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A Correction of the Literature Concerning Reactions of Polyarylated Carbinols. A Novel Suprafacial [1,5] Sigmatropic Rearrangement

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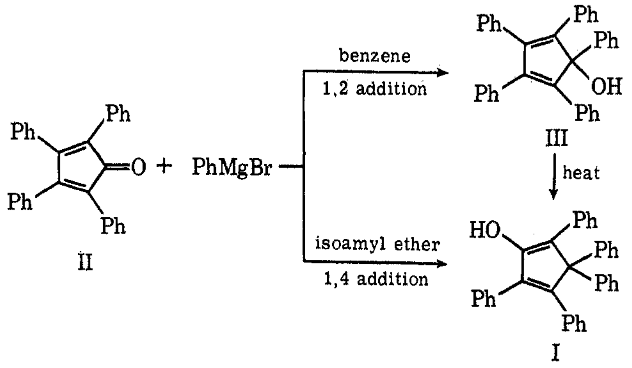
1,2 addition of phenylmagnesium bromide to tetraphenylcyclopentadienone in benzene affords the magnesium bromide salt of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol. Replacing the benzene with isoamyl ether and refluxing for 8 hr converts the above salt into the magnesium bromide salt of 1,1,2,3,4-pentaphenyl-2,4-cyclopentadien-5-ol by a symmetry-allowed suprafacial [1,5] sigmatropic phenyl shift. Hydrolysis produced 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (IV) *via* the keto-enol tautomerization of the intermediate 1,1,2,3,4-pentaphenyl-2,4-cyclopentadien-5-ol (VII). Heating 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol in isoamyl ether for 6 hr produced IV *via* the same sigmatropic shift and enol intermediate VII. Investigation of the mechanism of this rearrangement in ionic solvents and in the presence of a radical inhibitor eliminated the possibility of any ionic or radical character to the rearrangement. Treatment of IV in acetic acid with 48% hydrobromic acid afforded 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (VIII). Addition of phenylmagnesium bromide to VIII produced 1,2,3,4,5,5-hexaphenyl-2-cyclopenten-1-ol, which can be dehydrated with either acetyl chloride or acetic anhydride to produce 1,2,3,4,5,5-hexaphenyl-1,3-cyclopentadiene. This work is used to correct several errors in the existing literature.

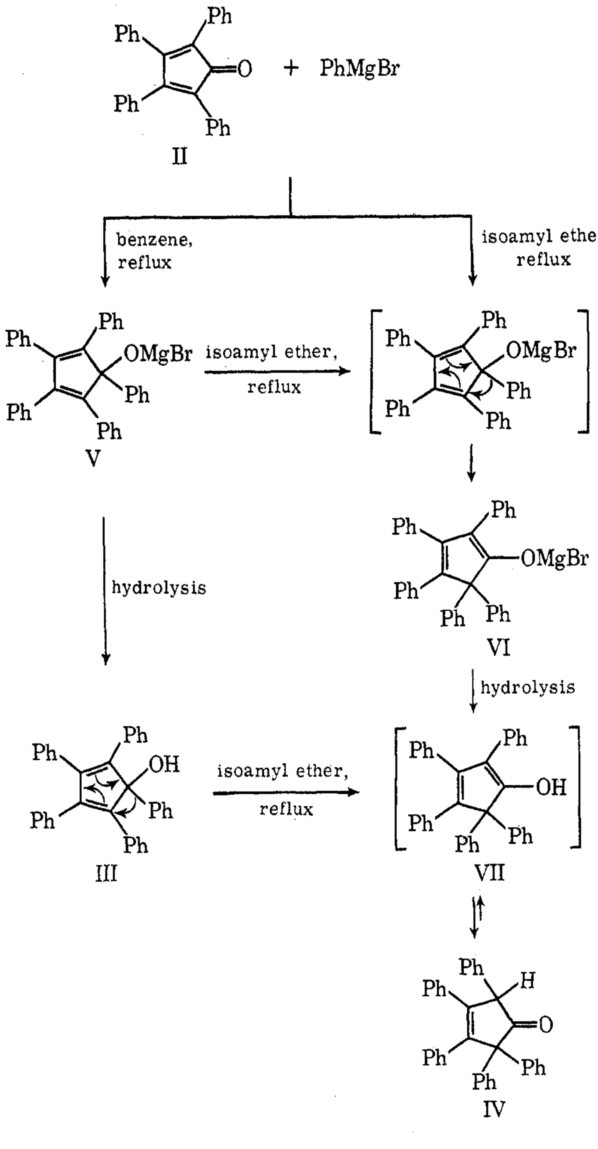
In 1943 Allen and VanAllan[1] reported that 2,3,3,4,5-pentaphenyl-1,4-cyclopentadien-1-ol (I) could be prepared by two methods: by direct 1,4 Grignard addition of phenylmagnesium bromide in isoamyl ether (isopentyl ether, bp 173°) to tetraphenylcyclopentadienone (tetracyclone, II), and by thermal isomerization of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (III) formed by 1,2 Grignard addition of phenylmagnesium bromide in benzene to tetracyclone (II).



In 1961, Dufraisse, *et al.*,[2] reinvestigated the thermal isomerization of III, in the absence of solvent, and found that, in addition to two other minor products which were formed, the correct structure of the major product produced was not I but IV, 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one.[3] They explained the formation of IV *via* a pinacol rearrangement of III.

We have reinvestigated both the 1,4 Grignard addition of phenylmagnesium bromide to II and the thermal isomerization of III, and we have established that both reactions produce IV not *via* a pinacol rearrangement as previously reported, but *via* a symmetry-allowed suprafacial [1,5] sigmatropic phenyl shift. In addition we have repeated all the reactions which involve interconversions in the pentaphenylated cyclopentadienol system originally reported by Allen and VanAllan, and we have corrected the structures of all the products subsequently produced.

SCHEME I



Addition of phenylmagnesium bromide in refluxing isoamyl ether to II, followed by hydrolysis, afforded a 65% yield of IV (Scheme I). The structural assignment of the product was aided by the spectral properties of a sample of IV independently synthesized[3] and by a mixture melting point comparison which showed

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[1] C. F. H. Allen and J. A. VanAllan, *J. Amer. Chem. Soc.*, **65**, 1384 (1943).

[2] C. Dufraisse, G. Rio, and A. Ranjon, *C. R. Acad. Sci.*, **253**, 2441 (1961).

[3] R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 3727 (1961).

no depression. To establish that IV is formed by thermal isomerization of the magnesium bromide salt V formed by 1,2 addition of phenylmagnesium bromide to II, we prepared V and investigated its reaction upon heating. Grignard addition of phenylmagnesium bromide to II in benzene afforded the desired magnesium bromide salt V, since quenching an aliquot of this solution afforded the dienol III. Replacing the solvent in the remaining unhydrolyzed reaction mixture with isoamyl ether and allowing the solution to reflux for 8 hr before hydrolysis and work-up afforded 65% (corrected for aliquot removed) of enone IV.

These results indicate that a direct 1,6 addition of phenylmagnesium bromide to II did not occur, but that the 1,2-addition product V initially formed when phenylmagnesium bromide is added to II thermally rearranges to VI. This rearrangement probably proceeds through a phenyl migration by a symmetry-allowed suprafacial [1,5] sigmatropic shift. This is the first such rearrangement reported for magnesium salts obtained from Grignard reactions and it is striking that such a rearrangement is so facile and that it affords such a good yield of rearranged product. Hydrolysis of the magnesium bromide salt VI affords only IV, probably through the dienol VII, which indicates that in this keto-enol tautomerization the keto form IV is highly favored (Scheme I).

In an effort to establish if such a sigmatropic shift is possible in the cyclopentadienol system we prepared III[1,3,4] by the 1,2 Grignard addition of phenylmagnesium bromide to II. Isolation of III (90%) and then placing it under reflux for 6 hr in isoamyl ether produced a 90% conversion of III to IV, probably through the dienol intermediate VII. The ease with which the dienol III is isomerized to the enone IV is very striking and it takes place much cleaner and in higher yield in the presence of solvent than in the absence[1,2] of solvent.

In order to study the mechanism of this phenyl shift and to establish that this rearrangement is indeed sigmatropic, and that it proceeds without any ionic or radical character, we performed the following reactions. Allowing III to reflux in isoamyl ether for 6 hr with a strong stream of oxygen bubbling through the refluxing solution continuously did not affect the yield of IV, since a 90% conversion of III to IV was again obtained. These results are exactly the same as those obtained when the reaction was performed without oxygen. This indicates that the observed phenyl shift is not radical in nature, since the presence of a radical inhibitor did not affect the yield of IV obtained. To eliminate the possibility of there being any ionic character to the rearrangement, we first allowed III to reflux in isoamyl ether for only 3 hr and by chromatography separated and isolated the ketone IV and the starting alcohol III. Under these conditions only 20% of IV was produced, while unrearranged alcohol III accounted for the remaining 80% of the reaction mixture. Repeating this reaction using dimethyl sulfoxide (DMSO) as the solvent and heating for 3 hr at 173°, followed by chromatography, afforded exactly the same yields of ketone IV and recovered unrearranged alcohol III, even though changing the solvent caused the reaction to be run in a medium of considerably increased dielectric constant: isoamyl ether, ϵ 2.82;[5] DMSO, ϵ 46.6.[6] These results indicate that it is highly unlikely that there is any ionic character to the phenyl migration observed. Having eliminated the possibility of any ionic or radical character to the observed rearrangement, it is left to be characterized as a [1,5] sigmatropic phenyl shift which must be suprafacial if it is thermally induced and if it is to obey the Woodward–Hoffmann rules.[7]

Once the correct structure of IV and its mechanism of formation was established, we turned our attention to its reactions. In Scheme II, we have listed the reactions performed and the structures assigned by Allen and VanAllan;[1] directly below their work we have represented the same reactions with the correct structures of the starting materials and products as established by this work. Attempted reaction of phenylmagnesium bromide with IV afforded only recovered starting material, as would be expected if our assigned structure (the presence of a proton α to the keto group) is correct for IV. Treatment of the unconjugated enone IV in glacial acetic acid with 48% hydrobromic acid afforded 73% of the conjugated enone 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one[2] (VIII). This product most likely arises from protonation of IV at C_3 followed by proton elimination from C_5.

The enone VIII was dissolved in benzene, added to a benzene solution of phenylmagnesium bromide, allowed to reflux overnight, and hydrolyzed to yield 85% of the enol IX, 1,2,3,4,5,5-hexaphenyl-2-cyclopenten-1-ol.

Dehydration of IX using excess acetyl chloride afforded 96% of X, 1,2,3,4,5,5-hexaphenyl-1,3-cyclopentadiene,[1] after refluxing for 24 hr, while dehydration of IX using acetic anhydride afforded 90% of X after refluxing for 3 days.

Experimental Section

1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (III).—Into a 1-l., three-necked flask equipped with a mechanical stirrer and a reflux condenser was added 1.96 g (0.080 g-atom) of magnesium turnings and 13.36 g (0.080 mol) of bromobenzene in 150 ml of dry ether. After the reaction was complete, the ether was replaced by 50 ml of dry benzene and the mixture was brought to reflux. Tetracyclone (II, 7.70 g, 0.020 mol) dissolved in 100 ml of benzene was added dropwise to the refluxing Grignard solution. After the addition was complete the mixture was refluxed and stirred for 2 hr, cooled by means of an ice bath, and hydrolyzed with 200 ml of 10% ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted twice with 20-ml portions of benzene, and the benzene solutions were combined, washed with water, and dried over magnesium sulfate. Concentration of the benzene solution to essential dryness and recrystallization of the residue from petroleum ether (bp 30–60°) gave 8.40 g (0.0182 mol, 91%) of pale yellow crystals, mp 175–176° (lit.[4] mp 175–176°).

2,2,3,4,5-Pentaphenyl-3-cyclopenten-1-one (IV). A. By Grignard Reaction.—Using the same set-up and amounts of reagents as described above, an ether solution of phenylmagnesium bromide was prepared. After the reaction was complete, the ether was replaced with freshly distilled and dried isoamyl ether (isopentyl ether, bp 173°), the mixture was cooled to room temperature, and 3.84 g (10.0 mmol) of II was added as a solid. The mixture was then heated under reflux for 8 hr,

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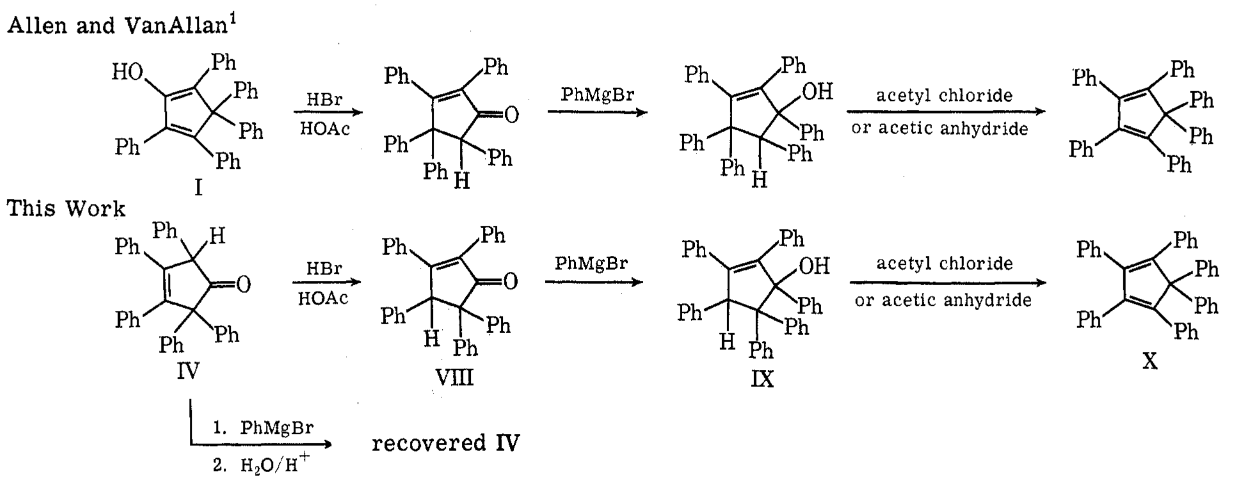
[4] K. Ziegler and B. Schnell, *Justus Liebigs Ann. Chem.*, **445**, 266 (1925).

[5] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Techniques of Organic Chemistry," Vol. VII, Interscience, New York, N. Y., 1955, p 123.

[6] E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 269.

[7] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 114–132.

Scheme II



cooled by means of an ice bath, hydrolyzed, and worked up as described above. Removal of the solvent under vacuum afforded a viscous brown oil which was crystallized from benzene and petroleum ether to give 3.00 g (6.47 mmol, 64.7%) of white crystals, mp 194.5–196° (lit.[2,3] mp 194–195°). A mixture melting point with an authentic sample prepared as in D below showed no depression. The spectral data, ir,[2,3] uv,[2,3] and nmr,[3] for this compound agreed with the literature. The compound gave satisfactory carbon and hydrogen analyses and its molecular weight (mass spectrum) was 462 (calcd 462).

B. By Thermal Isomerization.—Into a 100-ml round-bottomed flask equipped with a condenser was placed 1.00 g (2.16 mmol) of III and 50 ml of isoamyl ether. The solution was refluxed for 6 hr and cooled, and the solvent was removed under vacuum to yield a viscous brown oil which was crystallized from benzene and petroleum ether to give 0.90 g (1.94 mmol, 90%) of white crystals identical in all respects with the product obtained in A above.

C. By Thermal Isomerization of the Intermediate Magnesium Bromide Salt.—Into a 500-ml three-necked round-bottomed flask equipped with a mechanical stirrer and a condenser was placed 0.96 g (0.039 g-atom) of magnesium turnings and 6.28 g (0.040 mol) of bromobenzene in 100 ml of ether and the mixture was stirred until the Grignard reagent had completely formed. The ether was then replaced with 100 ml of benzene, and 1.50 g (0.0039 mol) of II in 50 ml of benzene was added dropwise. When the addition was complete, the reaction mixture was refluxed for 2 hr, and a 20-ml aliquot was removed. Hydrolysis and work-up of the aliquot afforded 0.24 g (0.51 mmol, 13%) of III. The benzene in the remaining reaction mixture was replaced with isoamyl ether, refluxed with stirring for 8 hr, cooled by means of an ice bath, and hydrolyzed with 10% ammonium chloride solution. Work-up as described above afforded 0.97 g (2.1 mmol, 53%) of IV.

D. Independent Synthesis of IV.—Using the procedure described by Breslow, *et al.*,[3] afforded a pure sample of IV which was used to establish the structure of the product obtained from reactions A, B, and C above.

Thermal Isomerization of III in the Presence of a Radical Inhibitor.—Into a 250-ml three-necked round-bottomed flask equipped with a reflux condenser, a mechanical stirrer, and a gas-dispersion tube was placed 75 ml of isoamyl ether. The solvent was heated to reflux while a strong stream of oxygen was passed through the solution by means of the gas-dispersion tube which protruded below the surface of the solution. At this point 2.00 g (4.3 mmol) of III was added as a solid (which immediately dissolved), and the solution was refluxed for 6 hr while the oxygen stream was continued. After this time the oxygen stream was stopped, the solution was cooled to room temperature, and the solvent was removed under reduced pressure. This afforded a viscous brown oil which was crystallized from benzene and petroleum ether to give 1.80 g (3.88 mmol, 90%) of white crystals identical in all respects with the product obtained in A above.

Thermal Isomerization of III for Only 3 Hr. A. In Isoamyl Ether.—Into a 250-ml round-bottomed flask equipped with a condenser was placed 75 ml of isoamyl ether and the solvent was heated to reflux. At this point 2.00 g (4.3 mmol) of III was added as a solid (which immediately dissolved) and the mixture was refluxed for 3 hr. After this time the solution was cooled to room temperature and the solvent was removed under vacuum, affording a viscous brown oil which was taken up in carbon tetrachloride and chromatographed on Woelm acid alumina using carbon tetrachloride as eluent. Collection of the light yellow band which separated and concentration of the eluent afforded 0.40 g (0.86 mmol, 20%) of white crystals identical in all respects with the product obtained from A above. Changing the eluent to a 9:1 mixture of carbon tetrachloride–chloroform brought down a second yellow band. Concentration of the eluent afforded 1.59 g (3.43 mmol, 80%) of starting alcohol III.

B. In Dimethyl Sulfoxide.—This reaction was performed on the same scale, at the same temperature, and in the same manner as the one described above except that DMSO was used as the solvent. After the reaction was complete, the solution was cooled to room temperature, poured into 200 ml of water, and extracted three times with benzene. The benzene solutions were combined, washed three times with water, dried over anhydrous magnesium sulfate, and concentrated under vacuum to afford a yellow residue which was dissolved in carbon tetrachloride and chromatographed as described above. The first yellow band eluted with carbon tetrachloride afforded 0.40 g (0.86 mmol, 20%) of IV, while elution of the second yellow band with a 9:1 carbon tetrachloride–chloroform mixture afforded 1.59 g (3.43 mmol, 80%) of starting alcohol III.

Reaction of IV with Phenylmagnesium Bromide.—Into a 500-ml three-necked round-bottomed flask equipped with a condenser and a mechanical stirrer was placed 0.50 g (0.020 g-atom) of magnesium turnings and 3.14 g (0.020 mol) of bromobenzene in 100 ml of dry ether. After the Grignard reagent had completely formed the ether was replaced by 100 ml of benzene, and 8.31 g (0.018 mol) of IV in 75 ml of benzene was added slowly. After the mixture was refluxed for 20 hr, it was hydrolyzed and worked up in the usual manner to afford a quantitative recovery of IV.

2,3,4,5,5-Pentaphenyl-2-cyclopenten-1-one[2] (VIII).—Into a 50-ml round-bottomed flask equipped with a condenser was added 1.50 g (3.24 mmol) of IV, 2.5 ml of 48% hydrobromic acid, and 10 ml of glacial acetic acid and the mixture was refluxed for 3.5 hr. The reaction mixture was then cooled, poured into 500 ml of cold water, and extracted with benzene, and the benzene was separated and dried over anhydrous magnesium sulfate. Concentration of the benzene afforded a yellow oil which was crystallized from benzene and petroleum ether to give 1.10 g (2.37 mmol, 73%) of pale yellow crystals, mp 166–167° (lit.[2] mp 169–170°). The ir and uv spectral data for this compound agreed with the literature;[2] nmr (CCl_4) τ 2.79 (m, 15, ArH), 4.85 (s, 1, CH); mol wt (mass spectrum) 462 (calcd 462).

1,2,3,4,5,5-Hexaphenyl-2-cyclopenten-1-ol (IX).—Into a 500-ml three-necked round-bottomed flask equipped with a mechanical stirrer and reflux condenser was placed 0.96 g (0.040 g-atom) of magnesium turnings and 6.28 g (0.040 mol) of bromobenzene in 75 ml of dry ether. After the Grignard reagent had completely formed, the ether was replaced with 100 ml of benzene and 2.3 g (0.0050 mol) of VIII in 50 ml of benzene was added slowly. The mixture was allowed to reflux overnight, hydrolyzed, and worked up in the usual manner to yield 2.29 g (0.0042 mol, 85%) of pale yellow crystals: mp 245–248°; ir (CCl_4) 3635 cm^{-1} (OH); nmr (CCl_4) τ 3.10 (m, 30, ArH), 4.50 (s, 1, OH), 7.26 (s, 1, CH).

Anal. Calcd for $C_{41}H_{32}O$: C, 91.07; H, 5.96; mol wt, 540. Found: C, 90.78; H, 6.06; mol wt, 540 (mass spectrum).

1,2,3,4,5,5-Hexaphenyl-1,3-cyclopentadiene[1] **(X). A. Using Acetyl Chloride.**—Into a 100-ml round-bottomed flask equipped with a condenser was placed 1.00 g (1.8 mmol) of IX and 25 ml of acetyl chloride, and the mixture was refluxed for 24 hr. After cooling to room temperature the mixture was carefully diluted with 100 ml of water and extracted with benzene and the benzene was dried over magnesium sulfate. Removal of the solvent under vacuum afforded a yellow oil which was crystallized from benzene and ethanol to yield 0.88 g (1.68 mmol, 96.5%) of white crystals: mp 175–177° (lit.[1] mp 172°); uv (CH_3CN) 335, 275 (sh), 247 mμ.

Anal. Calcd for $C_{41}H_{30}$: C, 94.21; H, 5.77; mol wt, 522. Found: C, 94.27; H, 5.93; mol wt, 522 (mass spectrum).

B. Using Acetic Anhydride.—Using the same procedure and amounts of reagents as described above but allowing the mixture to reflux for 3 days afforded 90% of product identical with that described above.

Registry No.—III, 2137-74-8; IV, 34759-47-2; VIII, 34759-48-3; IX, 34759-49-4; X, 34759-50-7.

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The Synthesis and Transformations of 2-Nitro-1-phenyl-1-hydroxyindene and Its Isomer

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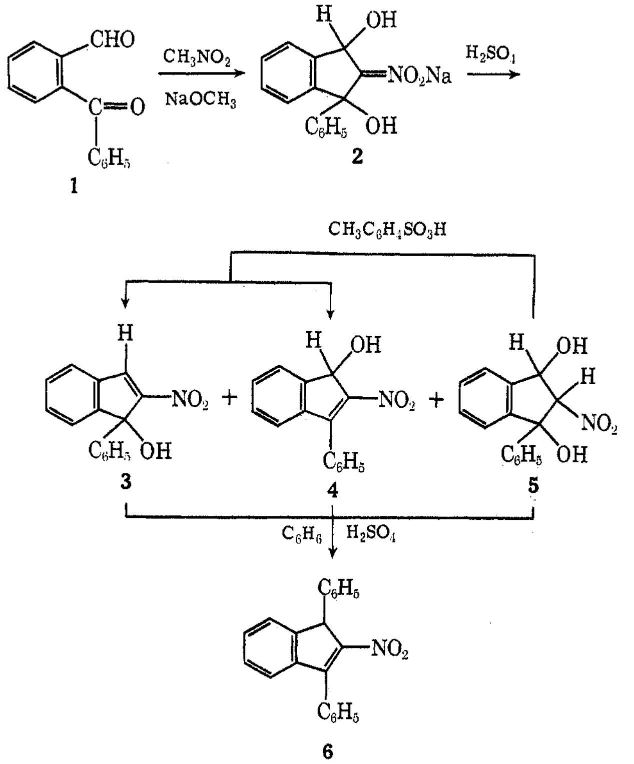
Condensation of 2-benzoylbenzaldehyde (**1**) with nitromethane in the presence of sodium methoxide gave, after acidification, 2-nitro-1-phenyl-1-hydroxyindene (**3**), 2-nitro-3-phenyl-1-hydroxyindene (**4**), and 2-nitro-1-phenyl-1,3-dihydroxyindan (**5**). The first two compounds were converted to the corresponding acetates **7** and **8**, which on treatment with primary or secondary amines gave the nitroenamines **9** and the ammonium salts **11** of the 2-nitro-1-phenyl-3-indanone (**12**), respectively. Hydrolysis of **9** or **11** afforded **12**. Treatment of the acetate **7** with alcohols yielded 2-nitro-3-phenyl-1-alkoxyindene (**17**). After prolonged reflux the isomeric 2-nitro-1-phenyl-3-alkoxyindene (**18**) was obtained. A catalytic amount of triethylamine rearranges **17** to **18**.

The condensation of 1,4, 1,5, and 1,6 dialdehydes with nitromethane in an alkaline medium followed by acidification is a general method for the synthesis of five-, six-, and seven-membered ring systems.[1] However, little is known about the reactivity of diketones or keto aldehydes toward nitromethane.[1] This led us to study the condensation of *o*-benzoylbenzaldehyde[2] with nitromethane under alkaline conditions.

Treatment of *o*-benzoylbenzaldehyde with nitromethane in the presence of 1 equiv of sodium methoxide in methanol generated within 2 min a white, crystalline precipitate of the 1-phenyl-1,3-dihydroxy-2-acinitroindan sodium salt **2**. Acidification of **2** with sulfuric acid in ice yielded two isomeric 2-nitrophenylhydroxyindenes (**3** and **4**) as well as 2-nitro-1-phenyl-1,3-dihydroxyindan (**5**). Structures were readily assigned from an interpretation of the nmr spectra for the three compounds. Dehydration of **5** with *p*-toluenesulfonic acid in refluxing benzene gave a mixture consisting mainly of **4** and a small amount of **3**. Treatment of either **3**, **4**, or **5** with sulfuric acid in benzene as dehydrating agent gave 1,3-diphenyl-2-nitroindene (**6**)[3] (Scheme I).

Acetylation of **3** was found to be temperature dependent. At −5°, the acetate **7** was obtained usually accompanied by **8**. The thermodynamically more stable product **8** was produced either at room temperature from **3**, by direct acetylation of **4**, or by treatment of **7** with glacial acetic acid at room temperature (Scheme II).

SCHEME I



Addition of primary or secondary amines to a solution of **7** resulted in an immediate color change from light yellow to green with the formation of nitroenamines of type **9**.[4] Most likely Michael addition with

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[1] F. W. Lichtenthaler, *Angew. Chem., Int. Ed. Engl.*, **3**, 211 (1964).

[2] W. Metlesics, T. Anton, M. Chaykovsky, V. Toome, and L. H. Sternbach, *J. Org. Chem.*, **33**, 2874 (1968).

[3] C. F. Koelsch, *ibid.*, **26**, 4238 (1961).

[4] See also F. W. Lichtenthaler and N. Majer, *Tetrahedron Lett.*, **411** (1969).