Carboxylation of Quinquephenyl.—Attempts to prepare quinquephenyldicarboxylic acid were unsuccessful. These experiments were run on 1-g. samples of quinquephenyl[12] using large excesses of oxalyl chloride and aluminum chloride in carbon disulfide solvent. After reaction over the weekend at room temperature, the reaction mixture was decomposed and worked up as in previous examples.

Anal. Calcd. for $C_{32}H_{22}O_4$: O, 13.6. Calcd for $C_{31}H_{22}O_2$: O, 7.5. Found: O, 8.5.

Sublimation of this product in a high vacuum at 300° separated a small amount of pale yellow product containing 0.6% oxygen. The residue now contained 9.4% oxygen. This would correspond to an average of about 1.2 carboxyls per quinquephenyl units.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Polyphosphoric Acid As a Reagent in Organic Chemistry. X. Two Yellow Hydrocarbons from Acetophenone

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RECEIVED NOVEMBER 23, 1959

The action of polyphosphoric acid on acetophenone produces two crystalline yellow hydrocarbons (A and B) of the formula $C_{32}H_{24}$; other products isolated are benzoic acid, dypnone and a yellow substance (C) melting above 300°. The lower-melting yellow hydrocarbon (A) is isomerized to a colorless hydrocarbon (D). Studies of the reactions and spectra of A and D are made and structures are suggested for these hydrocarbons.

In an earlier paper of this series[1] it was shown that in the presence of polyphosphoric acid certain hindered aliphatic–aromatic ketones combine with reactive aromatic hydrocarbons to produce 1,1-diarylalkenes. For example, acetomesitylene and mesitylene give 1,1-dimesitylethylene. When acetophenone and benzene were treated with polyphosphoric acid the reaction took an entirely different course. The benzene functioned only as a solvent, and the acetophenone underwent self-condensation and hydrolysis. The five products isolated were benzoic acid, dypnone, two isomeric yellow hydrocarbons (A and B) of the molecular formula $C_{32}H_{24}$, and a high-melting yellow solid (C) which was so insoluble that no method for its purification was found.

The two yellow hydrocarbons, A and B, melted at 181 and 227°, respectively. The lower melting isomer (A) generated a beautiful deep green color in the presence of acids. For example, it dissolved in concentrated sulfuric acid to give a solution so deeply colored as to appear black, but on dilution with water the yellow hydrocarbon A was regenerated. It could be extracted from benzene solution with concentrated sulfuric acid, and in this way could be separated from the higher-melting isomer (B), which remained in the benzene.

The conditions found to be most satisfactory for the preparation of the yellow hydrocarbon A involved a reflux period of seven hours. The hydrocarbon was produced in 14.5% yield in a relatively pure state. The amount of dypnone isolated from the reaction mixture was dependent on the reaction time. With a reflux period of one hour, dypnone was obtained in 34% yield, 58% conversion, and the yields decreased with longer reflux periods. The possibility that dypnone is an intermediate in the formation of A and B was tested by treating a benzene solution of dypnone with polyphosphoric acid. In addition to small amounts of compound C and benzoic acid, A was isolated from the reaction. The crude yellow product, however, had a wide melting point range, and some of the material melted at 175–205°. Presumably a mixture of A and B was formed. Similar results were obtained when a mixture of acetophenone and dypnone in a 2 to 1 molar ratio was used. Thus, it appears likely that dypnone is an intermediate in the formation of both A and B as well as C, but the possibility remains that any of the products was formed from acetophenone liberated by the hydrolysis of the dypnone used in these experiments. In an effort to obtain a substituted compound related to A or B, *p*-bromoacetophenone was treated with polyphosphoric acid, but the only material isolated was 4,4′-dibromodypnone. The yield was 35%.

The yellow hydrocarbon A exhibits a high degree of reactivity in comparison to the diarylalkenes[1] which were obtained from similar reactions. The substance decolorizes bromine and potassium permanganate solutions and turns green-black in the presence of strong acids. The oxidation of A with dilute nitric acid gave benzoic and *p*-nitrobenzoic acid. When chromic anhydride in acetic acid was employed as the oxidizing agent, a neutral yellow material that melted with decomposition was obtained. However, the product could not be purified by recrystallization or chromatography.

A tetrahydro derivative of A was obtained by employing a Raney nickel catalyst and hydrogen at 1400 p.s.i. and 100°. It was found that the treatment of A with lithium aluminum hydride caused the immediate formation of a dark green color. After hydrolysis of the reaction mixture a colorless substance was isolated, the analysis of which corresponded to a dihydro derivative. The same dihydro derivative was obtained by reduction with hydriodic acid in refluxing acetic acid solution. A colorless hexahydro derivative was obtained by reduction of A with a solution of sodium in liquid ammonia. When A was treated with butyllithium and carbonated, an acid having the empirical formula $C_{37}H_{34}O_2$ was formed. The

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[1] H. R. Snyder and R. W. Roeske, THIS JOURNAL, **74**, 5820 (1952).

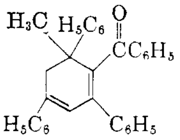
methyl ester was prepared by treatment of the acid with diazomethane.

The yellow color of the hydrocarbon A suggests a structure with a system of conjugated double bonds, and it was observed that the substance formed a monoadduct with maleic anhydride at 80°. When A was treated with maleic anhydride under the more severe conditions used in the reaction of 1,1-diarylethylenes with the Diels–Alder reagent,[2] a tetraadduct was formed.

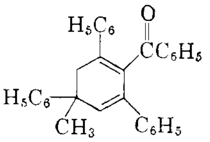
The addition of sodium nitrite to a mixture of A and acetic acid at room temperature produced an unidentified colorless substance which melted at 135° with decomposition. However, when the reaction was carried out in boiling acetic acid a brilliant orange material was obtained. The infrared spectrum and carbon–hydrogen analysis are consistent with an α,β-unsaturated nitro compound possessing the empirical formula $C_{32}H_{23}NO_2$. Treatment of the colorless material with 10% hydrochloric acid converted it to the same nitro derivative.

In the course of an early investigation[3] designed to elucidate the structure of benzene, Delacre obtained from derivatives of acetophenone several hydrocarbons having the empirical formula $C_{32}H_{24}$. One of the hydrocarbons was prepared by treatment of "α-dypnopinacolone," which was later shown[4] to have the structure I, with hydrochloric acid in a sealed tube. Two other hydrocarbons were obtained by the treatment of "α-isodypnopinacolone,"[3c,5] which is believed to have the structure II,[6] with sulfuric acid. Although the structures of the hydrocarbons themselves were not ascertained, it seemed desirable to determine the relationship, if any, between the yellow hydrocarbon A and the hydrocarbons of Delacre, and to test compounds I and II as possible intermediates in the formation of A. The hydrocarbon derived from I and the higher-melting isomer from II were prepared and their ultraviolet spectra were determined. There appears to be little resemblance of the spectrum of either of the hydrocarbons of Delacre to that of A. However, the spectrum of the hydrocarbon derived from II closely resembles that of 2,3-dimethyl-9-phenylfluorene. A fluorene derivative could be formed from II by a cyclization followed by dehydration and rearrangement.

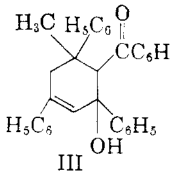
"Dypnopinacol"[3b] (III), the immediate precursor of "α-dypnopinacolone," was treated with polyphosphoric acid under conditions similar to those which resulted in the formation of A and B from acetophenone. Only the yellow substance C was obtained from the reaction. This fact suggests that the action of polyphosphoric acid on acetophenone produces some "dynopinacol," which proceeds immediately to C. Treatment of I with polyphosphoric acid gave some C, and a portion of I was recovered. Surprisingly, it was observed that polyphosphoric acid had no effect on II, even at elevated temperature. Thus, it is apparent that the formation of A and B does not involve I, II or III as intermediates.



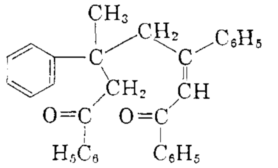
I



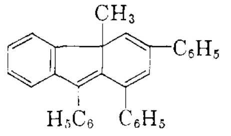
II



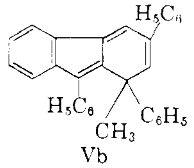
III



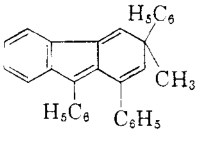
IV



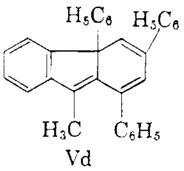
Va



Vb



Vc



Vd

If the action of polyphosphoric acid upon acetophenone does give some "dypnopinacol," then the diketone IV is a probable intermediate in its formation. Cyclization involving an aldol condensation of the α,β-unsaturated carbonyl group with the methylene group would give III. On the other hand, the initial cyclization could involve the attack of the non-conjugated aromatic nucleus by the other carbonyl carbon; subsequent dehydration would give an indene derivative. A second similar cyclization followed by dehydration would give Va. In view of the rapid cyclization of hydrocinnamic acid[7] and the reaction of carbonyl compounds with aromatic nuclei by the use of polyphosphoric acid, it does not seem unreasonable to suppose that the formation of an indene derivative from IV is a competing reaction with the formation of III. Structure Va may then be considered a possibility for the yellow hydrocarbon A. The spectra and chemical behavior of A and its derivatives are consistent with structure Va. The infrared spectrum of A in Nujol shows the usual absorption bands of a monosubstituted phenyl group; its spectrum in carbon tetrachloride exhibits a band characteristic of a methyl group at 1382 cm.$^{-1}$. The ultraviolet spectrum of A is found to be very similar to the spectra of substances with a 1,3,5-triene system conjugated to a benzene ring in a nearly planar configuration.[8] The ultraviolet spectra of the dihydro derivative of A and the methyl ester of the product of the butyllithium reaction of A are strikingly similar and are consistent with the presence of a 1,3-diene system conjugated with an aromatic nucleus.[9] Reductions involving either of the terminal double bonds of

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[2] F. Bergmann, J. Szmuszkowicz and G. Faway, THIS JOURNAL, **69**, 1773 (1947).

[3] M. Delacre, (a) *Bull. acad. roy. Belg.*, [3] **20**, 463 (1890); (b) [3] **22**, 470 (1891); (c) [3] **29**, 849 (1895).

[4] D. Ivanov and T. Ivanov, *Ber.*, **77B**, 173 (1944).

[5] E. Terlinck, *Bull. acad. roy. Belg.*, 1049 (1904).

[6] D. Ivanov, T. Ivanov and C. Ivanov, *Compt. rend.*, **231**, 1240 (1950).

[7] H. R. Snyder and F. X. Werber, THIS JOURNAL, **72**, 2965 (1950).

[8] *Cf.*, for example, the spectra of β-dihydrothebaine methine and 6-methoxythebentriene; K. W. Bentley, R. Robinson and A. E. Wain, *J. Chem. Soc.*, 958 (1952).

[9] *Cf.* the spectra of thebainone-B methine and β-codeimethine given in ref. 8 and those of α- and β-dihydrorubremetine, H. T. Openshaw and H. C. S. Wood, *J. Chem. Soc.*, 391 (1952).

the triene system of Va or a 1,6-addition would all result in such a structure. The catalytic reduction and the spectrum of the hydrogenation product are consistent with that structure. The addition of one mole of maleic anhydride to a compound of structure Va would produce a structure possessing a 3-phenylindene and a styrene system. As expected, the curve obtained by adding the molar extinction coefficients of α-methylstyrene and the tetrahydro derivative is similar to the curve for the monoadduct of A with maleic anhydride. The formation of the tetraadduct can be explained on the basis of structure Va by the reversibility of the Diels-Alder reaction. That the formation of the monoadduct is reversible was shown by the isolation of A during an attempted recrystallization of the monoderivative from acetic anhydride. The regenerated hydrocarbon could react in a manner similar to that of the addition of maleic anhydride to diphenylethylene.[2] Since Va has two groups vinylogously related to diphenylethylene, the formation of a tetraadduct is not implausible.

The nuclear magnetic resonance spectrum of A exhibits a peak at + 3.08 p.p.m. (with respect to water), which is in accord with an allylic methyl group. A peak at −1.82 p.p.m., approximately two-thirds the area of the + 3.08 p.p.m. peak, is in agreement with the two conjugated olefinic hydrogens of Va.

It should be noted that if IV is not assumed to be the precursor of A, then the physical and chemical data presented are also consistent with another structure, Vb. The four structures Va,b,c and d are all derivable by postulation of aldol or Michael reactions of two molecules of dypnone followed by cyclization and dehydration. Numerous other $C_{32}H_{24}$ compounds could conceivably be formed from acetophenone. However, structures which contain condensed aromatic nuclei or which lack conjugated aliphatic double bonds must be discarded in view of the spectra and the abnormal reactivity of the hydrocarbon A. As a possible structure for compound A, Vc may be excluded because the arrangement of its diene system could not allow the formation of a monoadduct with maleic anhydride. Structure Vd is rendered improbable in light of the nuclear magnetic resonance spectrum of the isomer of A which is discussed below.

Attempts to rearrange A to a fluorene derivative with polyphosphoric acid at 170°, with a mixture of sulfuric and acetic acids or of hydrochloric and acetic acids, or with aluminum chloride failed. It was observed that these reagents caused the formation of a characteristic green-black color. When an acetic acid solution of A was treated with hydrobromic acid and refluxed the green-black color faded. A colorless isomeric hydrocarbon (D) was formed, which exhibited fluorescent properties suggestive of a fluorene derivative.

If A has the structure Va, rearrangement would be expected to occur either by a 1,3-shift of the methyl group to give 9-methyl-1,3,9-triphenylfluorene or by a 1,2-shift to give 4-methyl-1,3,9-triphenylfluorene. A synthesis of 9-methyl-1,3,9-triphenylfluorene showed that D was not this hydrocarbon. However, the similarity of the infrared and ultraviolet spectra of 9-methyl-1,3,9-triphenylfluorene and D supports the presence of a 1,3,9-triphenylfluorene system in D. The presence of a hydrogen atom of reactivity similar to that in 1,3,9-triphenylfluorene was demonstrated by the formation of a methyl derivative (E) by successive treatment of D with butyllithium and methyl iodide. Oxidation of D by excess potassium permanganate formed a carbinol. The infrared spectrum of the carbinol indicated that it has a highly hindered hydroxyl group. The same carbinol was obtained by the treatment of D with one equivalent of N-bromosuccinimide and hydrolysis of the bromide thus obtained.

Nuclear magnetic resonance spectroscopy affords confirmation of the 4-methyl-1,3,9-triphenylfluorene structure for hydrocarbon D. The spectrum of this compound exhibited a peak at +2.10 p.p.m. (with respect to water), in agreement with a methyl group on a biphenyl nucleus, and a peak at −0.35 p.p.m. approximately one-third the area of the +2.10 p.p.m. peak. The −0.35 p.p.m. peak is attributed to the proton in the 9-position since the same chemical shift was observed in the spectrum of 1,3,9-triphenylfluorene, while in the spectrum of E, the −0.35 p.p.m. peak was replaced by a peak at +3.23 p.p.m., in agreement with a 9-methyl group.

If, however, hydrocarbon A has the structure Vb, isomerization involving a 1,3- or 1,2-methyl shift would result in 9-methyl- or 2-methyl-1,3,9-triphenylfluorene, respectively. The results of the nuclear magnetic resonance study could not be used to distinguish between 4-methyl- and 2-methyl-1,3,9-triphenylfluorene.

Isomerization of Vd to a fluorene derivative would involve a phenyl rather than a methyl migration. The nuclear magnetic resonance peak of D at +2.10 p.p.m. clearly excludes any structures in which the methyl group would not be attached to an aromatic ring.

The weight of the evidence for the structure of hydrocarbon A thus supports the formulation Va, although Vb cannot be decisively eliminated from consideration.

Acknowledgment.—Grateful acknowledgment is made of partial support of this work by a grant from the National Science Foundation (G6223) and of a Fellowship (1951–1952) to D.B.B. provided by the Atomic Energy Commission.

Experimental[10,11]

Reaction of Acetophenone with Polyphosphoric Acid.—A mixture of 1062 g. of polyphosphoric acid, 492 g. of acetophenone and 600 ml. of benzene was refluxed with vigorous stirring for 7 hours. The mixture turned green-black within 10 minutes and remained that color throughout the reflux period. The hot mixture was poured into 1.5 l. of ice-water. After the ice had melted, the mixture was filtered. The residue consisted of about 10 g. of a yellow substance (C), m.p. >300°. The yellow benzene layer of the filtrate was separated and extracted with two portions of dilute sodium hydroxide. Acidification of the basic extracts

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[10] All melting points are corrected and boiling points are uncorrected.

[11] Microanalyses by Miss Emily Davis, Mrs. Jean Fortney, Mrs. Esther Fett, Mrs. Katherine Pih and Mr. Josef Nemeth. Infrared spectra by Miss Elizabeth Petersen, Miss Helen Miklas and Mr. James Brader. Ultraviolet spectra by Mr. Homer Birch. Nuclear magnetic resonance spectra by Mr. Ben Shoulders.

caused the separation of 24 g. of colorless material, m.p. 106–113°. The solvent was removed from the yellow solution by distillation under reduced pressure. The residue was treated with 100 ml. of low-boiling petroleum ether and filtered. The yellow solid obtained was washed thoroughly with 150 ml. of low-boiling petroleum ether. The material (A) weighed 60.5 g. and melted at 176–179°. A sample was recrystallized four times from a mixture of benzene and cyclohexane; m.p. 180–181°.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92; mol. wt., 408. Found: C, 94.03; H, 6.17; mol. wt., 390, 430, 434 (ebullioscopic in benzene).

A mixture of 117 g. of acetophenone, 180 ml. of cyclohexane and 309 g. of polyphosphoric acid was subjected to the same treatment described above except that the reflux period was 6 hours. The yellow product (A) was washed with 30 ml. of cyclohexane; weight 15 g., m.p. 177–178.5° and mixed m.p. 177–179°.

The yellow substance (C), m.p. >300°, was treated with boiling benzene for 15 minutes and filtered. The yellow residue was dissolved in dimethylformamide and treated with Darco. Dilution with water caused the separation of a yellow material; this partially purified sample was dried thoroughly and submitted for infrared analysis. The spectrum exhibited absorption bands at 1650 and 1680 cm.$^{-1}$.

When the reaction was carried out employing 120 g. of acetophenone, 188 ml. of benzene and 300 g. of polyphosphoric acid with a reflux period of 5 hours, distillation of the organic layer gave approximately 25 g. of a yellow liquid, b.p. 130–147° (0.09–0.45 mm.). The yellow oil was treated with 2,4-dinitrophenylhydrazine reagent, and a brilliant red material was obtained. Four recrystallizations from 95% ethanol gave red crystals, m.p. 166–167°. No depression was observed in the melting point of a mixture of the compound with the 2,4-dinitrophenylhydrazone of dypnone.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.67; H, 4.51; N, 13.93. Found: C, 65.51; H, 4.67; N, 14.14.

When the same conditions were employed with the exception that the mixture was refluxed for one hour, 234 g. of acetophenone gave 75 g. of dypnone, and 97 g. of acetophenone was recovered.

A collection of crude samples of B obtained from several different runs was recrystallized from a benzene–cyclohexane mixture; a yellow crystalline material (B), m.p. 225–226°, was obtained. Four recrystallizations raised the melting point to 226–227°.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92; mol. wt., 408. Found: C, 94.06; H, 5.96; mol. wt., 411 (Rast camphor method).

The benzoic acid, obtained from the basic extraction of the yellow organic layer, was recrystallized twice from water; m.p. 121–122°, mixed m.p. 121–122°.

Reaction of Dypnone with Polyphosphoric Acid.—A mixture of 22.2 g. of dypnone, 50 ml. of benzene and 57 g. of polyphosphoric acid was refluxed for 7 hours. Efficient stirring was effected by the use of a Hershberg stirrer. The green-black mixture was poured into ice-water. Filtration yielded approximately 0.5 g. of yellow solid (C). The organic layer of the filtrate was washed with 10% sodium bicarbonate solution; about 0.5 g. of benzoic acid was obtained. The yellow benzene solution was evaporated to dryness under an air stream and triturated with 95% ethanol. Filtration yielded 3.2 g. of yellow solid, m.p. 160–168°. The solvent was removed from the filtrate and 2.5 g. of a yellow substance, m.p. 175–205°, was obtained. The lower-melting portion was recrystallized from a mixture of benzene and cyclohexane; m.p. 171–177°. A mixture of this sample with A melted at 174–177°.

Reaction of Dypnone with Acetophenone in the Presence of Polyphosphoric Acid.—A mixture of 11.1 g. of dypnone, 12.0 g. of acetophenone and 79 g. of polyphosphoric acid was subjected to the treatment just described. Trituration of the resulting oil with low-boiling petroleum ether gave 4.5 g. of bright yellow material, m.p. 157–190°. Recrystallization from a benzene–cyclohexane mixture yielded 2.5 g. of yellow solid, m.p. 165–175°, mixed m.p. with A 165–175°. From the filtrate of the recrystallization 1.5 g. of yellow material, m.p. 165–200°, was obtained.

4,4'-Dibromodypnone.—In a flask fitted with a thermometer, Hershberg stirrer and reflux condenser were placed 87 g. of *p*-bromoacetophenone, 68 g. of benzene and 210 g. of polyphosphoric acid. The mixture was refluxed for 5 hours at 85° and then poured into 300 ml. of water. The yellow compound which separated after about 12 hours was recrystallized repeatedly from methanol and submitted for analysis; 24 g. (35% yield) of material which had m.p. 105–107° was obtained.

Anal. Calcd. for $C_{16}H_{12}Br_2O$: C, 50.55; H, 3.20; Br, 42.05. Found: C, 50.56; H, 3.41; Br, 41.93.

Oxidation of the Yellow Hydrocarbon (A) with Nitric Acid.—Four grams of A was mixed with 40 ml. of concentrated nitric acid and 80 ml. of water, and the mixture was refluxed for 4 days. The yellow compound turned orange and finally became an orange-red oil. The mixture was decanted and the aqueous solution was allowed to cool. Filtration yielded a tan solid, which was recrystallized twice from water and once from benzene; m.p. 231–236°. Sublimation of the benzene-insoluble portion gave ivory crystals, m.p. 233–235°, mixed m.p. with *p*-nitrobenzoic acid 235–239°. The identity of this product was confirmed by a comparison of its infrared spectrum with that of *p*-nitrobenzoic acid.

Concentration of the filtrate obtained from the separation of the *p*-nitrobenzoic acid caused the separation of a colorless material. Three recrystallizations from water and one treatment with Darco gave white crystals, m.p. 120.5–121°, mixed m.p. with benzoic acid 121–122°.

The insoluble oil from the reaction mixture could not be purified by recrystallization from 95% ethanol.

Oxidation of the Yellow Hydrocarbon (A) with Chromic Anhydride.—To a mixture of 5 g. of A in about 50 ml. of boiling acetic acid was added in small portions a solution of 5 g. of chromic anhydride in 25 ml. of acetic acid. The reaction mixture remained a dark green color throughout the addition. The solution was refluxed for 20 minutes after the addition was completed and diluted with water. The mixture was filtered and the residue washed with water. An amorphous yellow material was obtained; m.p. 70–95° dec. The solid was dissolved in benzene and the benzene solution was washed thoroughly with dilute sodium bicarbonate solution. Acidification of the extracts gave a small amount of colorless material that melted above 300°. Attempted crystallizations from 95% ethanol and from benzene were unsuccessful. Attempted chromatographic purification with an alumina column gave similar results.

Hydrogenation of the Yellow Hydrocarbon (A).—A solution of 2.6 g. of A in 100 ml. of methylcyclohexane was hydrogenated at a pressure of 1400 p.s.i. and 100° for 3 hours in the presence of a Raney nickel catalyst. The catalyst was removed by filtration, and the filtrate was distilled until a residue of 10 ml. remained. Gray crystals formed in the residue. After two recrystallizations from a mixture of benzene and high-boiling petroleum ether, the colorless crystals melted at 175–176° and weighed 0.8 g.

Anal. Calcd. for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found: C, 93.22; H, 6.73.

Reaction of the Yellow Hydrocarbon (A) with Lithium Aluminum Hydride.—To a mixture of 2 g. of A and 100 ml. of dry ether was added 0.5 g. of lithium aluminum hydride. The immediate formation of a green-black color was noted. The reaction was stirred under a nitrogen atmosphere for 6.5 hours. After the addition of another 100-ml. portion of ether, dilute hydrochloric acid was used to decompose the mixture. The ether solution was extracted with dilute hydrochloric acid and evaporated to dryness. The remaining yellow oil was treated with boiling alcohol, and the mixture was filtered. The residue consisted of a colorless solid, m.p. 180–184°. It was recrystallized four times from acetic acid; m.p. 185–186°.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.37, H, 6.33.

Reduction of the Yellow Hydrocarbon (A) with Hydriodic Acid.—To a solution of 2 g. of A in 80 ml. of acetic acid was added 1 ml. of hydriodic acid (1.5 sp. gr.), and the mixture was warmed on the steam-bath for 10 minutes. The green-black solution was refluxed for one hour. The resulting dark red solution was diluted with an equal volume of water. Saturated sodium sulfite solution was added until the iodine color was removed. The colorless flocculent precipitate was removed by filtration and thoroughly washed with water. Recrystallization afforded two crops of light yellow crystals. Both crops had m.p. 184–185°. Further recrystallization afforded a product of m.p. 185–186°. No depression in melting point was observed with the dihydro derivative obtained by the lithium aluminum hydride reduction of A.

Reduction of the Yellow Hydrocarbon (A) with Sodium in Liquid Ammonia.—A solution of 10 g. of A in 150 ml. of toluene was prepared in a Dewar flask. Liquid ammonia was added until the total volume was approximately 350 ml.; 10 g. of sodium metal was added and the mixture stirred until solution was complete. (The first reductions were carried out using no organic solvent.) The solution turned blue for an instant, then deep maroon. At the top of the flask where the ammonia evaporated, the residue was white. After 3.5 hours, 100 ml. of water was added dropwise to destroy the excess sodium. The layers were separated, the solvent was evaporated and the product was recrystallized from methanol.

The first crystals of this material were very difficult to obtain. Chromatography on alumina was required before crystals could be obtained from the high-boiling petroleum ether solution.

Anal. Calcd. for $C_{32}H_{30}$: C, 92.69; H, 7.32. Calcd. for $C_{32}H_{32}$: C, 92.26; H, 7.74. Found: C, 92.41; H, 7.33.

Infrared analysis showed that the aliphatic double bonds of A had been saturated. Ultraviolet analysis showed absorption nearly equal to that of 1-methyl-3-phenylindane plus two molecules of phenylcyclohexane.

Reaction of the Yellow Hydrocarbon (A) with Butyllithium.—A mixture of 3.7 g. of A, 50 ml. of ether and 33 ml. of a 0.6*M* solution of butyllithium in ether was stirred for 1 hour under a nitrogen atmosphere. The solution, which remained green-black throughout the reaction period, was poured into a mixture of Dry Ice and ether and allowed to come to room temperature. Water was added to the ether solution and the aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether. The combined ether solutions were evaporated to dryness. Trituration with benzene of the resulting mixture of colorless solid and red liquid and filtration afforded about 0.5 g. of a yellow crystalline material. Two recrystallizations from absolute ethanol gave colorless crystals, m.p. 279–281°.

Anal. Calcd. for $C_{37}H_{34}O_2$: C, 87.02; H, 6.71; neut. equiv., 510. Found: C, 86.77, 86.85; H, 6.95, 6.87; neut. equiv., 505.

To an ether solution of diazomethane prepared from 6 g. of nitrosomethylurea was added 0.4 g. of the acid described above. The excess diazomethane was decomposed with acetic acid and the ether was removed by evaporation (hood). Filtration gave brilliant colorless crystals, which were recrystallized twice from methanol; m.p. 251–252°.

Anal. Calcd. for $C_{38}H_{36}O_2$: C, 87.00; H, 6.92. Found: C, 86.90; H, 6.87.

Reaction of the Yellow Hydrocarbon (A) with Maleic Anhydride.—A solution of 2 g. of A and 5 g. of maleic anhydride in 35 ml. of benzene was refluxed for 3 hours. The solution was evaporated to dryness and the resulting solid material was recrystallized from acetic acid; m.p. 203–205°. The colorless crystals turned yellow at the melting point.

Anal. Calcd. for $C_{36}H_{26}O_3$: C, 85.35; H, 5.17. Found: C, 85.51; H, 5.10.

During an attempted recrystallization from acetic anhydride, a mixture of colorless and yellow crystals separated. Physical separation was effected; the colorless substance melted at 203–205° and the yellow material at 177–179°, mixed m.p. with A 177–179°.

The method of Bergmann and Szmuszkowicz[2] was also employed. A mixture of 2.0 g. of A and 12.5 of maleic anhydride was heated for 3 hours at 160°. To the cooled reaction mixture was added 20 ml. of 95% ethanol. Filtration gave a slightly brown crystalline material, two recrystallizations of which yielded brilliant colorless crystals, m.p. 321° dec.

Anal. Calcd. for $C_{48}H_{32}O_{12}$: C, 72.00; H, 4.03. Found: C, 72.17; H, 4.26.

Reaction of the Yellow Hydrocarbon (A) with Nitrous Acid.—To a mixture of 0.5 g. of A partially dissolved in 25 ml. of acetic acid, 1 g. of sodium nitrite was added in small portions. The evolution of a brown gas was observed and a black substance which was soluble in the solvent formed in the upper part of the flask. The mixture was heated to the boiling point after the addition was complete. The solution turned black and produced an orange precipitate when it was diluted with water. Three recrystallizations from 95% ethanol yielded bright orange crystals, m.p. 193.5–194.5°.

Anal. Calcd. for $C_{32}H_{23}NO_2$: C, 84.74; H, 5.11; N, 3.09. Found: C, 84.52; H, 5.15; N, 3.18.

When the reaction was repeated without heating the mixture, dilution with water gave a colorless solid. Treatment with Darco and three recrystallizations from 95% ethanol yielded a product that melted at 133–135° dec., the analysis of which did not correspond to any logical empirical formula. The treatment of the colorless material with boiling 10% hydrochloric acid for 15 minutes converted it into an orange mass. Recrystallization from a 95% ethanol–acetic acid mixture gave the orange product described above, m.p. 194–195°, mixed m.p. 194–195°.

Action of Polyphosphoric Acid on "Dypnopinacol" (III).—A mixture of 5 g. of III,[12] m.p. 160–162°, 70 ml. of benzene and 53 g. of polyphosphoric acid was refluxed with stirring for 5.5 hours. The color of the mixture remained yellow during this period. A brilliant yellow precipitate formed in the aqueous layer when the reaction mixture was poured into water. Separation and evaporation of the nearly colorless benzene solution gave only a trace of oil. The yellow solid was partially purified by the same procedure previously described for C. The infrared spectrum showed it to be identical with C.

Action of Polyphosphoric Acid on "α-Dypnopinacolone" (I).—This reaction was carried out in the same manner described above; 1 g. of I,[3c] m.p. 135–137°, and about 30 g. of polyphosphoric acid were employed. In addition to A, an oil was obtained by evaporation of the benzene solution. Trituration with low-boiling petroleum ether caused the crystallization of a yellow solid, m.p. 134–136°, mixed m.p. with I 134–136°.

Action of Polyphosphoric Acid on "α-Isodypnopinacolone" (II).—One gram of II,[3c] m.p. 134–135°, was added to 95 g. of polyphosphoric acid at 80°. The temperature of the mixture was raised to 150° and the brown-black liquid was stirred at this temperature for 20 minutes. When the mixture was poured into 300 ml. of water, a yellow solid separated. Recrystallization from 95% ethanol gave a nearly colorless product, m.p. 132–134°, mixed m.p. with II 133–135°. The reaction was also attempted under conditions similar to those employed in the preparation of A, and II was recovered unchanged from the benzene solution.

Rearrangement of the Yellow Hydrocarbon (A).—Twenty grams of A was suspended in 150 ml. of acetic acid. The mixture was heated to reflux and treated with 10 ml. of 48% hydrobromic acid. After two hours the mixture was allowed to cool to room temperature. The green-black color of the mixture at the beginning of the reaction had been replaced by a faint yellow color. The colorless crystals were removed by filtration, m.p. 163–164°, yield 19 g.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 94.03; H, 6.03.

9-Methyl-1,3,9-triphenylfluorene.—To a solution of *n*-butyllithium prepared from 5.5 g. of *n*-butyl bromide and 0.27 g. of lithium in 150 ml. of absolute ether was added a solution of 3.3 g. of 1,3,9-triphenylfluorene[13] in 200 ml. of absolute ether. The resulting solution immediately became deep red. After stirring the solution for 15 minutes under a nitrogen atmosphere, 1 ml. of methyl iodide in 25 ml. of absolute ether was added. The solution was then refluxed for 7 hours after which time the color of the solution was light yellow. The ether layer was separated, dried over calcium chloride and distilled *in vacuo*. The residue was crystallized from ether-pentane and afforded two crops of colorless crystals, the first 1.23 g. of m.p. 161–167° and the second 0.40 g. of m.p. 162–166°. Further recrystallization of the combined material afforded colorless crystals of m.p. 171–172°, mixed m.p. with D 150–169°.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 94.01; H, 9.57.

Methyl Derivative of Hydrocarbon (D).—To a solution of *n*-butyllithium prepared from 3.5 g. of *n*-butyl bromide and 0.65 g. of lithium in 150 ml. of absolute ether was added a solution of 3.0 g. of D in 150 ml. of absolute ether and 50 ml. of benzene. The resulting solution was stirred for 15 minutes under an atmosphere of dry nitrogen. Then a solu-

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(12) D. Ivanov, *Compt. rend.*, **199**, 729 (1934).

(13) E. P. Kohler and L. W. Blanchard, Jr., THIS JOURNAL, **57**, 367 (1935).

tion of 4.7 g. of methyl iodide in 25 ml. of absolute ether was slowly added to the deep red colored solution with vigorous mechanical stirring. The solution was refluxed for 6.5 hours. During this time the color of the solution became light yellow. Any unreacted butyllithium was destroyed by the addition of 50 ml. of ethanol. The ether solution was washed with water until neutral and dried over calcium chloride. The ether was distilled *in vacuo* and the oil residue crystallized from benzene–methanol. Colorless crystals, m.p. 170–175°, 1.16 g., were obtained. A sample was recrystallized twice from ether–pentane. The melting point of the purified product was 163–164°. Further recrystallization failed to give material of higher m.p. A mixture of the purified material with D melted at 150–158°.

Anal. Calcd. for $C_{33}H_{26}$: C, 93.80; H, 6.20. Found: C, 93.63; H, 6.20.

Oxidation of Hydrocarbon (D). (a). To a solution of 1 g. of D in 20 ml. of pyridine was added 1.2 g. of finely powdered potassium permanganate and 1 ml. of water. The mixture was swirled and allowed to stand at room temperature for an hour. The excess permanganate was destroyed by the addition of 25 ml. of methanol. The oxides of manganese were removed by filtration through a sintered glass funnel. The filtrate was diluted with 25 ml. of water and made acid (litmus) with hydrochloric acid. A colorless solid separated; 0.7 g., m.p. 97–166°. The precipitate was dissolved in 50 ml. of ether, and the ether solution was extracted with three 20-ml. portions of saturated sodium bicarbonate solution. Acidification of the extracts failed to yield a solid acid. The neutral fraction was dried over sodium sulfate. The ether solution was concentrated and then diluted with low-boiling petroleum ether. A colorless crystalline precipitate separated, m.p. 172–173°. A mixture with the hydrolysis product below melted at 173–173.5°.

(**b**).—To a solution of 19 g. of D in 200 ml. of carbon tetrachloride were added 8.5 g. of N-bromosuccinimide and 0.58 g. of benzoyl peroxide. The solution was refluxed for 4 hours. The succinimide was removed by filtration. The filtrate was dried over sodium sulfate. The solvent was evaporated and the viscous residue was dissolved in 250 ml. of acetone. To the acetone solution 50 ml. of water was added and the resulting solution was refluxed for 15 hours. To this was added 8.5 g. of silver nitrate dissolved in aqueous acetone of the same concentration as the hydrolysis solution. The precipitated silver bromide was removed by filtration. The acetone solution was treated with Darco and filtered again. Ten grams of colorless crystals was obtained by dilution with water, m.p. 172–173°. The analysis corresponded to a dimeric ether.

Anal. Calcd. for $(C_{32}H_{23})_2O$: C, 92.50; H, 5.58. Found: C, 92.48; H, 5.87.

To a solution of 9.5 g. of the above ether in 100 ml. of dioxane was added a solution of 10 ml. of concd. sulfuric acid in 150 ml. of water. The mixture was refluxed for 4 days. The cooled solution was diluted with water and extracted with six 50-ml. portions of ether. The combined ether extracts were washed with 5% sodium bicarbonate solution and water. The ether was distilled and the residue crystallized from acetone. The colorless crystals had m.p. 172–173° and weighed 3.22 g. An additional 0.75 g., m.p. 174–175°, was obtained by allowing the filtrate to stand. The two crops were combined and recrystallized from acetone, m.p. 174–175°. No depression in m.p. was observed upon mixing with the carbinol obtained by permanganate oxidation of D.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.28; H, 5.87.

Nuclear Magnetic Resonance Spectra.—The nuclear magnetic resonance spectra were run at 40 megacycles and 20° on a Varian model V-4200 B instrument. Methylene chloride was employed as an external standard, and the scale was determined by the sideband method using a Hewlett–Packard model 200-CD audio oscillator. The chemical shifts are expressed in parts per million with respect to pure water, the positive values being on the side of higher frequency.

The spectrum of hydrocarbon A, run as a saturated solution in carbon tetrachloride, showed peaks at −1.82 and +3.08 p.p.m. in addition to highly split absorption below −2.22 due to the aromatic hydrogens. The ratio of the area of the +3.08 p.p.m. peak to that of the −1.82 p.p.m. peak is 3.0 to 2.1.

The spectrum of compound D as a 20% solution in carbon tetrachloride exhibited peaks at +2.10 and −0.35 p.p.m., having areas in the ratio 3.0 to 1.25, in addition to the aromatic absorption below −2.00 p.p.m. Peaks of compound E as a 20% solution in carbon tetrachloride were observed at +2.08 and +3.23 p.p.m., having areas in the ratio 3.0 to 2.0, as well as aromatic absorption below −2.15 p.p.m. The spectrum of 1,3,9-triphenylfluorene as a 20% solution in carbon tetrachloride showed only one peak above −2.00 p.p.m., a peak at −0.35 p.p.m.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MASSACHUSETTS]

O-Acylhydroxylamines. II. O-Mesitylenesulfonyl-, O-*p*-Toluenesulfonyl- and O-Mesitoylhydroxylamine[1]

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RECEIVED DECEMBER 5, 1959

O-Mesitylenesulfonyl- and O-*p*-toluenesulfonylhydroxylamine have been prepared by the hydrofluoric acid and perchloric acid cleavages of the corresponding *t*-butyl N-arenesulfonoxycarbamates. The structures of the O-arenesulfonylhydroxylamines were established by (a) iodometric analysis, (b) reaction with acetone which gave the corresponding O-sulfonylacetoximes and (c) infrared examination. O-Mesitoylhydroxylamine was prepared similarly from *t*-butyl N-mesitoyloxycarbamate. Reaction of O-mesitoylhydroxylamine with dibenzylamine gave 1,1-dibenzylhydrazine.

Prior to the current study the only simple N-unsubstituted O-sulfonylhydroxylamine known was hydroxylamine-O-sulfonic acid[2] (HOS, I, R = H). In connection with work on amination reactions[3] it was desirable to have available O-sulfonyl derivatives of hydroxylamine which might be soluble in

H_2NOSO_2OR I

H_2NOCOR

IIa, R = C_6H_5—

IIb, R = 2,4,6-$Me_3C_6H_2$—

organic solvents. Keller and Smith[4] attempted to prepare the methyl and ethyl esters of HOS (I, R = CH_3 and C_2H_5) with only partial success. In the present study we have succeeded in preparing O-arenesulfonylhydroxylamines by a method analogous to that which had been used in the synthesis of O-acylhydroxylamines.

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(2) F. Sommer, O. F. Schulz and M. Nassau, *Z. anorg. u. allgem. Chem.*, **147**, 142 (1925).

(3) L. A. Carpino, C. A. Giza and B. A. Carpino, THIS JOURNAL, **81**, 955 (1959).

(4) R. N. Keller and P. A. S. Smith, *ibid.*, **68**, 899 (1946).