Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 82.4; H, 5.9. Found: C, 82.2; H, 6.2.

1-(2-Biphenylyl)-2-phenylethylene.—An intimate mixture of 7.5 g. of 1-(2-biphenylyl)-2-phenylethanol and 20 g. of potassium hydrogen sulfate was heated and the product isolated as described in previous dehydration experiments. Distillation at 190–210° (4–5 mm.) gave 5.6 g. (80%) of a yellow oil. Evaporative distillation at 140–150° (0.01 mm.) gave a colorless oil which could not be crystallized and which would not form a picric acid or trinitrobenzene derivative.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.4; H, 6.1.

Acknowledgment.—The technical assistance of W. Stroup and W. Selcer in a portion of this work is gratefully acknowledged. The authors are indebted to the Research Institute of The University of Texas (Project 186) for a grant to the senior author which made this work possible. They also wish to thank the Monsanto Chemical Company for the gift of a generous quantity of *o*-aminobiphenyl.

Summary

The synthesis of some *o*-alkenylbiphenyls is described.

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[Contribution from the Chemistry Department of Emory University]

sym-Tetraphenylacetone. A Study of its Synthesis[1]

By Douglas O. Dean, William B. Dickinson, Osborne R. Quayle and Charles T. Lester[2]

For some time we have been interested in the synthesis of tetraphenylacetone. We have tried a variety of methods for its synthesis. Among these are: (1) sodium and ethyl diphenylacetate,[3] (2) sodium and diphenylacetyl chloride, (3) diphenylmethylpotassium and diphenylacetyl chloride and (4) diphenylmethylpotassium and diphenylketene. Method (1) we consider the best, since it gives good yields and requires the least attention.

The Synthesis of Tetraphenylacetone. (1) Sodium and Ethyl Diphenylacetate.[4]—A mixture of 60 g. (0.25*M*) of ethyl diphenylacetate, 600 ml. of dry ether and 10 g. of sodium wire was allowed to sit at room temperature for four days. The mixture was cooled to 0° and the residual sodium destroyed with ethanol. The mixture was diluted with 500 ml. of water, the ether layer removed and washed with 200 ml. of 5% sodium bicarbonate solution. The ether was removed by distillation, the oily residue treated with 50 ml. of 5% sodium hydroxide solution[5] and this mixture steam distilled until organic material was no longer present in the distillate. The crystalline residue was filtered and recrystallized from hot ethanol, yielding tetraphenylacetone, m. p. 133–134°.[3,6] The steam distillate was extracted with ether, the ether dried over sodium sulfate, decanted and removed by distillation. The residue was identified as diphenylmethane by m. p., 27°, and by oxidation to benzophenone. When all the aqueous layers accumulated in this process were acidified, diphenylacetic acid was recovered. Average yields based on five such preparations: tetraphenylacetone, 17.5 g., 38.8%; diphenylmethane, 13 g., 31%; diphenylacetic acid, 16 g., 30%.[7]

(2) Sodium and Diphenylacetyl Chloride.—A mixture of 11.5 g. (0.05*M*) of diphenylacetyl chloride and 2.8 g. (0.12*M*) of powdered sodium in 200 ml. of dry toluene was heated with stirring for six hours. It was then processed as in (1), yielding 3.6 g., 40%, tetraphenylacetone, 2.0 g., 23.7%, diphenylmethane and 3.6 g., 35.6%, diphenylacetic acid.

(3) Diphenylmethylpotassium and Diphenylacetyl Chloride.—An approximately 0.2*M* suspension of diphenylmethylpotassium in 200 ml. of dry toluene was prepared as previously described.[8] After cooling to −30°, 0.2*M* of diphenylacetyl chloride was added as rapidly as possible with vigorous stirring. The mixture was allowed to warm spontaneously to room temperature, refluxed for thirty minutes and processed as in (1), yielding 5.6 g., 31%, tetraphenylacetone.

(4) Diphenylmethylpotassium and Diphenylketene.—An ether solution of diphenylketene was prepared from 5.85 g. (0.025*M*) of diphenylacetyl chloride and 3.3 g. (0.025*M*) of triethylamine.[9] After standing overnight and filtering, the solution was added dropwise to a suspension of approximately 0.05*M* diphenylmethylpotassium in 125 ml. of toluene. The mixture was heated at reflux for two and one-half hours, allowed to sit overnight and processed as in (1), yielding 1.3 g., 15% (based on diphenylacetyl chloride), tetraphenylacetone.

Although the reaction of ethyl diphenylacetate with sodium to produce tetraphenylacetone superficially resembles a Claisen condensation, followed by a ketonic cleavage, such a path is at variance with present ideas concerning the reaction of an ester and sodium.[10] In order to determine the course of this reaction we have investigated several possible paths by (a) attempting self-condensation of the ester with sodium hydride and potassium amide, (b) preparing the β-keto-ester that would result from self-condensation and attempting ketonic cleavage, (c) attempting cleavage of the ester with excess sodium hydride and lithium aluminum hydride and (d) making a quantitative study of the products of the reaction of ester and sodium.

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(1) Parts of this work were taken from the Master's Theses of Douglas O. Dean, Emory University, 1948, and William B. Dickinson, Emory University, 1947.

(2) Address communications concerning paper to this author.

(3) Vorlander, *Ber.*, **56**, 1125 (1923).

(4) Rehberg, Master's Thesis, Emory University, 1937.

(5) Unless the base is added at this point, unreacted ester remains with the ketone. This necessitates a tedious purification by crystallization, ref. 4.

(6) All melting points reported are uncorrected.

(7) Almost identical quantities of ketone, hydrocarbon and acid were obtained when the reaction was run in toluene at 80° for five hours or Eastman Kodak Co. "Heptane" at reflux for eight hours. When Vorlander's original procedure was followed (*cf.* ref. 3) the yield of ketone was 14% and the yield of hydrocarbon 51%.

(8) Hauser and Yost, This Journal, **69**, 2325 (1947).

(9) Staudinger, *Ber.*, **40**, 1148 (1907).

(10) Hauser and Hudson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 273; McElvain, *ibid.*, Vol. IV, 1948, p. 261.

Attempted Self-Condensation of Ester. (a) Sodium Hydride.—A mixture of 0.05*M* of sodium hydride, 0.05*M* of ethyl diphenylacetate and 100 ml. of anhydrous ether containing four drops of ethanol[11] was heated with stirring for eighteen hours (until sodium hydride had all disappeared and gas was no longer evolved). An additional 0.05*M* of ester was then added to the flocculent suspension of the sodium salt and the resulting mixture heated at reflux for nine hours. The mass was then poured on ice and dilute hydrochloric acid, the ether layer separated, washed with water, dilute sodium bicarbonate and water. On drying and removing the ether, the ester was quantitatively recovered. Acidification of the sodium bicarbonate wash gave no diphenylacetic acid.

(b) **Potassium Amide.**—When the potassium salt of the ester was prepared[8] and treated in the same manner (toluene as the solvent), the ester was also quantitatively recovered.[12]

The Acylation of Ethyl Diphenylacetate and *t*-Butyl Diphenylacetate.—The esters (0.1*M* of each) were metalated and acylated with diphenylacetyl chloride as previously described.[8] The esters were purified by crystallization from Eastman Kodak Co. "Heptane." From ethyl diphenylacetate was obtained 10 g., 23%, ethyl α,α,γ,γ-tetraphenylacetoacetate, m. p. 93–94°. *Anal.* Calcd. for $C_{30}H_{26}O_3$: C, 82.95; H, 5.99. Found: C, 82.79; H, 5.69. From the *t*-butyl ester was obtained 9.7 g., 21%, *t*-butyl α,α,γ,γ-tetraphenylacetoacetate, m. p. 97–98°. *Anal.* Calcd. for $C_{32}H_{30}O_3$: C, 83.08; H, 6.54. Found: C, 83.15; H, 6.20.

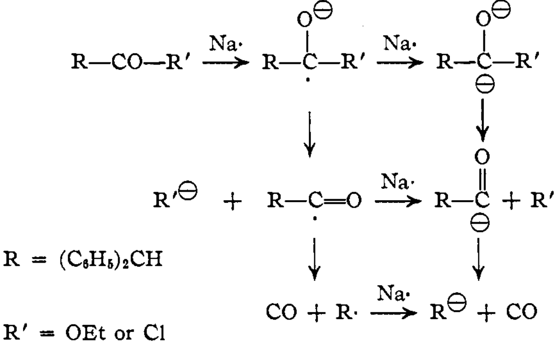
Hydrolysis of the β-Ketoesters.—A 1-g. sample of each ester was refluxed with both 5% alcoholic potassium hydroxide and an acetic acid–hydrogen iodide solution.[8] In all four experiments diphenylacetic acid was produced quantitatively. This is in sharp contrast to the behavior of the benzoyl derivatives of these esters.[8]

Reaction of Ethyl Diphenylacetate with Excess Sodium Hydride.—A mixture of 0.1*M* of ethyl diphenylacetate and 0.24*M* of sodium hydride was stirred in boiling toluene for twenty hours and processed as described in the preparation of tetraphenylacetone. This gave 18.5 g. of diphenylacetic acid (94% of original ester) and 0.8 g., 5%, *sym*-tetraphenylethane, identified by mixed m. p. with an authentic sample. The odor of diphenylmethane was pronounced but it was not isolated.

Reaction of Ester and Acid with Lithium Aluminum Hydride.—By a previously described procedure[13] 0.1*M* of ethyl diphenylacetate and 0.1*M* of diphenylacetic acid were reduced to β,β-diphenylethanol, m. p. 60–61°, in 82 and 88% yield, respectively. The literature gives values for the m. p. of this alcohol ranging from 59 to 65°.[14]

Quantitative Study of Products of Reaction of Ester and Sodium.—In a 500-ml., three-neck flask, with stirrer, dropping funnel and condenser was placed 5.8 g., 0.25*M*, of powdered sodium. The system was swept out with dry nitrogen, a solution of 24 g., 0.1*M* of ethyl diphenylacetate in 200 ml. of dry toluene added, the system heated to 80°, connected to a reservoir and the gas evolved collected over water. After one and one-half hours heating the mixture changed abruptly from a pale yellow to a dark green color, accompanied by a tremendously increased rate of gas evolution. In a matter of minutes the color faded and gas evolution almost ceased. After gas evolution ceased entirely (five hours), heating was discontinued and the mixture processed as previously described, yielding 2.5 g., 0.021*M*, 21%, diphenylmethane and 6.8 g., 0.019 *M*, 38%, tetraphenylacetone. The gas was analyzed in an Orsat apparatus and found to be entirely carbon monoxide, 0.037*M*, when reduced to standard conditions. Average values obtained from three such experiments were: diphenylmethane, 0.027*M;* tetraphenylacetone, 0.020*M;* carbon monoxide, 0.044*M*. A similar experiment with sodium and diphenylacetyl chloride gave: diphenylmethane, 0.0137*M;* tetraphenylacetone, 0.0094*M;* carbon monoxide, 0.0227*M*.[15]

It has been reported that diphenylmethylsodium will add to methyl diphenylacetate to produce tetraphenylacetone[16]: $2(C_6H_5)_2CHNa + (C_6H_5)_2CHCOOMe \rightarrow Na^+ [(C_6H_5)_2CHCOC(C_6H_5)_2]^- + (C_6H_5)_2CH_2$. This seems a likely mode of reaction in the present case, the diphenylmethylsodium being formed by any one or all of several steps[17]



These suggestions are in accord with: (1) the close agreement in moles of carbon monoxide and the sum of moles of diphenylmethane and tetraphenylacetone: 0.044 to 0.047 for ester; 0.0227 to 0.0221 for acid chloride; (2) the substantially equimolar quantities of ketone and hydrocarbon produced; and (3) the startling color changes observed.

We are investigating the scope of this interesting cleavage by studying the reaction of sodium with other derivatives of substituted acetic acids.

Acknowledgment.—We wish to thank Mr. E. C. Suratt for help in carbon and hydrogen analyses and Dr. E. E. Royals for many helpful suggestions.

Summary

1. Several syntheses of *sym*-tetraphenylacetone have been tried.

2. The synthesis of the ketone by the reaction of sodium and ethyl diphenylacetate has been found satisfactory.

3. A study of the mode of this reaction has been made.

4. A mechanism has been proposed, involving a free radical intermediate.

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[11] Daub and Johnson, THIS JOURNAL, **70**, 419 (1948).

[12] Frostick and Hauser, *ibid.*, **71**, 1350 (1949), report that diisopropylaminemagnesium bromide failed to self-condense ethyl diphenylacetate.

[13] Nystrom and Brown, *ibid.*, **69**, 2548 (1947).

[14] (a) Bergmann, *J. Chem. Soc.*, 413 (1936); (b) Tellegen, *Rec. trav. chim.*, **57**, 667 (1938); (c) Kharasch, Sternfeld and Mayo, *J. Org. Chem.*, **5**, 362 (1940); Whitmore, *et al.*, THIS JOURNAL, **63**, 652 (1941).

[15] The tetraphenylacetone was recrystallized before weighing. The diphenylmethane was simply steam distilled and dried before weighing. This gives low values for ketone and high values for hydrocarbon.

[16] Schlenk, Hilleman and Rodloff, *Ann.*, **487**, 152 (1931).

[17] This mechanism was proposed by one of the referees. A similar intermediate has been proposed for the reaction of esters and sodium in liquid ammonia, *cf.* ref. 14(c). The over-all reaction of ester and sodium is similar to the reaction of diphenylcarbamine chloride and sodium; *cf.* Pearl, Evans and Dehn, THIS JOURNAL, **60**, 2478 (1938).