(60%) of crude ketoether, b. p. 89–95° at 4 mm. resulted. This product was transformed in good yield into its 2,4-dinitrophenylhydrazone, m. p. 159.5–160.5°.

Anal. Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.8; H, 4.7; N, 16.2. Found[c]: C, 55.9; H, 4.7; N, 16.3.

α-Methoxypinacolone.—When a solution of 4.9 g. of α-diazopinacolone in 40 ml. of methanol was treated with 0.3 g. of boron fluoride etherate at 25° the nitrogen (96%) was evolved in 20 min. Distillation yielded 3.0 g. (59%) of α-methoxypinacolone, b. p. 81–83° at 48 mm. A sample of the same ketone was prepared in 2% yield by treating *t*-butylmagnesium bromide with methoxyacetonitrile. Both samples yielded identical 2,4-dinitrophenylhydrazones, m. p. and mixed m. p. 188.0–189.2°.

Anal. Calcd. for $C_{13}H_{18}O_5N_4$: C, 50.3; H, 5.8; N, 18.1. Found[k]: C, 50.7; H, 5.8; N, 18.2.

Di-(4-phenyl-2-ketobutyl) Sulfate.—A solution of 5.0 g. of β-phenethyl diazomethyl ketone, obtained in 97% yield as a viscous yellow oil from the acid chloride, in 100 ml. of dry ether was treated dropwise with 2.6 g. of concentrated sulfuric acid. Gas evolution was vigorous, 650 cc. of nitrogen being liberated in five minutes. After washing this solution with sodium bicarbonate solution, the ether was dried over sodium sulfate. On removing the ether under reduced pressure the residue solidified almost completely as colorless needles. On several recrystallizations from benzene–petroleum ether (low boiling) without attempting to avoid losses there were obtained colorless needles of the neutral sulfate, m. p. 51–52°.

Anal. Calcd. for $C_{20}H_{22}O_6S$: C, 61.5; H, 5.7; S, 8.5. Found[c]: C, 61.3; H, 5.9; S, 8.5.

Summary

The decomposition of α-diazoketones is shown to be non-protonic acid catalyzed. In the absence of alcohols, only tar results from this treatment but in the presence of typical primary, secondary and tertiary alcohols, the corresponding alkoxy ketones are obtained.

In one case, a neutral sulfate was obtained by treating an α-diazoketone with ethereal sulfuric acid.

COLUMBUS, OHIO RECEIVED MAY 22, 1950

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

An Improved Wolff Rearrangement in Homogeneous Medium[1]

BY MELVIN S. NEWMAN AND PHILIP F. BEAL III

In our experience, the Wolff rearrangement of α-diazo ketones using methanol and silver oxide[2] has proved to be somewhat erratic. In different runs using the same diazo ketone large variations in yield were experienced for no apparent reason. Accordingly we undertook to develop a procedure whereby the rearrangement might take place in a homogeneous medium. In this paper we report a new procedure by which this rearrangement may be carried out in solution and under conditions milder than those which usually obtain.[2]

The new reagent consists of a solution of silver benzoate in triethylamine. When a few milliliters of this reagent are added to a solution of diazomethyl ketone in methanol at room temperature nitrogen evolution soon starts and the solution darkens owing to the precipitation of metallic silver. As nitrogen evolution slackens the addition of more silver reagent is made. Usually only a few additions are needed before the theoretical amount of nitrogen is evolved. To effect completion only a small proportion of silver is needed. The methyl ester of the acid to be expected is then isolated by suitable means from the reaction mixture in quite acceptable yields which are easily duplicated.

A number of experiments designed to elucidate the requirements for successful reaction were executed. When α-diazopropiophenone was treated under the same conditions which led to successful rearrangement of α-diazoacetophenone no reaction occurred, even after a silver precipitate and mirror were produced by addition of a small amount of formalin. These experiments

$$C_6H_5COCHN_2 + CH_3OH \xrightarrow[(C_2H_5)_3N]{C_6H_5COOAg} C_6H_5CH_2COOCH_3 + N_2$$

$$C_6H_5COCN_2CH_3 + CH_3OH \xrightarrow{\text{same}} \text{No reaction}$$

indicate that the alpha hydrogen is necessary.

When a solution of hydroquinone was added to a reaction that was running smoothly gas evolution ceased abruptly. On further addition of the silver solution, in excess of the equivalent amount of hydroquinone remaining, the evolution of nitrogen started again. This stopping and starting could be repeated several times by making the necessary additions of hydroquinone and silver solutions. The hydroquinone probably stops the reaction by reducing the silver ion, or a necessary reaction intermediate.

The necessity for triethylamine (or a similar base) was demonstrated by the following experiment. A solution of silver trifluoroacetate in benzene was added to a solution of diazoacetophenone in methanol. No reaction occurred. However, when triethylamine was added, evolution of nitrogen commenced. Thus triethylamine is important not only because of its solvent action on silver benzoate but also because of its basic properties.

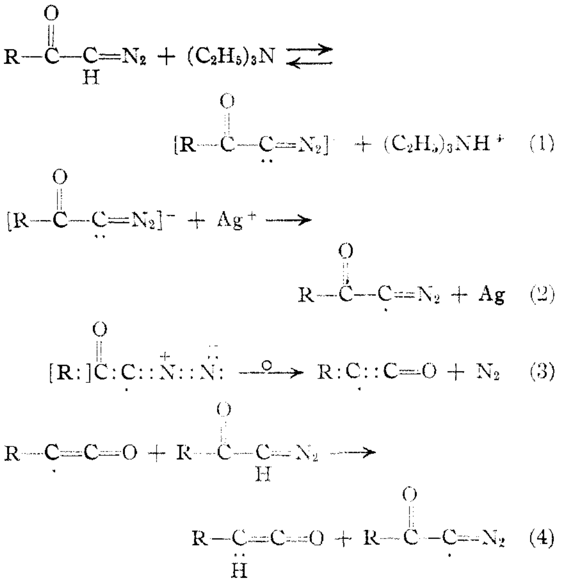
It thus appears that a base and catalytic amount of an oxidizing agent is required in this modification of the Wolff rearrangement. A

---

[1] Taken from the Ph.D. thesis of P. F. B. Ohio State University, 1949.

[2] W. E. Bachman and W. S. Struve, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1942, p. 52.

scheme which is consistent with these requirements is shown[3]



$$R-\overset{\overset{O}{\|}}{C}-\underset{H}{C}=N_2 + (C_2H_5)_3N \rightleftarrows [R-\overset{\overset{O}{\|}}{C}-\underset{\cdot\cdot}{C}=N_2]^- + (C_2H_5)_3NH^+ \quad (1)$$

$$[R-\overset{\overset{O}{\|}}{C}-\underset{\cdot\cdot}{C}=N_2]^- + Ag^+ \longrightarrow R-\overset{\overset{O}{\|}}{C}-\underset{\cdot}{C}=N_2 + Ag \quad (2)$$

$$[R:]\overset{\overset{O}{\|}}{C}:\underset{\cdot}{C}::\overset{+}{N}::\overset{\cdot\cdot}{N}: \xrightarrow{\circ} R:\underset{\cdot}{C}::C=O + N_2 \quad (3)$$

$$R-\underset{\cdot}{C}=C=O + R-\overset{\overset{O}{\|}}{C}-\underset{H}{C}=N_2 \longrightarrow R-\underset{\underset{H}{\cdot\cdot}}{C}=C=O + R-\overset{\overset{O}{\|}}{C}-\underset{\cdot}{C}=N_2 \quad (4)$$

$$R-CH=C=O + CH_3OH \longrightarrow RCH_2COOCH_3 \quad (5)$$

This procedure for carrying out the Wolff rearrangement has been applied successfully to a variety of diazoketones by other workers in this Laboratory. The information concerning these experiments will be given in appropriate articles. In applying this procedure to diazoketones which react sluggishly at room temperature it is important to replace the methanol with *t*-butyl alcohol. When solutions of silver benzoate in triethylamine and methanol are heated, the silver is reduced thus destroying its effectiveness in promoting the Wolff rearrangement. However heating of *t*-butyl alcohol solutions of silver benzoate does not cause reduction of silver, even at reflux temperature, and a good yield of *t*-butyl *p*-nitrophenylacetate was obtained from *p*-nitrophenyl diazomethyl ketone.

Other experiments indicated that cuprous salts may be used to less advantage than silver but we have not studied this approach to any great extent.

Experimental

Silver benzoate was prepared by mixing equivalent solutions of silver nitrate and sodium benzoate. The precipitate was collected, washed and dried in a vacuum oven. Extreme dryness of silver benzoate is desirable as moisture causes precipitation of silver oxide on dissolving in triethylamine. The reactions described below were carried out in three-neck flasks fitted with dropping funnel, sealed stirrer and reflux condenser connected to an azotometer.

Methyl Phenylacetate.—A solution of 1.0 g. (0.004 mole) of silver benzoate in 9.1 g. of triethylamine was prepared and filtered to remove a small amount of precipitate. Soon after the addition of a few drops of this solution to a solution of 5.12 g. (0.035 mole) of diazoacetophenone in 55 ml. of absolute methanol at room temperature the reaction mixture turned black and evolution of nitrogen commenced. As soon as the evolution of nitrogen slackened a new addition of silver solution was made. A total of 3.8 g. of silver benzoate solution was added during two hours, when 92% of the theoretical amount of nitrogen had been collected and the reaction would proceed no further. The mixture was heated to reflux a few minutes after the addition of charcoal and filtered. The solvents were removed from the filtrate and the residue taken into ether and washed with sodium bicarbonate solution. On distillation there was obtained 4.3 g. (82%) of methyl phenylacetate, b. p. 98–101° at 5 mm., $n^{24}D$ 1.5050. This ester was converted in high yield into the corresponding amide, m. p. 156–157°, and acid, m. p. 76–77°. These melting points were not depressed when mixed with authentic samples.

Another experiment similar to the above was carried out except that five minutes after the first addition of silver reagent, and while the evolution of nitrogen was steady, the reaction was stopped by adding a small amount of a solution of hydroquinone in methanol. The reaction was then reactivated by adding more silver reagent. This stopping and starting procedure was repeated three times, the total period of the experiment involving 145 minutes. The yield of methyl phenylacetate, however, still amounted to 75%.

When a solution of 5.0 g. of diazoacetophenone in 100 ml. of methanol was treated with a slurry of 0.25 g. (0.001 mole) of cuprous chloride in 5 ml. of triethylamine a rapid reaction ensued. In two minutes about 90% of the theoretical nitrogen was collected. The reaction product on distillation yielded 3.15 g. of an impure distillate, b. p. 130–145° at 16 mm., $n^{24}D$ 1.5269. On alkaline saponification 1.69 g. of this mixture yielded 0.90 g. (over-all yield 37%) of phenylacetic acid and 0.67 g. of unidentified neutral fraction. In a similar experiment involving cuprous acetate[4] (0.04 g.), triethylamine (3 ml.), diazoketone (5.0 g.) and methanol (100 ml.), 93% of nitrogen was evolved in thirty minutes and the solution turned deep red. By vacuum distillation and alkaline saponification there was isolated only 19% of phenylacetic acid. Two neutral fractions were also obtained but not further studied. Although this reaction occurred more rapidly than the corresponding one involving the silver benzoate it was not investigated further because the yield of desired phenylacetic acid was considerably less.

Methyl *p*-Methoxyphenylacetate.—A solution of 0.5 g. (0.002 mole) of silver benzoate in 5 ml. of triethylamine was added to a solution of 5.28 g. (0.030 mole) of *p*-methoxy-α-diazoacetophenone in 50 ml. of methanol. Later 0.39 g. of powdered silver benzoate was added in two portions. After 200 minutes 91% of nitrogen had been collected and no more reaction would take place. On distillation there was obtained 4.48 g. (84%) of methyl *p*-methoxyphenylacetate,[5] b. p. 114–116° at 10 mm. The acid, m. p. 85–86°, and the amide,[6] m. p. 188–189°, were prepared in almost quantitative yields and agreed in melting point with the literature values.

Methyl Hydrocinnamate.—A solution of 6.0 g. of silver benzoate in 20 ml. of triethylamine was added over a period of two hours to a solution of 14.0 g. of benzyl diazomethyl ketone in 100 ml. of methanol. Only 78% of the theoretical nitrogen was obtained. On distillation there was obtained 10.1 g. (70%) of methyl hydrocinnamate, b. p. 88–92° at 7 mm. This was quantitatively hydrolyzed to hydrocinnamic acid, m. p. and mixed m. p. 49–50°.

***t*-Butyl *p*-Nitrophenylacetate.**—To a refluxing solution of 5.0 g. of *p*-nitro-α-diazoacetophenone in 80 ml. of *t*-butyl alcohol was added during 70 minutes 6.0 g. of a solution of 2.0 g. of silver benzoate in 11 g. of triethylamine. The nitrogen evolution was the theoretical. On distillation there was obtained 3.4 g. (57%) of *t*-butyl *p*-nitrophenylacetate, b. p. 164–168° at 10 mm.

Anal. Calcd. for $C_{12}H_{15}O_4N$: C, 60.7; H, 6.4; N, 5.9. Found: C, 60.7; H, 6.1; N, 6.0.

---

[3] The authors wish to express their appreciation to Dr. Harry Walborsky and Ralph Kaplan for suggesting this reaction scheme.

[4] F. Pechard, *Compt. rend.*, **136**, 505 (1903).

[5] R. Pschorr, *et al.*, *Ber.*, **33**, 172 (1900).

[6] H. Salkowski, *ibid.*, **22**, 2140 (1890).

The ester was quantitatively hydrolyzed to *p*-nitrophenylacetic acid,[7] m. p. 153.4–154.6°, by heating for twenty minutes with concentrated hydrochloric acid.

Summary

A new modification of the Wolff rearrangement of α-diazomethylketones involving a homogeneous reaction medium is described. This involves treating an α-diazoketone in an alcohol with a solution of silver benzoate in triethylamine. The necessity for a hydrogen alpha to both the carbonyl and the diazo group, for silver ion, and for the base, triethylamine, are demonstrated. A possible mechanism involving ionic and free radical intermediates is presented.

COLUMBUS, OHIO RECEIVED JUNE 12, 1950

---

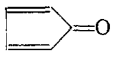
(7) G. R. Robertson, "Organic Syntheses," Coll. Vol. I, p. 406, 1941.

[COMMUNICATION NO. 1343 FROM THE KODAK RESEARCH LABORATORIES]

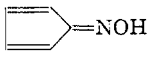
Dimerization of Cyclopentadienones

BY C. F. H. ALLEN AND J. A. VANALLAN

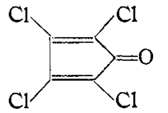
Cyclopentadienone (I) is unknown. Its oxime (II)[1,2] and tetrachloro-substitution product (III) occur only as dimers (type of IV).[3,4,5] Attempts to prepare 2,3,4-trichloro-5-methyl-[6] and 2,3,5-trichloro-4-methyl-,[7] and 3,5-dichloro-2,4-dimethyl-[8] derivatives result in dimeric forms, analogous to IV, only. The same is true of most aryl derivatives, including the acid (V).[9] Only the monomeric 2,3,4,5-tetraphenylcyclopentadienone (VI) is known.[10]



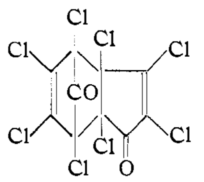
I



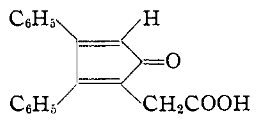
II



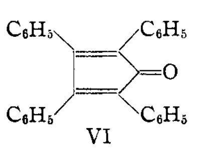
III



IV

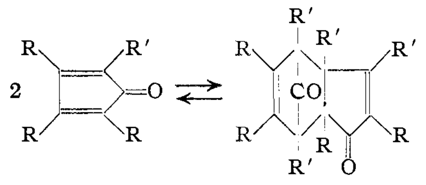


V

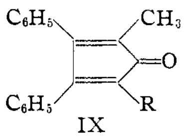


VI

The dimeric products (VII) from 2,5-dimethyl-3,4-diphenyl-[11] and 2,3,5-triphenylcyclopentadienone[12] dissociate readily in solution, while the 2-methyl-3,4-diphenyl derivative, at 200°, gives two products with maleic anhydride, one of which is derived from the monomeric form (VIII), thus showing that there is some dissociation at the elevated temperature of the reaction.[13] The purpose of the work described in this paper was to determine the limits of the reaction of dimerization of cyclopentadienones.



VIII VII



IX

2-Methyl-5-*n*-propyl-3,4-diphenylcyclopentadienone (IX, R = $n\text{-}C_3H_7$) is a white substance but its solutions are a brilliant red; molecular weight determinations in benzene show that it is a reversible dimer. If the propyl group is replaced by phenyl, a monomeric substance (IX, R = C_6H_5) only results. The 2,5-diethyl-, 2,5-di-*n*-propyl-, and 2,5-di-*n*-hexyl-3,4-diphenylcyclopentadienones (VIII, R = C_6H_5, R′ = alkyl) are also monomeric. They are bright red solids and give red solutions. It appears, then, that the diethyl compound is the limiting member of the series.

For convenience in consideration, the cyclopentadienones can be arranged in three groups (Table I), between each of which there is a sharp line of demarcation. The first group consists of those that are known only in the dimeric form; they are colorless in solution regardless of the temperature, show the expected molecular weight, and do not react by addition to dienophiles in benzene solution. Members of the second group are colorless solids which give colored solutions, the intensity increasing to a maximum as the temperature is

---

(1) Thiele, *Ber.*, **33**, 669 (1900).

(2) Alder and Stein, *Ann.*, **496**, 205 (1932).

(3) Zincke and Fuchs, *Ber.*, **26**, 515 (1893).

(4) Zincke, *Ann.*, **367**, 1 (1909).

(5) Zincke and Pfaffendorf, *ibid.*, **394**, 7 (1912).

(6) Bergmann and Francke, *ibid.*, **296**, 167 (1897).

(7) Prentzell, *ibid.*, **296**, 189 (1897).

(8) Francke, *ibid.*, **296**, 209 (1897).

(9) Japp and Murray, *J. Chem. Soc.*, **71**, 149 (1897). The "oxime," m. p. 122–123°, which the authors were unable to identify, is, therefore, the dihydroxylamine salt of the dimer, $C_{38}H_{34}N_2O_8$. Calcd.: C, 70.7; H, 5.1; N, 4.4. Found: C, 69.8; H, 5.6; N, 4.1.

(10) Allen, *Chem. Rev.*, **37**, 209 (1945).

(11) Allen and VanAllan, THIS JOURNAL, **64**, 1260 (1942).

(12) Ziegler and Schnell, *Ann.*, **445**, 276 (1925).

(13) Allen and VanAllan, *J. Org. Chem.*, **10**, 333 (1945).