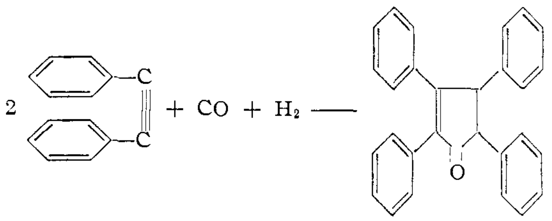
The stoichiometry of formation of this dihydrotetracyclone may be represented as



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

BY RAYMOND T. MERROW AND ROBERT H. BOSCHAN

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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.

68% yield from benzhydrol and hydrogen chloride in dry ether, essentially by the method of Montagne.[4]

Benzhydryl Nitrate.—Twenty-six grams (0.13 mole) of the chloride was dissolved in 35 ml. of anhydrous ether and the solution was stirred for ten hours with 30 g. of powdered silver nitrate, while precautions were taken to exclude moisture. The silver chloride and excess silver nitrate were filtered and washed with dry ether. The filtrate was chloride-free, as indicated by testing with alcoholic silver nitrate. After distillation of the ether at reduced pressure, there remained 25 g. (0.11 mole, assuming pure benzhydryl nitrate) of a rather viscous yellow liquid. Trial runs had shown that the nitrate decomposed on attempted distillation, with the evolution of NO_2. This residual liquid was therefore used without any purification. The liquid gave a strong brown-ring test for nitrate with ferrous sulfate and sulfuric acid, and the infrared spectrum showed strong absorption peaks, characteristic of nitrate esters, at 6.06 and 7.82 μ.

A sample was analyzed immediately after distillation of the ether. *Anal.* Calcd. for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84. Found: C, 69.76; H, 5.30.

On standing for an hour at room temperature or overnight at 0°, in stoppered flasks, the nitrate decomposed, giving a quantitative yield of dibenzhydryl ether, m.p. 107–108° (lit.[5] 109–109.5°).

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.11; H, 6.33; N, 0.00. Found: C, 88.78; H, 6.17; N, 0.00. The infrared spectrum of this material did not show absorptions at 6.06 and 7.82 μ.

Treatment of the nitrate with 95% hydrazine resulted in some gas evolution, heating and reddening, which varied from one run to another, and which may have been due to oxides of nitrogen present as a result of partial autodecomposition of the nitrate. In every trial, however, dibenzhydryl ether was formed in good yield in a few minutes at room temperature. The ether was also formed, but more slowly, when small amounts of the nitrate were added to ethanol, methanol or water.

To establish the stoichiometry of the hydrolysis of benzhydryl nitrate, the following procedure was used. The chloride-free ether solution of the nitrate ester made from 12.0 g. (59.11 mmoles) of benzhydryl chloride was added to 120 ml. of water, and the mixture was stirred and warmed to remove the ether. After four hours additional stirring, the layers were separated and the aqueous solution titrated for acidity with standard NaOH. The non-aqueous material was stirred for eight hours with another portion of water, and the layers separated and treated as before. After a third 8-hour treatment, the non-aqueous material was entirely crystalline, and was filtered, washed with ethanol and dried *in vacuo*. Total acidity in the combined aqueous solutions was 43.75 milliequivalents. Weight of the solid dibenzhydryl ether, m.p. 107–108°, was 7.75 g. (22.14 mmoles). This indicated approximately 75% conversion of chloride to nitrate ester, and further indicated that the stoichiometry of the hydrolytic reaction could be represented as

$$2(C_6H_5)_2CHONO_2 + H_2O \longrightarrow (C_6H_5)_2CHOCH(C_6H_5)_2 + 2HNO_3$$

Triphenylmethyl Nitrate.—To a solution of 2.0 g. (0.0072 mole) of trityl chloride in 30 ml. of anhydrous ether was added 2.0 g. (0.12 mole) of powdered silver nitrate. The mixture was stirred overnight, with precautions taken to exclude moisture. The silver chloride was filtered off, and the filtrate was found to be chloride free. The ether was evaporated at water aspirator pressure. A white solid crystallized as the volume of solution decreased, and turned yellow and finally orange as the ether was completely evaporated. The original white solid melted with decomposition at 90–91°.[6] The yield of the orange-yellow solid was 2.2 g. (100% if assumed to be pure trityl nitrate). The original white solid gave a brown-ring nitrate test. No analysis was possible because of the extreme instability of this ester.[1] Triphenyl carbinol, m.p. 160–161°, was isolated when a sample of this compound was refluxed for a few minutes in either anhydrous benzene or anhydrous carbon tetrachloride. The melting point was not depressed by mixing with an authentic sample of the carbinol.

When 95% hydrazine was dropped slowly onto solid trityl nitrate, a violent reaction took place, and only a dark red tarry residue was obtained. When the hydrazine was added to an ether suspension of the nitrate, the mixture became cloudy and warmed sufficiently to reflux the ether. After one hour, a small amount of white solid had precipitated. It first melted at 194–195° dec. after softening at 188°. After purification by recrystallization from benzene–ethanol, followed by washing with ether, the m.p. was 206–207° (uncor.). An authentic sample of 1,2-bis-(triphenylmethyl)-hydrazine prepared by the method of Wieland[7] melted at 207–208°; there was no depression of the m.p. on mixing with the product from the trityl nitrate–hydrazine reaction.

Anal. Calcd. for $C_{38}H_{32}N_2$: C, 88.33; H, 6.24; N, 5.42. Found: C, 88.01, 88.26; H, 5.50, 5.35; N, 5.90.

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[4] P. J. Montagne, *Rec. trav. chim.*, **25**, 379 (1907).

[5] C. M. Welch and H. A. Smith, THIS JOURNAL, **72**, 4748 (1950).

[6] The melting point sample was obtained by dipping a capillary into the white solid beneath the surface of the ether, so that the solid was not exposed to the air until it was in the melting point tube.

[7] H. Wieland, *Ber.*, **42**, 3020 (1909).

Further Investigation of the Solvolytic Reactivity of Nortricyclyl, Dehydronorbornyl and Norbornyl Halides[1]

BY JOHN D. ROBERTS[2] AND W. BENNETT

RECEIVED APRIL 23, 1954

In a previous paper,[3] we reported solvolytic reactivities in 80% ethanol–20% water (by volume) of nortricyclyl (I), *endo*-dehydronorbornyl (II), *exo*-dehydronorbornyl (III), *endo*-norbornyl (IV) and *exo*-norbornyl (V) halides. In subsequent publications,[4] it was shown that the ratios of the reactivities of the *endo*-compounds II and IV to those of the *exo*-compounds III and V are much greater with the *p*-bromobenzenesulfonates than reported[3] for the corresponding halides.

We have prepared new samples of the chlorides II and IV and redetermined their solvolytic reactivities. The results (Table I) are in reasonable agreement with those obtained for the *p*-bromobenzenesulfonates[4] and these chlorides are far less reactive than previously reported.[3] The earlier erroneous results were due to insufficient reaction times and the presence of reactive impurities other

TABLE I

SOLVOLYSIS RATES OF CHLORIDE (RCl) IN 80% ETHANOL–20% WATER (BY VOLUME) SOLUTION AT 85.0 ± 0.1°

R	k_1, hr.$^{-1}$	% Purity[a] (approx.)
Nortricyclyl (I)	0.019	100
endo-Dehydronorbornyl (II)	< .0005	83
exo-Dehydronorbornyl (III)	.078[b]	83[b]
endo-Norbornyl (IV)	~ .002	84
exo-Norbornyl (V)	.14[b]	100[b]

[a] Determined by the method of H. C. Brown and R. S. Fletcher, THIS JOURNAL, 71, 1845 (1949). [b] Ref. 3.

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[1] Supported in part by the program of research of the U. S. Atomic Energy Commission under Contract AT(30-1)-905.

[2] Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, Calif.

[3] J. D. Roberts, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950).

[4] (a) S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950); (b) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. S .Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).