis of V (4.0 g.) at higher temperatures, 200–220°, and under reduced pressure, was complete in about one hour. The dark glassy material was processed as described above. The products were 1.37 g. of the cyclopropane VI and 1.10 g. of a mixture which melted at 158° and which probably consisted largely of VI.

Diphenacyldiphenylmethane (VIII).[8]—Freshly prepared, powdered sodamide[19] (4.0 g.) was added, in small portions, to a cold (0°) solution of benzophenone (9.0 g., 0.0495 mole) and acetophenone (12.0 g.) in dry ether (25 cc.). The mixture was allowed to stand in the ice-bath overnight and gradually allowed to come to room temperature. It was transferred to a separatory funnel and shaken with two 20-cc. portions of water. The water was drawn off and the solid was shaken with ether (20 cc.) and filtered. It weighed 11.24 g. (56%) and melted at 177–179°. The crude material was purified by two crystallizations from a 2:1 mixture of ethyl acetate and benzene (35 cc. for 4.2 g.

(19) Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

of solid). It then melted at 183°, in agreement with the value in the literature. The loss in the purification was about 50%.

1,3-Dibenzoyl-1,3-dibromo-2,2-diphenylpropane (IX).[9] —A solution of bromine (1.82 g.) in carbon bisulfide (10 cc.) was added dropwise to a cold (0°) solution of VIII (2.3 g.) in carbon bisulfide (25 cc.). There was a brief induction period, after which the bromination proceeded smoothly. The solvent was allowed to evaporate spontaneously at room temperature, and the residue (m. p. 118-122°) was crystallized twice from ethanol (10 cc.). It then weighed 0.95 g. (30%), and melted at 132-133°. A high melting by-product was obtained; this was not investigated.

1,1-Diphenyl-2,3-dibenzoylcyclopropane (VI).—The dibromo compound VIII (0.6 g.) was dissolved in ethanol (50 cc.), potassium iodide (0.6 g.) was added, and the solution was refluxed for seven and one-half hours. Free iodine was removed by addition of sodium bisulfite solution (2 cc., 10%) and then the solution was diluted with an equal volume of water. The solid (0.45 g.) was removed and dissolved in benzene (5 cc.). Petroleum ether (7 cc., b. p. 38-48°) was added and the mixture, when chilled, deposited 71 mg. of the cyclopropane, m. p. and mixed m. p. 179°.

The cyclopropane was indifferent to prolonged (two days) action of hot 2% sulfuric acid, or to boiling alkaline permanganate (four hours), and was recovered unchanged in both cases. Action of zinc for thirty minutes on a solution of VI in hot acetic acid produced an intractable oil from which a small amount of unchanged material was the only product obtained; zinc was without action upon VI dissolved in equal volumes of methanol and acetic acid. Action of hydrobromic acid in acetic acid converted VI into a yellow resin, and action of acetic anhydride containing sulfuric acid gave a black tar. Hydrogenation over Raney nickel gave an oil and a very small amount of a hygroscopic solid, m. p. 49°. The cyclopropane was recovered unchanged after it was subjected to the action of sodiomalonic ester for twenty-four hours. No carbonyl derivatives could be obtained; action of hydroxylamine, 2,4-dinitrophenylhydrazine, or l-menthyl N-aminocarbamate under the usual conditions either produced tarry materials or else led to recovery of unchanged cyclopropane.

Addition of Phenyldiazomethane.—*trans*-Dibenzoylethylene (4.72 g., 0.02 mole) was dissolved in a mixture of ethyl acetate (10 cc.) and chloroform (20 cc.) and the solution was added to phenyldiazomethane (2.7 g., 0.022 mole). The orange-red color of the solution became somewhat lighter after thirty minutes. After the solution had stood overnight, the solvents were evaporated under reduced pressure. The yellow, sticky residue was dissolved

in ethyl acetate (10 cc.), petroleum ether (2-5 cc., b. p. 28-38°) was added, and the solution was chilled. The light yellow solid was removed; it weighed 0.34 g., melted at 109°, and was unchanged starting material. No further solid material could be isolated from the filtrates, and after removing the solvents there remained the residue of light yellow oil from which no definite compounds could be isolated.

Summary

1. Diazomethane and diphenyldiazomethane have been added to *cis*- and *trans*-dibenzoylethylene. Both diazo compounds reacted much more rapidly and completely with the *trans*-ethylene than with the *cis*-isomer, but the products from the two isomers were identical.

2. From diazomethane and the diketones there was obtained Δ^1-3,4-dibenzoylpyrazoline, which was converted into the Δ^2-isomer and into the pyrazole, although the alkylation product, 1,2-dibenzoylpropylene, may have been present. No cyclopropane could be obtained from these pyrazolines.

3. From diphenyldiazomethane and the diketones there were obtained directly Δ^1-3,3-diphenyl-4,5-dibenzoylpyrazoline and 1,1-diphenyl-2,3-dibenzoylcyclopropane. This is the first example of the direct formation of a cyclopropane in a reaction of this sort. Oxidation of the Δ^1-pyrazoline by permanganate gave the cyclopropane; pyrolysis of the Δ^1-pyrazoline gave the cyclopropane and the pyrazole.

4. No carbonyl derivatives could be obtained from any of these products—pyrazolines, pyrazoles, or from the cyclopropane. The lack of formation of carbonyl derivatives made it impossible to attempt a resolution of the cyclopropane and so to establish the configuration.

5. Phenyldiazomethane failed to give a solid product with *trans*-dibenzoylethylene.

6. In their reactions with aliphatic diazo compounds, the unsaturated 1,4-diketones behave generally as do the other α,β-unsaturated carbonyl compounds, including the quinones.