The presence of this compound of undetermined structure in this solution shows that diphenyliodonium ion can undergo some reversible reaction with the reagents present in the other runs, and therefore the reaction must be more complicated than reactions 1 and 2 alone would indicate, in complete accord with the results deduced from the yield measurements.

Experimental

Materials.—Diphenyliodonium iodate was made essentially by the method of Lucas and Kennedy.[6] The chloride was made from this by precipitation from solution with sodium chloride and recrystallization from alcohol. *Anal.* Calcd. for $C_{12}H_{10}ICl$: Cl, 11.2. Found: Cl, 11.2 (by titration with mercuric nitrate).

Rate Measurements.—An appropriate solution of sodium hydroxide, sometimes containing sodium nitrate to adjust the ionic strength, was heated in a thermostat to 59.1 ± 0.04° and solid diphenyliodonium chloride was then dissolved in this as rapidly as possible. Samples were then taken at various times and analyzed for iodonium ion. This analysis consisted in pipetting the sample into a cold solution of sodium iodide, filtering the resulting diphenyliodonium iodide on a weighed filtering crucible, washing with water and ether, then drying in a vacuum desiccator and weighing. On known solutions of concentrations within the range used this analysis was about 2% low. Solutions of the iodonium chloride were apparently stable in the absence of hydroxide ion, and in the presence of 0.1 *N* bromide ion no perceptible reaction (less than 10%) occurred in 40 hr. at 100°.

Product Analysis.—Phenol was determined by bromination in reaction mixtures in which no phenol or sodium phenoxide was used as a starting material. Diphenyl ether was estimated by a bromination method after separation from phenol by repeated partition of the reaction mixture between carbon tetrachloride and aqueous sodium hydroxide followed by removal of most of the solvent. At room temperature in two hours diphenyl ether in a small amount of carbon tetrachloride reacted with 1.00 ± 0.05 mole of bromine derived from an acidified standard solution of sodium bromate and sodium bromide. The excess bromine was determined iodometrically. The product of this reaction is presumably mostly *p*-bromodiphenyl ether,[7] but it was not isolated. The accuracy of this analysis is not high; an indication of the accuracy can be obtained from the two runs where phenol was also determined, in these cases phenol and diphenyl ether together accounted for 94 and 98% of the total reaction product.

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(6) H. J. Lucas and E. R. Kennedy, *Org. Syntheses*, **22**, 52 (1942).

(7) A. Mailhe and M. Murat, *Compt. rend.*, **154**, 601 (1912); C. M. Suter, THIS JOURNAL, **51**, 2381 (1929).

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The Anomalous Carbonylation of Diphenylacetylene[1]

BY GEORGE P. MUELLER[2] AND FRANK L. MACARTOR

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Shortly after descriptive reports of carbonylation of olefins and acetylenes became available[3,4] we became interested in predicting the direction of addition of hydrogen and carboxyl to the unsaturated center. Since the other groups in substituted ethylenes and acetylenes would be most likely to influence both the rate and direction of carbonylation, a number of symmetrical and unsymmetrical acetylenes were chosen for study. The work was prematurely interrupted and results of more extensive investigations of this kind have since been published.[5] Our experience with ethyl tetrolate, phenylacetylene and diphenylacetylene is in accord with the results and predictions of the British group. Although our reaction medium was not the same as that employed in the standard conditions adopted by them,[5a] we also noted that certain carbonylations proceeded slowly with no temperature rise while others were exothermic. The latter were always accompanied by a deep blood-red color changing instantly to the pale green of the nickel solution with exhaustion of either the acetylene or the nickel carbonyl. In addition we wish to report the curious behavior of diphenylacetylene on carbonylation in dioxane medium.

The non-availability of detailed experimental procedures at the inception of this work necessitated casting about for suitable conditions in each case. Diphenylacetylene in ethanol and benzene gave the expected ethyl α-phenylcinnamate in 34% yield, some starting material being recovered. When dioxane and ethanol were used as solvents, this ester was also produced, but the principal reaction product was a white, granular material, which after recrystallization melted at 161–162°. This compound was neutral and unsaponifiable, permanganate and bromine tests for unsaturation were negative, and no carbonyl derivative could be obtained in spite of determined efforts to prepare an oxime, phenylhydrazone or 2,4-dinitrophenylhydrazone. The infrared spectrum in Nujol was prepared and interpreted through the courtesy of Dr. H. S. Gutowsky of the University of Illinois, who suggested the presence of a carbonyl group, a double bond possibly conjugated with the former, and one or more phenyl groups.

The compound proved to be 2,3,4,5-tetraphenylcyclopenta-2-en-1-one which, though previously known, was not suspected in this case because our analytical results gave consistently low carbon values. The identity was noted from a comparison of physical data and the review of chemical reactivity of this compound given by Sonntag, *et al.*[6] Our product seemed to be the same in all respects, chemical properties, ultraviolet and infrared absorption, except for the carbonyl absorption reported at 5.85 μ. We had found this band at 5.91 μ. An authentic sample was supplied through the courtesy of Dr. Becker. This was identical in physical appearance, melting point and mixed melting point. The infrared curves of both compounds obtained using potassium bromide discs[7] were superimposable and showed the carbonyl absorption at 5.92 μ.

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(1) Part of this work is abstracted from the thesis submitted by Frank L. MacArtor to the faculty of the University of Tennessee in partial fulfillment of requirements for the M.S. degree in chemistry.

(2) G. D. Searle and Co., Skokie, Ill.

(3) "A New Synthesis of Acrylic Acid," J. W. Reppe, (translation by I. G. Callomon and G. M. Kline), *Modern Plastics*, **23**, 162 (1945).

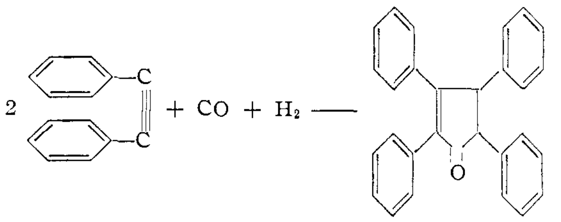
(4) C. Schuster and A. Simon, U. S. Department of Commerce, Office of Technical Service, PB No. L70326 (2) (April 23, 1940) (see "Bibliography of Scientific and Industrial Reports," Vol. 8, No. 1, July 4, 1948, p. 6).

(5) (a) E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, 230 (1950); (b) *ibid.*, 48 (1951); (c) *ibid.*, 763 (1951).

(6) N. O. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, THIS JOURNAL, **75**, 2283 (1953).

(7) We wish to thank Dr. R. T. Dillon, G. D. Searle and Co., for these determinations.

The stoichiometry of formation of this dihydrotetracyclone may be represented as



The hydrogen is formed in the straight-forward carbonylation by reaction between metallic nickel and acid, thus

$$RC{\equiv}CR + 4R'OH + Ni(CO)_4 + 2HCl \longrightarrow 4RHC{=}CRCOOR' + NiCl_2 + H_2$$

Reppe has pointed out[3] that considerable hydrogenation of the desired acrylic esters to propionic esters occurred in non-aqueous media, but this reaction is forestalled in the presence of aqueous hydrohalic acids. He noted further that the fate of hydrogen liberated in the aqueous media has never been determined. The reduction of tetracyclone has been thoroughly studied[6] with the result that 2,3,4,5-tetraphenylcyclopenta-2-en-1-one is formed under a variety of conditions. It therefore seems probable that carbonylation of diphenylacetylene in dioxane produced tetracyclone which was subsequently reduced by hydrogen. The factors responsible for the initial tetracyclone formation or that of another intermediate, remain to be investigated.

Experimental

Carbonylation in Benzene–Ethanol.—A solution of 17.8 g. of diphenylacetylene in 100 ml. of benzene and 63 ml. of absolute ethanol was placed in a 500-ml. flask fitted with a sealed stirrer, addition funnel and reflux condenser and flushed with dry nitrogen. The solution was warmed to 40°; 10 ml. of concentrated hydrochloric acid was added, followed by 5.0 g. of nickel carbonyl[8] added during five minutes. A temperature rise did not occur so the mixture was warmed to 62° within 20 minutes. It was then cooled to 40°, another 5.0-g. portion of nickel carbonyl added, and warmed to 50° for 40 minutes. Again cooled to 35°, it was allowed to stand and the layers separated. The lower layer was stripped of benzene and nickel carbonyl at 30° and 40 mm., filtered from metallic nickel and extracted with ether. The brown liquid remaining after removal of the ether was distilled and 12.0 g. of liquid collected, b.p. 164–200° (13 mm.). By saponification equivalent this contained 71.5% of ethyl α-phenylcinnamate, an over-all yield of 34%. Ether extraction of the alkaline diethylene glycol saponification liquors gave recovery of about 2 g. of diphenylacetylene, while acidification precipitated α-phenylcinnamic acid, 6.5 g. The melting point was 171–172°, after recrystallization from dilute methanol.

Carbonylation in Dioxane–Ethanol.—A solution containing 17.8 g. of diphenylacetylene in 50 ml. of dioxane was treated with 10 ml. of concentrated hydrochloric acid and 7.6 ml. of absolute ethanol. The air was displaced with nitrogen and 5.0 g. of nickel carbonyl was added at 30°. The temperature was raised to 50° during 30 minutes, lowered to 40° and 17 g. of nickel carbonyl added. The temperature was raised to 65° and held there for two hours. The cooled mixture was filtered from solid nickel chloride and the organic layer stripped of solvent *in vacuo* at room temperature leaving a yellow solid. The latter dissolved readily in 100 ml. of ether but soon precipitated crystals of 1,2,3,4-tetraphenylcyclopenta-2-en-1-one, 5.5 g. The ethereal liquors were evaporated and the residual semisolid crystallized from alcohol to give an additional 1.8 g., or a total yield of 37%. The residue after evaporation of the alcoholic liquors was extracted with cold ligroin to give 2 g. (8%) of a viscous oil. This was saponified in diethylene glycol to α-phenylcinnamic acid, m.p. 171–172°.

The crude cyclopentenone was recrystallized repeatedly from petroleum ether or alcohol, m.p. 161–162°, $\lambda^{\max}_{\mathrm{MeOH}}$ 292 mμ (ε 12,970).

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.12; H, 5.74. Found: C, 89.57, 89.52; H, 5.99, 6.25.

An authentic sample, m.p. 158.5–160.0°, when mixed with this product melted at 159.5–162.5°. The infrared spectrum was identical with that obtained from Dr. Becker's sample. This spectrum in potassium bromide is likewise identical in location of principal absorption bands with the Nujol spectrum obtained for us by Dr. Gutowsky but differs from the published spectrum[5] in the placement of bands in the 5-7 μ region.

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[8] This was generously supplied by The International Nickel Company, Inc., New York, N. Y.

Benzhydryl and Triphenylmethyl Nitrates

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RECEIVED MARCH 29, 1954

In connection with our studies of the reactions of nitrate esters, it appeared desirable to prepare two hitherto unknown esters, benzhydryl and triphenylmethyl (trityl) nitrates.[1] Both of these compounds were prepared in good yield by the action of silver nitrate on solutions of the corresponding chlorides in anhydrous ether, and both appeared to be extremely unstable when freed of solvent.

Benzhydryl nitrate decomposed, even at 0°, to give dibenzhydryl ether and oxides of nitrogen. The ether was also isolated from the reaction of the nitrate with water, ethanol, methanol and hydrazine. No alkylated hydrazine derivatives were isolated from the latter reaction, in contrast to the results obtained with benzyl nitrate.[2]

Trityl nitrate was converted very readily to the carbinol on exposure to the air for even a very short time.[1] Refluxing of the nitrate for a few minutes in either anhydrous benzene or anhydrous carbon tetrachloride gave the carbinol, apparently as a result of the abstraction of a hydrogen from another molecule of the nitrate or from the solvent in the case of benzene. Like benzyl nitrate,[2] this ester (in ether suspension) acted as an alkylating agent toward hydrazine, yielding 1,2-bis-(triphenylmethyl)-hydrazine.

Because these unstable nitrates would decompose in the time required to weigh samples, no very good analyses were obtained and no quantitative reaction studies could be carried out.

Experimental[3]

Benzhydryl Chloride.—This compound was prepared in

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[1] After this work was complete, S. J. Cristol and J. E. Leffler reported in a private communication the preparation of trityl nitrate; see THIS JOURNAL, **76**, 4468 (1954). NOTE ADDED IN PROOF.—G. W. Cheeseman, *Chemistry & Industry* 281 (1954), has recently reported the prepartion of benzhydryl and triphenylmethyl nitrates. J. W. Baker and T. G. Heggs, *ibid.*, 464 (1954), have isolated benzhydryl nitrate as a crystalline solid, m.p. 36.7-37.2°, and have obtained satisfactory carbon, hydrogen, and nitrogen analyses.

[2] R. T. Merrow and R. W. Van Dolah, Abstracts of Papers Presented at the 123rd National Meeting of the American Chemical Society, Los Angeles, March, 1953, p. 53M.

[3] All melting points are corrected except where noted otherwise. The authors are indebted to Mrs. L. B. Oliver for the combustion analyses, and to R. H. Pierson for the infrared spectra.