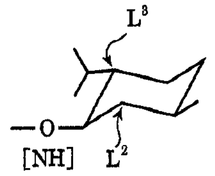
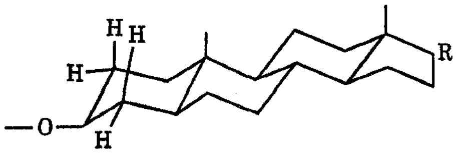
the amide examples fit the general scheme of L^2 being smaller than L^3.

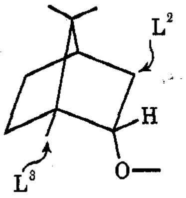
The carbinyl carbon in cholesterol (**7**) is flanked on each side by a methylene group; accordingly one might anticipate that there would be little difference in the α-CF$_3$ nmr resonances for these MTPA diastereomers. This is what we observe.



6, *l*-menthyl



7, cholesteryl



8, *d*-bornyl

However, we have checked both (−)- and (+)-bornyl MTPA esters and confirm that the *d*-bornyl ester with the *S* configuration at the carbinyl carbon shows the α-CF$_3$ resonance of the (*R*)-MTPA ester downfield with respect to that of the (*S*)-MTPA ester. In borneol the methylene group at C-2 is clearly designated L^2 (smaller) while the quaternary carbon at C-2 is L^3 (larger). Thus this lone example stands as a clear exception to the general correlation scheme for the α-CF$_3$ resonances.

Finally, the presence of heteroatoms in either L^2 or L^3, as in entries 6 and 7, Table I, may profoundly change the molecular conformations upon which the correlation is based. The fact that the correlation does hold in a case such as ethyl lactate does not necessarily mean that this will be generally so for all α-hydroxy esters. These examples must be taken only as indication that it may be possible to successfully extend the correlation to these types by further study.

Experimental Section

Instruments.—All ^{19}F resonance measurements were made on a Varian XL-100 nmr spectrometer[19] at 94.1 MHz using 5-mm nmr tubes, CDCl$_3$ solvent, and external trifluoroacetic acid (TFA) as standard. The TFA was contained in a sealed, precision ground, coaxial cell which was necked down at the bottom to a concentric 25 × 2 mm o.d. capillary stem containing the degassed TFA.

Reagent.—(+)-α-Methoxy-α-trifluoromethylphenylacetyl chloride, (+)-MTPA-Cl, was prepared from (*R*)-(+)-α-methoxy-α-trifluoromethylphenylacetic acid,[5] (*R*)-(+)-MTPA, according to the previously described method.[3c,4]

MTPA Derivatives.—The MTPA esters and amides were prepared from (+)-MTPA-Cl according to the previously described procedure.[4] Two derivatives were usually prepared, one from enantiomerically pure carbinol and amine and (+)-MTPA-Cl and a second using MTPA-Cl which was about 70% (+)-MTPA-Cl and 30% (−)-MTPA-Cl. This permitted the unequivocal establishment of the nmr chemical shift for each diastereomer.

Chiral Carbinols and Amines.—These compounds were available from previous studies in these laboratories by the methods indicated by the references to Table I.

Acknowledgment.—We are grateful to Dr. Lois Durham, Director of the Stanford Chemistry Department Nmr Laboratories, for her continued help and cooperation.

[19] We gratefully acknowledge Grant GP 28142 from the National Science Foundation to the Stanford Chemistry Department for the purchase of this instrument.

The 2:1 Adduct from Diphenylketene and 1,1-Diphenylethylene. 3,4-Dihydro-1,4,4-triphenyl-2-naphthyl Diphenylacetate[1,2]

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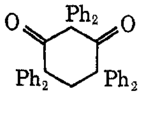
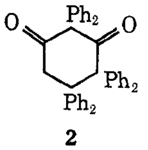
Received December 29, 1972

The 2:1 adduct from the thermal reaction of diphenylketene and 1,1-diphenylethylene has been conclusively identified as 3,4-dihydro-1,4,4-triphenyl-2-naphthyl diphenylacetate, and part of the degradation of the adduct reported in 1958 by Farooq and Abraham has been repeated and reinterpreted.

The 2:1 adduct derived from the reaction of diphenylketene with 1,1-diphenylethylene at 150° was first obtained by Staudinger and Suter[3] in 1920. Their original structural proposal, 2,2,4,4,6,6-hexaphenylcyclohexane-1,3-dione (**1**), was revised by Farooq and Abraham[4] in 1958 to 2,2,4,4,5,5-hexaphenylcyclohexane-1,3-dione (**2**).



1



2

The later proposal was bolstered by results obtained through a degradation of the 2:1 adduct, a degradation which led eventually to some 1,1,4,4-tetraphenyl-1-butene, claimed to be identical with an authentic, independently synthesized sample of this hydrocarbon. Salient features of degradation are outlined in Scheme I.

In the course of a thorough kinetic investigation of the cycloaddition reaction between diphenylketene and 1,1-diarylethylenes[5] we secured infrared and nmr spectral data on five adducts of this class. These data were inconsistent with cyclohexanedione structural postu-

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[1] Supported by the National Science Foundation and Hoffmann-La Roche Inc.

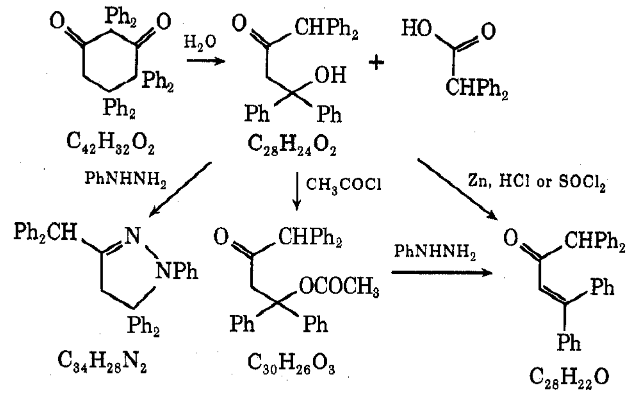
[2] A preliminary account of this work has appeared: J. E. Baldwin, M. F. Breckinridge, and D. S. Johnson, *Tetrahedron Lett.*, 1635 (1972).

[3] H. Staudinger and E. Suter, *Ber. Deut. Chem. Ges.*, **53**, 1092 (1920).

[4] M. O. Farooq and N. A. Abraham, *Bull. Soc. Chim. Fr.*, 832 (1958).

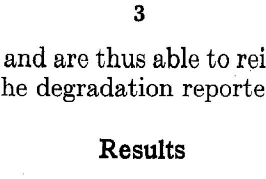
[5] J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **92**, 4868 (1970).

SCHEME I[4]



lates **1** and **2**, and led us to a repetition of the degradative studies reported by Farooq and Abraham.

We thereby found that the 2:1 adduct is 3,4-dihydro-1,4,4-triphenyl-2-naphthyl diphenylacetate (**3**),[2,6,7] and



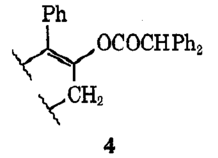
3

have unraveled and are thus able to reinterpret satisfactorily most of the degradation reported earlier.

Results

The 2:1 adduct from diphenylketene and 1,1-diphenylethylene has prominent infrared bands at 1745 and 1490 cm⁻¹ and, in addition to absorptions from 29 aromatic protons at τ 2.5–3.4, singlets at τ 5.10 and 6.55 with integrated intensities appropriate to one and two protons, respectively.

These data were viewed as suggestive of an enol diphenylacetate partial structure (**4**).



4

The diphenylacetate ester of 2,3,4-triphenyl-1-naphthol, by comparison, shows a singlet for the α H at τ 5.15.[8]

Hydrolysis of the 2:1 adduct with alcoholic sodium hydroxide and subsequent acidification gave diphenylacetic acid, while reduction of the adduct with lithium aluminum hydride gave 2,2-diphenylethanol. Both results are easily comprehended in terms of partial formula **4**.

There was initial surprise, however, when we found that, in addition to diphenylacetic acid or diphenylethanol, both hydrolysis and reduction gave the same product, mp 195–196°, having the formula $C_{28}H_{22}O_2$. Farooq and Abraham had identified this material, obtained through hydrolysis, as 4-hydroxy-1,1,4,4-tetraphenylbutan-2-one, $C_{28}H_{24}O_2$.

This two-hydrogen discrepancy between previously assigned and actual molecular formula, easily understandable since the earlier workers had depended on combustion analyses alone, was unmistakable through mass spectrometric molecular weight determinations. The discrepancy was sustained in the three degradation products from "$C_{28}H_{24}O_2$" in Scheme I; all three were found to have two hydrogens fewer than originally believed.

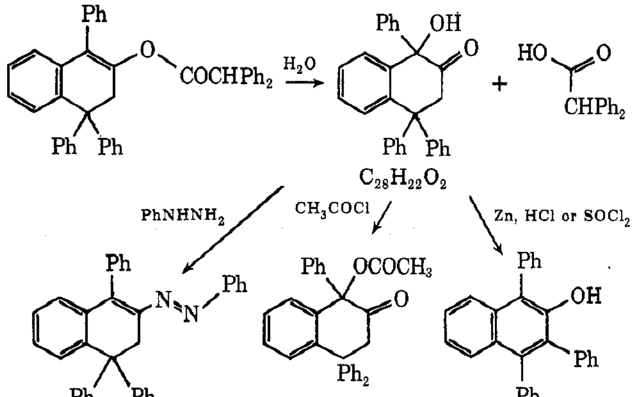
The nmr spectrum of the $C_{28}H_{22}O_2$ product showed absorptions from three nonaromatic protons: a singlet at τ 5.46 and an AB pattern centered at τ 6.35 with J_{AB} = 12.5 Hz. The singlet vanished when the solution of sample was shaken momentarily with D_2O.

In the infrared, there were indications of carbonyl (1725 cm⁻¹) and hydroxyl (3450 cm⁻¹) functionality. The hydroxyl reacted with acetyl chloride smoothly to give a keto ester (1743 and 1730 cm⁻¹) having nonidentical geminal protons as before, centered at τ 6.50 (J_{AB} = 16 Hz).

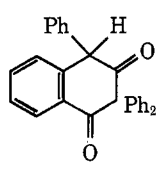
Reaction of the keto alcohol with phenylhydrazine gave an oxygen-free derivative in which the geminal protons now appeared as a sharp singlet at τ 6.1.

With these reactions and spectral data as guides, and conscious of the extreme ease with which a doubly benzylic and α-to-carbonyl hydrogen might suffer autoxidation by air, the structural postulates of Scheme II were made.

SCHEME II



The diphenylketene dimer **5** must be prepared and recrystallized under a nitrogen atmosphere to avoid air oxidation.[8] Heller and coworkers[6] have been able to isolate and observe nmr absorptions appropriate to the unoxidized hydrolysis products **6** and **7** by conducting the basic hydrolysis of **3** under an inert atmosphere.



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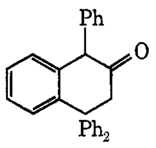

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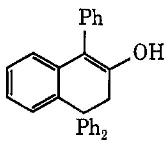

7

The final reaction in Scheme II, acid-catalyzed dehydration, would then require a molecular rearrangement. Acid-catalyzed formation of the enol form **8**

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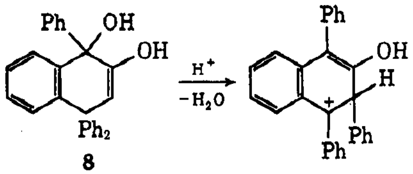
(6) An independent investigation has also led to the correct structural representation for the 2:1 adduct: J. S. Hastings, H. G. Heller, and R. M. Megit, The Chemical Society Autumn Meeting, University of York, Sept 27–30, 1971, Abstract A25.

(7) J. S. Hastings and H. G. Heller, *J. Chem. Soc., Perkin Trans. 1*, 1839 (1972).

(8) H. Das and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **84**, 965 (1965).

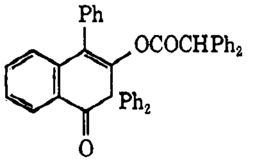
would greatly facilitate ionization of the protonated alcohol function with concomitant or rapidly following 1,2-phenyl shift to the other end of the allylic cationic system. Loss of a proton from **9** would then afford 1,3,4-triphenyl-2-naphthol.



8

9

The triphenylnaphthol we obtained had mp 232–233°. Das and Kooyman[8] secured a small amount of a triphenylnaphthol, mp 228–231°, from the reaction of the diphenylacetate **10** with red phosphorus and hydriodic acid in a sealed tube at 200–210° for 70 hr.

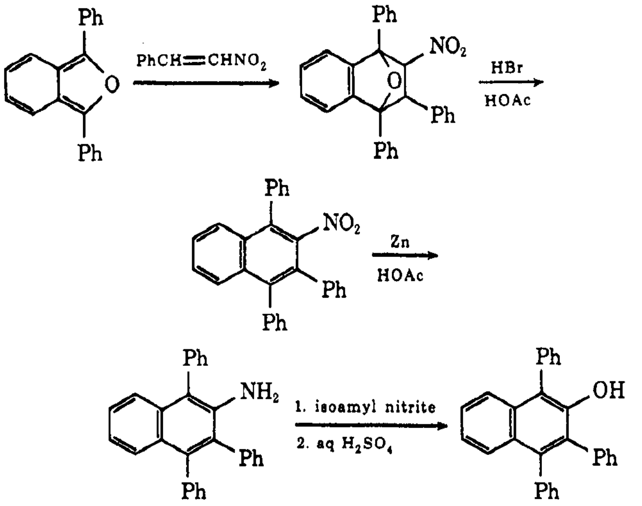


10

While they proposed[8] a mechanistic rationale for the formation of 1,3,4-triphenyl-2-naphthol derivatives under these reaction conditions, they carefully refrained from claiming a sure structural characterization of the degradation product.

To make our identification secure, then, we prepared an authentic sample through the route given in Scheme III.

SCHEME III



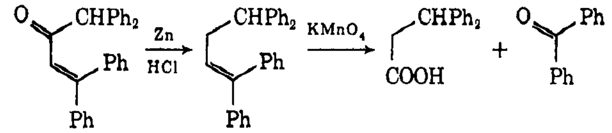
Diels–Alder reaction between β-nitrostyrene[9] and 1,3-diphenyl[c]benzofuran[10,11] gave the known oxidotetrahydronaphthalene adduct,[11] which was converted[12] through the four steps shown in Scheme III to the desired 1,3,4-triphenyl-2-naphthol, mp 231–233°. This material and the sample obtained through acid-catalyzed rearrangement of the $C_{28}H_{22}O_2$ product (Scheme II) proved to be identical in infrared and nmr spectral characteristics.

Thus the proposed revision (Scheme II) of the degradation first studied by Farooq and Abraham is anchored by a direct correlation between an authentic sample and a degradation product, and the other proposed formulations are thereby strengthened. Staudinger's 2:1 adduct now seems properly represented by structure **3**.

Discussion

Everything fits, except the report[4] that the product of mp 231°, thought to be 1,1,4,4-tetraphenyl-3-buten-2-one but now known to be 1,3,4-triphenyl-2-naphthol, may be reduced with zinc amalgam in acidic media to give 1,1,4,4-tetraphenyl-1-butene, identical with an authentic sample, and oxidized by permanganate to benzophenone and β,β-diphenylpropionic acid (Scheme IV).

SCHEME IV[4]

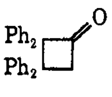


We have been unable to clarify this claim, since all our attempts to reduce the naphthol with zinc amalgam and hydrochloric acid have been unsuccessful.

Authentic 1,1,4,4-tetraphenyl-1-butene, mp 97–98°, was prepared by Farooq and Abraham[4] according to a procedure introduced by Wittig and Lupin.[13,14] A sample of mp 103° secured by other means in 1970,[15] which exhibited an appropriate nmr spectrum, is identical with 1,1,4,4-tetraphenyl-1-butene prepared according to Wittig and Lupin.[16] Thus either the zinc amalgam reduction of 1,3,4-triphenyl-2-naphthol reported earlier resulted in extensive isomerization or the comparison of the two samples of 1,1,4,4-tetraphenylbut-1-ene through a mixture melting point determination may have lacked adequate discriminatory sensitivity.

What mechanism may be responsible for formation of the 2:1 adduct **3**?

One possibility is through formation of a dipolar intermediate **12**, either directly or subsequent to a rate-determining cycloaddition producing the cyclobutanone **11**.



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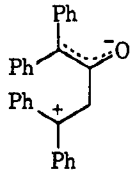
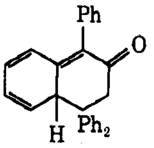


12



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The dipolar species **12** could cyclize intramolecularly, affording system **13**, which could easily react further in the presence of excess diphenylketene to yield the observed 2:1 product. Alternatively, **13** may be

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[9] D. E. Worrall, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N.Y., 1941, p 413.

[10] C. R. Hauser, M. T. Tetenbaum, and D. S. Hoffenberg, *J. Org. Chem.*, **23**, 861 (1958).

[11] M. S. Newman, *ibid.*, **26**, 2630 (1961).

[12] *Cf.* C. F. Allen, A. Bell, and J. W. Gates, Jr., *ibid.*, **8**, 373 (1943).

[13] G. Wittig and F. von Lupin, *Ber. Deut. Chem. Ges.*, **61**, 1627 (1928).

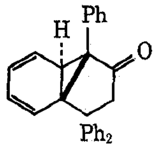
[14] G. Wittig, *ibid.*, **64**, 437 (1931).

[15] G. Köbrich and I. Stöber, *Chem. Ber.*, **103**, 2744 (1970).

[16] D. S. Johnson, unpublished work.

envisaged as arising directly through Diels–Alder combination of diphenylketene and 1,1-diphenylethylene.

Finally, the unusual behavior of diphenylketene in its cycloadditions with alkoxyacetylenes,[17,18] if repeated with 1,1-diphenylethylene, would give as the initial 1:1 adduct structure **14**, an assemblage of atoms just a six-centered hydrogen migration to oxygen away from the enol **15**. As a variation on this possibility, the initial adduct **14** could react with diphenylketene with realization of its potential for a cyclopropylcarbinyl to homoallylic skeletal rearrangement to give **16** and, in turn, through a hydrogen transfer, **3**.



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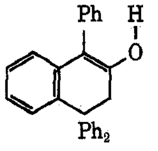

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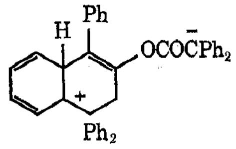

16

Clarification of the structure of the 2:1 adduct thus does not settle any mechanistic problems; it merely poses them. Several reasonable possibilities exist; choices among them may be made only through additional and carefully engineered experimental tests.

Experimental Section

Melting points were obtained on a Kofler micro heating stage using a calibrated thermometer; boiling points are uncorrected. Infrared spectra were recorded on a Beckman IR-7 or a Beckman IR-5A using chloroform solutions unless otherwise noted. Nuclear magnetic resonance spectra were obtained on Varian Associates T-60, HA-100, and XL-100 spectrometers using deuteriochloroform solutions unless otherwise noted and are reported in τ units, parts per million relative to tetramethylsilane at τ 10. Ultraviolet spectra were obtained using a Cary Model 15. Mass spectra were obtained on a CEC-110-21B and elemental analyses were determined by Dr. Susan Rottschaefer.

Diphenylketene was prepared through the dehydrohalogenation of diphenylacetyl chloride[19] with dry triethylamine in benzene;[5] it had bp 100–101° (1 mm) [lit.[20] bp 119–120° (3.5 mm)].

1,1-Diphenylethylene was prepared through reaction of phenylmagnesium bromide with ethyl acetate, followed by dehydration of the resultant carbinol with 20% sulfuric acid. The product had bp 129–131° (10 mm) [lit.[21] bp 113° (2 mm)].

Cycloaddition of Diphenylketene and 1,1-Diphenylethylene.—In a combustion tube were placed 8.75 g (42 mmol) of diphenylketene and 4.07 g (23 mmol) of 1,1-diphenylethylene. The tube was degassed on a vacuum line and sealed under 330 mm of nitrogen, then heated at 150° for 3 days. The tube was allowed to cool and was opened carefully. The reaction mixture was dissolved in a minimum of benzene, then petroleum ether (bp 30–60°) was added until precipitation seemed imminent. The following day a crystalline material was collected. This crude product, 7.4 g (58%), mp 170–173°, was washed with acetone and recrystallized from benzene–petroleum ether to afford material of mp 185–186° [lit.[4] mp 182°]; nmr absorptions at τ 2.7–3.5 (29 H), 5.10 (s, 1 H), and 6.55 (s, 2 H); mass spectrum M$^+$ *m/e* 568 (calcd for $C_{42}H_{32}O_2$, 568).

Anal. Calcd for $C_{42}H_{32}O_2$: C, 88.70; H, 5.67. Found:[4] C, 89.15; H, 5.72.

Lithium Aluminum Hydride Reduction of the 2:1 Adduct.—In a 250-ml round-bottomed flask were placed 1.0 g (26 mmol) of lithium aluminum hydride and 100 ml of THF. The flask was cooled and 3.75 g (6.6 mmol) of the 2:1 adduct dissolved in 50 ml of THF was added; the reaction mixture was stirred for 1 hr at room temperature. After cooling again, 1 ml of water was added, followed by 1 ml of 15% potassium hydroxide solution and 2 ml of water. The reaction mixture was filtered and the solid cake obtained was thoroughly washed with ether. The total filtrate was concentrated on a steam bath to 5 ml and was purified by column chromatography on Woelm acidic alumina to give 0.87 g (34%) of a solid having mp 195–196° [lit.[4] mp 195–196°]; ir (Nujol mull) 1725 (CO) and 3450 cm^{-1} (OH); nmr τ 2.5–3.3 (aromatic), 5.46 (s, 1 H), and 6.35 (AB pattern, J_{AB} = 12.5 Hz, 2 H); mass spectrum M$^+$ *m/e* 390 (calcd for $C_{28}H_{22}O_2$, 390).

Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.13; H, 5.68. Found:[4] C, 86.18; H, 5.62.

After elution was complete, the alumina was subject to continuous extraction with methanol for 8 hr. The resulting solution was concentrated and the residue was sublimed twice at 60° to give a product melting at 52–53°, identified as 2,2-diphenylethanol [lit.[22] mp 54–55°] through direct spectral comparisons with an authentic sample prepared through reduction of diphenylacetic acid with lithium aluminum hydride.

Alcoholic Sodium Hydroxide Hydrolysis of the 2:1 Adduct.—In a 100-ml round-bottomed flask were combined 0.2 g (9.9 mmol) of sodium, 20 ml of 95% ethanol, and a few drops of water. After all the sodium had reacted, 0.15 g (0.26 mmol) of the 2:1 adduct was added, and the mixture was heated to reflux for 1 hr. An additional 25 ml of ethanol was added and the mixture was heated to reflux for another 15 min. It was then concentrated to about 5 ml, allowed to cool, and diluted with 25 ml of water; the white precipitate which formed was collected and recrystallized from benzene–petroleum ether; there was obtained 0.10 g (95%) of product, mp 193–196° (lit.[4] mp 195–196°), identical with that obtained from the lithium aluminum hydride reduction. The filtrate was acidified with dilute acid and the resulting solid was filtered and dried; it had mp 144–146° (lit.[23] mp 148°); admixture of authentic diphenylacetic acid caused no melting point depression.

Acetylation of the Reduction Product.—In a 10-ml round-bottomed flask were placed 0.15 g (0.38 mmol) of the reduction product and 4 ml (4.4 g, 5.6 mmol) of freshly distilled acetyl chloride. The reaction mixture was heated to reflux overnight, and then the excess acetyl chloride was removed at reduced pressure. The crude product was dissolved in methylene chloride and precipitated by the addition of petroleum ether. After two recrystallizations there was obtained 0.11 g (65%) of product: mp 165–168° (lit.[4] mp 163°); ir (CCl$_4$) 1743 (CO), 1730 cm^{-1} (CO); nmr τ 2.6–3.2 (aromatic), 6.50 (AB pattern, J_{AB} = 16 Hz, 2 H), and 7.9 (s, 3 H); mass spectrum M$^+$ *m/e* 432 (calcd for $C_{30}H_{24}O_3$, 432).

Anal. Calcd for $C_{30}H_{24}O_3$: C, 83.31; H, 5.59. Found:[4] C, 83.43; H, 5.91.

Phenylhydrazone of the Reduction Product.—To 0.94 g (2.4 mmol) of the reduction product in a 10-ml round-bottomed flask was added 1 ml of acetic acid and 1 ml (1.1 g, 0.10 mmol) of phenylhydrazine. The mixture was heated at 100° for 15 min. The orange solid obtained was collected and recrystallized from methylene chloride–acetone. The purified derivative (0.60 g, 54%) had mp 278–281° (lit.[4] mp 171°); ir (CCl$_4$) 1448 (m), 1299 (m), 696 (s), and 683 cm^{-1} (s); nmr τ 2.4–3.2 (aromatic), 6.1 (s, 2); mass spectrum M$^+$ *m/e* 462 (calcd for $C_{34}H_{26}N_2$, 462).

Anal. Calcd for $C_{34}H_{26}N_2$: C, 88.28; H, 5.67; N, 6.06. Found:[4] C, 88.16; H, 5.58; N, 5.80.

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[17] H. Teufel and E. F. Jenny, *Tetrahedron Lett.*, 1769 (1971), and references cited therein.

[18] Another instance of such a "crisscross" thermal addition to a diene unit has been uncovered in the reaction of 1,8-dehydronaphthalene with cyclopentadiene: J. Meinwald and G. W. Gruber, *J. Amer. Chem. Soc.*, **93**, 3802 (1971).

[19] L. Hellerman, M. L. Cohen, and R. E. Hoen, *ibid.*, **50**, 1725 (1928).

[20] L. I. Smith and H. H. Hoehn, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 357.

[21] C. F. H. Allen and S. Converse, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 226.

[22] "Dictionary of Organic Compounds," Vol. III, 4th ed, Oxford University Press, New York, N. Y., 1965, p 1280.

[23] "Handbook of Tables for Organic Compound Identification," 3rd ed, compiled by Z. Rappoport, The Chemical Rubber Co., Cleveland, Ohio, 1967, p 202.

1,3,4-Triphenyl-2-naphthol.—Dry gaseous hydrogen chloride was bubbled through a solution of 100 mg (0.25 mmol) of the reduction product in 5 ml of acetic acid at reflux for 1.5 hr. The reaction mixture was cooled and poured into water. The aqueous solution was extracted with two 10-ml portions of ether; the ethereal solution was dried over sodium sulfate, filtered, and concentrated to give a crystalline material which, after being washed with cold, anhydrous ether, was collected. There was obtained 80 mg (84%) of 1,3,4-triphenyl-2-naphthol, mp 231°. Recrystallization from benzene–ligroin gave crystals of mp 232–233°; ir 3400 (s), 1190 (s), 1280 (s), and 950 cm^{-1} (s); nmr τ 2.4–3.0 (aromatic), 4.9 (s, 1 H); mass spectrum M$^+$ *m/e* 372 (calcd for $C_{28}H_{20}O$, 372).

Anal. Calcd for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 90.11; H, 5.55.

β-Nitrostyrene was prepared according to the "Organic Syntheses" procedure[9] on a 0.2-mol scale; after recrystallization from ethanol the product (23.7 g, 79%) had mp 58–59° (lit.[9] mp 59°).

3-Phenylphthalide from the reduction of *o*-benzoylbenzoic acid with zinc dust in aqueous acetic acid had mp 114–115° (lit.[10] mp 114–115°).

1,3-Diphenyl[*c*]benzofuran.—Phenylmagnesium bromide and 3-phenylphthalide in a solution of THF and ether led to the benzofuran product; after recrystallization from benzene–ethanol, it had mp 129–131° (lit.[10] mp 128–131°).

1,2,4-Triphenyl-3-nitro-1,4-oxido-1,2,3,4-tetrahydronaphthalene was prepared by heating 0.7 g (2.6 mmol) of 1,3-diphenyl[*c*]benzofuran, 0.4 g (2.6 mmol) of nitrostyrene, and 20 ml of ethanol at reflux for 3 hr. The reaction mixture was cooled and filtered; the pale yellow material collected (1.1 g, 100%) had mp 155–158° (lit.[12] mp 163°).

1,2,4-Triphenyl-3-nitronaphthalene.—A suspension of 0.85 g (2.0 mmol) of the oxidotetrahydronaphthalene addition product in 5 ml of 30–32% hydrobromic acid in acetic acid (Eastman Organic Chemicals) was allowed to stand for 4 hr. It was then heated to reflux for several minutes, cooled in an ice bath, and filtered. The tan, crystalline material was washed with acetic acid; the white, crystalline material obtained (0.40 g, 51%) had mp 206–210° (lit.[12] mp 216–218°).

1,2,4-Triphenyl-3-aminonaphthalene.—1,2,4-Triphenyl-3-nitronaphthalene (0.45 g, 1.1 mmol), 2 g (31 g-atoms) of zinc, and 20 ml of glacial acetic acid were heated at reflux for 3.5 hr. The reaction mixture was poured into water and extracted with ether. The ethereal solution was dried, filtered, and concentrated to give white, crystalline product (0.3 g, 75%) having mp 254–256° (lit.[12] mp 256–257°).

1,3,4-Triphenyl-2-naphthol was obtained by adding 0.3 g (0.9 mmol) of the corresponding amine to 3 ml of glacial acetic acid and 0.5 g (4.5 mmol) of isoamyl nitrite. The reaction mixture was allowed to stand for 15 min; it was then slowly poured into a boiling 10% aqueous solution of sulfuric acid. As soon as the addition was complete, the solution was cooled in an ice bath and the precipitate was collected, washed with cold ether, and dried. This material, mp 231–233°, was identical in spectral characteristics with that formed through the degradation of the 2:1 adduct.

Anal. Calcd for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 89.98; H, 5.62.

Registry No.—1, 39495-51-7; 2, 39495-52-8; 3, 38028-34-1; diphenylketene, 525-06-4; 1,1-diphenylethylene, 530-48-3; 3,4-dihydro-1-hydroxy-1,4,4-triphenyl-2(1*H*)-naphthalenone, 38028-35-2; 3,4-dihydro-1-hydroxy-1,4,4-triphenyl-2(1*H*)-naphthalenone acetate, 38028-36-3; 3,4-dihydro-1,4,4-triphenyl-2-naphthalenazobenzene, 38028-37-4; 1,3,4-triphenyl-2-naphthol, 38028-38-5; 1,3-diphenyl[*c*]benzofuran, 5471-63-6; β-nitrostyrene, 102-96-5; 1,2,4-triphenyl-3-nitro-1,4-oxido-1,2,3,4-tetrahydronaphthalene, 39495-59-5; 1,2,4-triphenyl-3-nitronaphthalene, 39495-60-8; 1,2,4-triphenyl-3-aminonaphthalene, 39495-61-9.

The Oxidative Hydrolysis of *p*-Hydroxyphenyl Phosphates[1]

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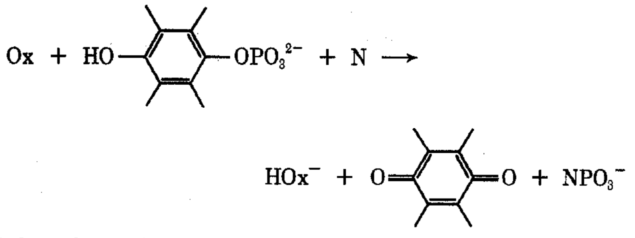
Periodic acid and its anions react with *p*-hydroxyphenyl phosphate (I) and the mono- (II) and dimethyl (III) esters, following second-order kinetics with no evidence for buildup of a periodate intermediate in high concentration. Both periodic acid and its monoanion are reactive species, and the reaction rates are greatest at low pH except for I, where the fastest reaction, at pH 7–8, involves a trianionic transition state, probably with elimination of a metaphosphate ion. Phosphorus–oxygen fission is important in the reaction of I at pH 1 and 6.5.

The oxidation of quinol phosphates can generate a phosphorylating agent, and the reaction has been examined and used synthetically.[2,3] The oxidants have generally been halogens or metal ions.

These reactions have been discussed as models for oxidative phosphorylation in biological systems, and the isolation of *p*-quinones from biological systems supported this hypothesis.[4] In addition, the involvement of quinones in biological phosphorylation has been demonstrated,[5] and quinone-induced phosphorylations have been observed in chemical systems.[6] Oxidatively induced chemical phosphorylations have recently been reviewed.[7] There are, however, certain weaknesses to this hypothesis, notably the difficulty of explaining the initial formation of the quinol phosphate and the observation that the oxidation in some



(where OX and N are respectively the oxidant and nucleophile)

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