Nitration of 3,4-Dimethylacetophenone and 3,4-Dimethylbenzophenone. Formation and Rearomatization of Adducts

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Nitration of 3,4-dimethylacetophenone in acetic anhydride gives a mixture of *cis*- and *trans*-2-acetyl-4,5-dimethyl-4-nitro-1,4-dihydrophenyl acetate as the main product, together with 3,4-dimethyl-2-, 3,4-dimethyl-5-, and 3,4-dimethyl-6-nitroacetophenone. Analogous products are obtained from 3,4-dimethylbenzophenone. Rearomatization of the adducts under mildly acidic conditions occurs via 1,4-elimination of nitrous acid to form 2-acetyl- and 2-benzoyl-4,5-dimethylphenyl acetate, respectively. In strongly acidic conditions elimination of acetic acid accompanied by 1,2- and 1,3-shifts of the nitro group occurs to form the 2- and 5-nitro derivatives of the parent ketones. The rearomatization to the nitro derivatives involves the intermediate formation of an *ipso*-cyclohexadienyl cation which may be trapped by anisole or mesitylene to form biphenyl derivatives.

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La nitration de la diméthyl-3,4 acétophénone dans l'anhydride acétique donne un mélange d'acétates d'acétyl-2 diméthyl-4,5 nitro-4 dihydro-1,4 phényle *cis* et *trans*; aux côtés de ces produits principaux, il se forme aussi de la diméthyl-3,4 nitro-2, de la diméthyl-3,4 nitro-5 et de la diméthyl-3,4 nitro-6 acétophénone. On obtient des produits analogues à partir de la diméthyl-3,4 benzophénone. La réaromatisation des produits d'addition dans des conditions d'acidité faible, s'effectue par une élimination 1,4 d'acide nitreux conduisant, suivant les cas, à la formation d'acétates d'acétyl-2 et de benzoyl-2 diméthyl-4,5 phényle. Dans des conditions d'acidité forte, il y a une élimination d'acide acétique accompagnée par des réarrangements 1,2 et 1,3 du groupe nitro, pour conduire aux dérivés nitro-2 et nitro-5 de la cétone de départ. La réaromatisation des dérivés nitrés implique la formation intermédiaire d'un cation *ipso*-cyclohexadiényle qui peut être piégé par l'anisole ou le mésitylène pour conduire à des dérivés biphényles.

[Traduit par le journal]

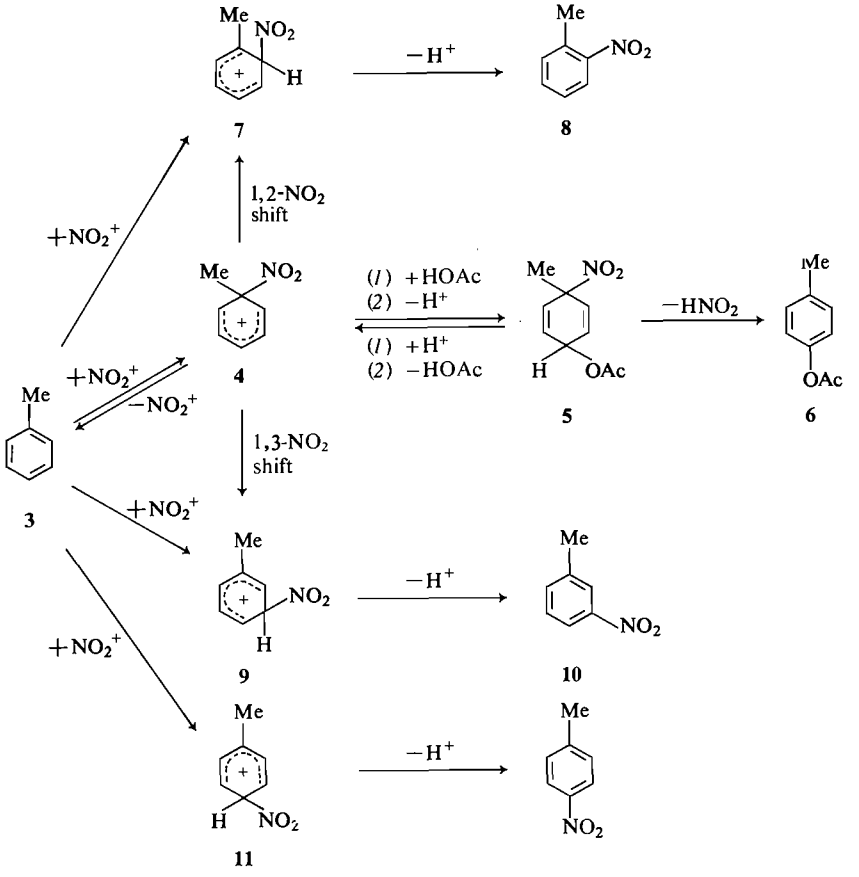
Introduction

Ipso nitration of methylbenzenes and their derivatives in acetic anhydride gives diastereoisomeric adducts which are derivatives of 4-nitro-1,4-dihydro-*p*-tolyl acetate (1, 2). Such adducts readily undergo rearomatization reactions. Secondary acetate adducts (to which discussion is confined in this report) afford aryl acetates by elimination of nitrous acid (1*a–e*) and nitroarenes by elimination of acetic acid accompanied by migration of the nitro group. Elimination of acetyl nitrate and reversion to the original aromatic is also observed with some adducts. Thus, the *o*-xylene adduct exhibits a 1,2-shift of the nitro group to form 3-nitro-*o*-xylene (3) whereas those from 3-chloro- (1*e*) and 3- and 4-cyano-*o*-xylene (1*d*) exhibit 1,3-shifts of nitro as well as the elimination of acetyl nitrate. Formation and potential rearomatization reactions of methylbenzene adducts are depicted for toluene, the parent methylbenzene, in Scheme 1. It should be noted that not all of the rearomatization reactions have actually been observed for any one of the adducts previously studied and, in particular, the nitro rearrangement and acetyl nitrate elimination reactions have neither been looked for, nor observed, in the case of the toluene adduct itself.

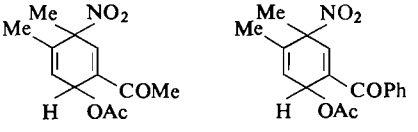
The present study, which is concerned with the effect of the oxo group, is a continuation of our investigations of substituent effects on the formation and rearomatization reactions of adducts of substituted *o*-xylenes.

Results and Discussion

Nitration of 3,4-dimethylacetophenone in acetic anhydride formed a mixture of 68% diene adducts, 20% 3,4-dimethyl-6-nitroacetophenone, and small amounts of the 2-nitro and 5-nitro isomers. The diastereoisomeric acetoxynitro adducts **1***a* and *b* were isolated by chromatography. The relative yields of the products and the absence of adducts resulting from attack at the 4-(*ipso*) position are consistent with the combined directing effects of the acetyl and the two methyl



SCHEME 1. Formation and potential rearomatization reactions of methylbenzene adducts.



1 2

a NO_2, OAc *trans*
b NO_2, OAc *cis*

substituents. The *ortho* methyl groups should favor electrophilic attack in the positional order 3 = 4 > 6 > 5 = 2. The acetyl group, which is deactivating, would be expected to reduce the reactivity at the 4-(*para*) position to a greater extent than at the 2- and 6-(*ortho*) positions and least of all at the 3- and 5-(*meta*) positions. The observed order, 3 > 6 > 5 ~ 2 > 4, is in accord with these expectations.

Nitration of 3,4-dimethylacetophenone with mixed acid was carried out by Buu-Hoî *et al.* (4) who reported that 3,4-dimethyl-6-nitroacetophenone, m.p. 120° was obtained in 75% yield together with 3,4-dimethyl-5-nitroacetophenone. Brändström and Carlsson (5) repeated this reaction and they obtained a 2:1:1 mixture of 3,4-dimethyl-2-nitroacetophenone, m.p. 122°, 3,4-dimethyl-6-nitroacetophenone, m.p. 80°, and 3,4-dimethyl-5-nitroacetophenone. They concluded that Buu Hoî *et al.* (4) incorrectly identified the isomer of m.p. 120°. The n.m.r. spectra clearly identify each isomer (see Experimental) and our work confirms Brändström and Carlsson's observations that the isomer of m.p. 120° is the 2-nitro compound and that the isomer having m.p. 80° is 3,4-dimethyl-6-nitroacetophenone. However, the relative yields of substitution products that they found, in which the 2-nitro isomer predominates, is quite different from the

relative yields that we observed, where the 6-nitro isomer predominates. We suggest that under both sets of conditions the nitronium ion is the active electrophile and that its relative rate of attack at the nuclear positions is the same. Under the highly acidic conditions pertaining in sulfuric acid (Brändström and Carlsson's conditions) diene adducts are not stable and, if formed, will be readily converted back to the precursor cyclohexadienyl cation (5-Ac-2-Me-**4**)[1] which, by shift of the nitro group, followed by loss of a proton, will give the 2-nitro and 5-nitro substitution products of 3,4-dimethylacetophenone (*cf.* Scheme 1: **4** → **7** → **8** and **4** → **9** → **10**, see below). Thus the predominant attack by nitronium ion at the 3-(*ipso*) position will under their conditions lead to an increased yield of the 2-nitro and 5-nitro isomers. If the ratio of attack at the 2, 3, 5, and 6 positions that we observed, ~6, 68, ~6, and 20%, respectively, is assumed to be the same in sulfuric acid, and if the 68% of *ipso* attack leads to the 2-nitro and 5-nitro derivatives in the same ratio that we found for the rearrangements (3:1) then the observed yields of 2-, 5-, and 6-nitro derivatives would be 57, 23, and 20%, respectively. This is quite close to the 2:1:1 ratio found by Brändström and Carlsson. This provides a clear illustration of how *ipso* attack followed by rearrangement can complicate the interpretation of positional reactivity determined from the isomer distribution of the final substitution products (3, 6, 7).

Nitration of 3,4-dimethylbenzophenone gave the diastereoisomeric adducts **2***a* and *b*, in approximately 70% yield, the three 3,4-dimethylnitrobenzophenone isomers, and 3,5-dinitro-*o*-xylene. Because of the complexity of the spectrum of the reaction product it was not possible to measure the yields of the individual nitro substitution products. The formation of 3,5-dinitro-*o*-xylene is indicative of attack by the nitrating electrophile, assumed to be the nitronium ion, at the position *ipso* to benzoyl. The resulting 4-nitro-*o*-xylene would be expected to nitrate in the vacant *meta* position to form the 3,5-dinitro-*o*-xylene. However, study of the nitration of 4-nitro-*o*-xylene has shown that it is quite unreactive towards nitric acid in acetic anhydride under the conditions used for nitration of the dimethylbenzophenone.[2] The mode of formation of the dinitro-*o*-xylene is thus unexplained.

Rearomatization of **1** and **2** under aprotic, weakly acidic (acetic acid) and moderately acidic conditions (5% sulfuric acid in acetic acid, trifluoroacetic acid) gave the corresponding acetates, 2-acetyl-4,5-dimethylphenyl acetate and 2-benzoyl-4,5-dimethylphenyl acetate, by 1,4-elimination of nitrous acid. During the course of the slow elimination reaction of **1** in acetic acid, epimerization was evident. Under more strongly acidic conditions (50% sulfuric acid in acetic acid, 78% aqueous sulfuric acid) or in the presence of the Lewis acid boron trifluoride, a mixture of the 3,4-dimethylacetophenone (29%) and its 2-(53%) and 5-nitro (18%) derivatives, or 3,4-dimethylbenzophenone (37%) and its 2-(36%) and 5-nitro (27%) derivatives was obtained, respectively. The two distinct pathways for rearomatization reflect those observed for the *o*-xylene adduct 2-Me-**5** (3), and its derivatives 6-Cl-2-Me-**5** (1*e*), and 5-CN-2-Me-**5** (1*d*).

Clearly, the outcome of the competition between the two rearomatization pathways depends upon the acidity of the reaction medium and the results are explicable in terms of the previously proposed mechanisms (1*d*, *e*, 3). In the 1,4-elimination (E2) of nitrous acid (Scheme 1: **5** → **6**) a basic species (normally a solvent molecule) is required to abstract the proton. Under conditions of very high acidity the ability of the solvent to abstract the proton is markedly reduced and the 1,4-elimination pathway is disfavored with respect to the second rearomatization process. This involves the acid-catalyzed unimolecular loss of acetate to (re)form the *ipso*-cyclohexadienyl cation **4** which can in principle undergo (*i*) loss of the nitro group as a nitronium ion, to reform **3**; (*ii*) a 1,2-nitro shift to form **7**, which is in turn deprotonated to the 2-nitro derivative **8**; and (*iii*) a 1,3-nitro shift to form **9**, in turn deprotonated to the 3-nitro derivative **10**. The acidity at which the transition from the E2 to cation pathway occurs depends upon the substituents present in the adduct. Thus in the intermediate acidity range (5% sulfuric acid in acetic acid, or trifluoroacetic acid), where the less deactivated 6-Cl-2-Me-**5** has already exhibited the E2 to cation transition (1*e*), **1** and **2** still follow the E2 pathway. For **1** and **2** the transition is effected

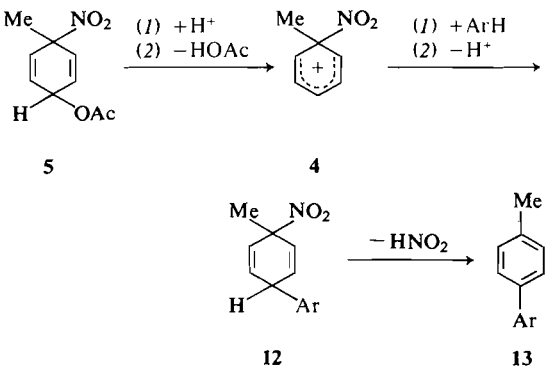
[1]When reference is made to compounds as derivatives of those depicted in Scheme 1 the numbering system follows that of toluene itself *i.e.* the position to which the methyl substituent is attached is always taken as the 1-position.

[2]Unpublished work with B. Fowler.

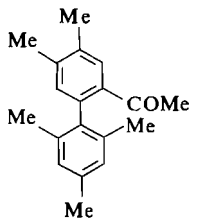
at higher acidities. The fact that epimerimization of **1***b* occurred in the course of the elimination reaction in acetic acid indicates that (reversible) cation formation does occur at low acidities. Presumably, the lifetime of the cation under these conditions is too short to allow the nitro shift processes (**4** → **3**, **7**, **9**) to occur.

The particular rearomatization processes which occur from the cation are determined by the substituents. For 2-Me-**4** only a 1,2-nitro shift, leading eventually to 3-nitro-*o*-xylene, is observed (*cf.* **4** → **7** → **8**). The other potential reactions of the *ipso*-cyclohexadienyl cation, *viz.* a 1,3-nitro shift followed by deprotonation to the isomeric nitro aromatic (*cf.* **4** → **9** → **10**), and the loss of the nitro group as nitronium ion, leading to parent aromatic (*cf.* **4** → **3**) but not the 1,2-nitro shift, are realized in the cases of 6-Cl-2-Me-**5**, (1*e*), 3-CN-2-Me-**5**, and 5-CN-2-Me-**5** (1*d*). In adducts **1** and **2**, which give rise to the cations 5-Ac-2-Me-**4** and 5-Bz-2-Me-**4**, respectively, all three processes are observed. The relative yields of the products indicate that in the case of 5-Ac-2-Me-**4** the 1,2-shift of the nitro group (**4** → **7**) is the most favored process; loss of the nitronium ion (**4** → **3**) occurs less readily and the 1,3-shift of the nitro group (**4** → **9**) occurs to the least extent. The data for **2** suggest that 1,2-shift of the nitro group in the cation is not so favored over the other processes as it is in the case of **1**. This may be attributed to the steric effect of the benzoyl substituent (larger than acetyl) which would be expected to inhibit the 1,2-nitro shift. For both **1** and **2** it is clear that the shift of the nitro group must be intramolecular. A dissociation–renitration process would give the 6-nitro derivative which is not observed; indeed in the case of **1**, 3,4-dimethyl-6-nitroacetophenone would be expected to be the major product, since the results of the nitration of 3,4-dimethylacetophenone show that of the unsubstituted positions the 6-position is the most activated. The fact that no 3,4-dimethyl-6-nitroacetophenone is obtained from the rearomatization of **1** (nor 3,4-dimethyl-6-nitrobenzophenone from **2**) although the precursor cyclohexadienyl cation (5-Ac-2-Me-**11**) is the most stable of the non-*ipso* cations also confirms the expectation that the direct 1,4-nitro shift is unlikely and shows that a non-*ipso* cation (5-Ac-2-Me-**9**) undergoes deprotonation (to 5-Ac-2-Me-**10**) much more rapidly than it rearranges to a more stable cation (*cf.* **9** → **11**). We suspect that this last is a general conclusion since no evidence for the rearrangement of a non-*ipso* nitrocyclohexadienyl cation has ever been adduced. Furthermore, the parallel observation that the only acetyl adducts which have ever been observed have the nitro group attached to an *ipso* position and the irreversibility of nitration, show that the *only* fate of a non-*ipso* nitrocyclohexadienyl cation is deprotonation.

ipso-Cyclohexadienyl cations from tertiary acetate precursors (*e.g.* 4-Me-**4**) are trappable by nucleophiles other than acetic acid (*e.g.* methanol) to give other adducts (1*f*, *g*). The epimerization observed in the course of the rearomatization of **1***a* in acetic acid indicates that the secondary acetate adducts can undergo exchange reactions by formation of the cation and its subsequent combination with a nucleophile. The coupling reactions with aromatic substrates presumably follow this process, illustrated for the parent adduct **5** (Scheme 2). The cation substitutes in the aromatic to form as the immediate product the nitroaryl adduct **12** which readily undergoes elimination of nitrous acid to form the biphenyl derivative **13**. The biphenyl derivatives **14**, **15**, and **16** obtained by reaction of **1** with mesitylene and with anisole and by reaction of **2** with mesitylene, as well as that (**17**) previously reported from reaction of 6-Cl-2-Me-**5** with mesitylene, all have precisely the structures expected if they were formed by the pathway shown in Scheme 2. In the nitration of 1,2-dialkylbenzenes (*e.g.* *o*-xylene) and of hemimellitene with 90% nitric acid at low temperatures, coupling occurs to form polyalkylbiphenyls, which may be further nitrated (8). It is significant that such coupling takes place with substrates which when reacted with nitric acid in acetic anhydride are known to, or would be expected to, give good



SCHEME 2



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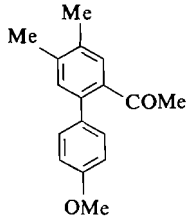

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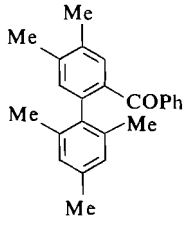

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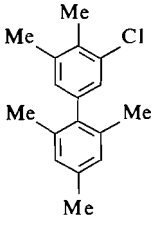

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yields of secondary acetate adducts, and does not occur with substrates which do not form adducts (*e.g.* mesitylene) or which form only tertiary acetate adducts (*e.g. p*-xylene). It seems clear that the mechanism of this coupling reaction is just that shown in Scheme 2 except that the *ipso*-cyclohexadienyl cation **4** is generated by *ipso* attack of nitronium ion on the hydrocarbon. The susceptible hydrocarbons have a highly activated *ipso* position *para* to an unsubstituted position. Toluene itself was not observed to couple (8*a*) but since only a small amount of *ipso* attack occurs with toluene (1*c*) only a very small amount of coupling product would be expected. Cross coupling of two different arenes also occurs but only if one of the components is of the type required for successful self-coupling. Clearly the second component is merely filling the role of the aromatic which is substituted, not that which becomes the active electrophile. The high yields of biphenyl derivatives which are obtained from **1** and **2** indicate that the reaction has potential synthetic utility. The reaction is obviously related to the Scholl reaction of dehydrogenation condensation of aromatics (9) but has the important advantage over the latter that it provides a mixed biaryl product.

Reaction of **1** and **2** with sodium methoxide in methanol resulted in rearomatization by 1,4-elimination of nitrous acid accompanied by cleavage of the ester function.

Experimental

Nuclear magnetic resonance spectra at 220 MHz were determined on the Varian HR 200 spectrometer at the Ontario Research Foundation, Sheridan Park, Ontario. Microanalyses were by Dr. D. McGillivray. Nitric acid was purified by distilling the fuming acid (300 cm^3) at 100 Pa from urea (10 g) and sulfuric acid (500 cm^3). Alumina was deactivated with 3% of 10% acetic acid. Ether and pentane were dried by distillation from sodium and phosphorus pentoxide, respectively.

Nitration of 3,4-Dimethylacetophenone

A solution of freshly distilled nitric acid (10 cm^3, 0.24 mol) in acetic anhydride (40 cm^3) was added to 3,4-dimethylacetophenone (20 g, 0.14 mol) in acetic anhydride (60 cm^3) at $-40°$. The yellow reaction mixture was allowed to stand at 2° overnight after which time the n.m.r. spectrum indicated that approximately 70% of dienes had been formed. The mixture was worked up in the normal manner (10) to yield an oil consisting of (by n.m.r.) 68% dienes, 20% 3,4-dimethyl-6-nitroacetophenone, and lesser amounts of 3,4-dimethyl-2-nitroacetophenone and 3,4-dimethyl-5-nitroacetophenone. Chromatography on alumina at $-20°$ and elution with pentane and ether–pentane mixtures gave a mixture of 3,4-dimethylnitroacetophenones (1.2 g, 6 mmol) in the 50–70% ether fractions, *trans*-2-acetyl-4,5-dimethyl-4-nitro-1,4-dihydrophenyl acetate (**1***a*, 10.7 g, 42 mmol) in the second 70% ether fraction, a mixture of **1***a* and *b* (5.4 g, 21 mmol) in the first 100% ether fraction, and *cis*-2-acetyl-4,5-dimethyl-4-nitro-1,4-dihydrophenyl acetate (**1***b*, 1.0 g, 4 mmol) in the second 100% ether fraction.

Recrystallization of **1***a* from chloroform–pentane gave colorless crystals, m.p. 95.5–97°; u.v. (CH_3OH) 212.5 nm (ε 1130 $m^2\ mol^{-1}$); i.r. (Nujol) 1730 and 1245 ($OCOCH_3$), 1680 ($COCH_3$), 1545 and 1380 (NO_2), and 930 cm^{-1}; n.m.r. ($CDCl_3$) τ 3.08 (d, 1, 3-*H*) 3.83 (m, 1, 1-*H*), 4.00 (m, 1, 6-*H*), 7.62 (s, 3, $COCH_3$), 7.98 (s, 3, $OCOCH_3$), 8.09 (s, 3, 4-CH_3), 8.15 (t, 3, 3-CH_3), J_{13} = 0.90, J_{16} = 4.07, $J_{1,5-CH_3}$ = 1.26, $J_{6,5-CH_3}$ = 1.31 Hz; irradiation at 8.15 collapsed the multiplet at 3.83 to a doublet of doublets and that at 4.00 to a doublet, allowing the initial assignment of chemical shifts and coupling constants to be made to simulate the spectrum, the simulation then being refined to give the listed parameters.

Anal. Calcd. for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.96; N, 5.53. Found: C, 56.61; H, 5.96; N, 5.45.

Recrystallization of **1***b* from chloroform–pentane gave colorless crystals, m.p. 120–120.5°; u.v. (CH_3OH) 213.5 nm (ε 1100 $m^2\ mol^{-1}$); i.r. (Nujol) 1730 and 1240 ($OCOCH_3$), 1680 ($COCH_3$), 1550 and 1380 (NO_2), 1020 and 940 cm^{-1}; n.m.r. ($CDCl_3$), τ 3.14 (d, 1, 3-*H*), 3.90 (m, 1, 1-*H*), 4.03 (m, 1, 6-*H*), 7.62 (s, 3, $COCH_3$) 7.95 (s, 3, $OCOCH_3$), 8.13 (t, 3, 5-CH_3). 8.17 (s, 3, 4-CH_3), J_{13} = 0.82, J_{16} = 3.83, $J_{1,5-CH_3}$ = 1.30, $J_{6,5-CH_3}$ = 1.28 Hz; irradiation at 8.08 collapsed the multiplet at 3.90 to a doublet of doublets and then at 4.30 to a doublet allowing the assignment of chemical shifts and coupling constants which were then refined as in the case of **1***a*.

Anal. Calcd. for $C_{12}H_{15}NO_5$ (M_r 253): C, 56.91; H, 5.96; N, 5.53. Found (249): C, 57.03; H, 5.93, N, 5.47.

Identical arguments to those adduced for the structure of the adduct from 3,4-dimethylbenzonitrile (**1***d*) can be made for the assignment of structure **1** to the 3,4-dimethylacetophenone adducts. The assignment is supported by the effect of the shift reagent tris-(1,1,1,2,2,3,3-heptafluoro-7,7-[$^2H_6$]dimethyl-4,6-[$^2H_3$]octanedionato)europium(III) {Eu([$^2H_9$]fod)$_3$} (Table 1). In both **1***a* and *b* the acetate methyl absorption moved downfield more rapidly

TABLE 1. Relative gradients (gradient 1-OAc = 1.00) of proton chemical shifts for diene adducts resulting from the addition of Eu([$^2H_9$]fod)$_3$

Compound	1-H	3-H	6-H	4-CH_3	5-CH_3	2-Ac	2′-H
1*a*	1.97	0.46	0.73	0.22	0.08	0.52	—
1*b*	1.94	0.40	0.73	0.08	0.09	0.51	—
2*a*	2.20	0.40	0.65	0.22	0.07	—	0.38
2*b*	2.40	0.40	0.66	0.04	0.08	—	0.42

than that of any of the other methyl groups, confirming the expectation of coordination of the reagent at the acetate function. The allylic hydrogen (1-H) peak moves downfield more rapidly than that of the adjacent vinyl hydrogen (6-H) which in turn moves more rapidly than that of the remote vinyl hydrogen (3-H), in accord with the increasing distance between the europium and the respective hydrogens. Similarly, in both **1***a* and *b*, the acetate methyl absorption moves more rapidly than that of the acetyl methyl which moves more rapidly than that of the 5-methyl, again in accord with the increasing distance between europium and the respective methyl groups. However, the 4-methyl peak in **1***a* moves more than twice as rapidly as the similar peak of **1***b* whereas the shift gradients for all other pairs of corresponding protons of **1***a* and *b* are not significantly different and on this basis the stereochemistry is assigned with 4-methyl and acetate *cis* in **1***a* and thus **1***a* as the *trans* adduct and the complementary assignment for **1***b*.

Nitro Compounds.

The residues from early column fractions containing the nitro compounds were combined and rechromatographed on alumina. 3,4-Dimethyl-6-nitro-acetophenone was eluted with 25% ether–pentane, m.p. 79–80° (lit. (5) m.p 80°); i.r. (Nujol) 1700 (C=O), 1545 and 1370 (NO_2); n.m.r. ($CDCl_3$), τ 2.15 (s, 1, 5-*H*), 2.72 (s, 1, 2-*H*), 7.50 (s, 3, $COCH_3$), 7.65 (s, 6, 3-CH_3 and 4-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 193 (32, M), 178 (100, *M* − CH_3), 151 (74), 103 (40), 91 (30), 43 (60). 3,4-Dimethyl-5-nitroacetophenone could not be obtained pure but was obtained in a mixture with the 6-nitro isomer: n.m.r. ($CDCl_3$), τ 1.85 (d, 1, *J* = 1.5 Hz, 6-*H*), 2.00 (d, 1, *J* = 1.5 Hz, 2-*H*), 7.40 (s, 3, $COCH_3$), 7.67 (s, 6, 3-CH_3 and 4-CH_3).

Anal. Calcd. for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.04; H, 5.60; H, 7.00.

3,4-Dimethyl-2-nitroacetophenone was isolated in a small amount from the 40% ether–pentane fraction on rechromatography of the nitro compounds. It was more readily obtained from the product of rearomatization of **1** using boron trifluoride (see below), m.p. 118° (lit. (5) m.p. 122°); i.r. 1700 (C=O), 1540 and 1350 cm^{-1} (NO_2); n.m.r. ($CDCl_3$) τ 2.45 (d, 1, *J* = 8 Hz, 6-*H*), 2.70 (d, 1, *J* = 8 Hz, 5-*H*), 7.48 (s, 3, $COCH_3$), 7.58 (s, 3, 3-CH_3), 7.80 (s, 3, 4-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 193 (6, M), 178 (100, *M* − CH_3), 151 (80), 103 (42), 91 (41), 43 (45), 42 (34).

Anal. Calcd. for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.00; H, 5.50; N, 7.48.

The three nitro substitution products have definitive n.m.r. spectra. 3,4-Dimethyl-2-nitroacetophenone has two *ortho* protons which give rise to a typical AB quartet with an 8 Hz coupling. Its 5-nitro isomer has *meta* protons and these give an AB quartet with a 1.5 Hz coupling. The 6-nitro isomer has *para* protons which appear as two singlets. None of the peaks overlap and this facilitates the detection of the individual isomers in mixtures.

2-Acetyl-4,5-dimethylphenol and 2-Acetyl-4,5-dimethylphenyl Acetate

Diene **1** (3 g) was added to a concentrated solution of sodium methoxide in methanol (5 cm^3). After neutralization with ammonium chloride and evaporation of excess methanol the residue was extracted with ether. Evaporation of the ether and recrystallization of the residue from petroleum ether gave 2-acetyl-4,5-dimethylphenol, m.p. 71.5–72.5° (lit. (11) m.p. 71°); i.r. (Nujol) 3300–3500 (OH), 1650 cm^{-1} ($COCH_3$); n.m.r. ($CDCl_3$) τ 2.50 (s, 1, 3-*H*), 3.20 (s, 1, 6-*H*), 7.45 (s, 1, $COCH_3$), 7.76 (s, 1, CH_3), 7.80 (s, 1, CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 164 (36, M) (100, *M* − CH_3), 121 (5), 91 (12), 77 (14), 43 (15).

The phenol (278 mg) was dissolved in acetic anhydride (5 cm^3), 5 drops of sulfuric acid were added, and the mixture maintained at 35° for 30 min. The mixture was neutralized and extracted with ether. Removal of the ether gave 2-acetyl-4,5-dimethylphenyl acetate which was recrystallized from ethanol–water, m.p. 59–60°; i.r. (Nujol) 1780 ($OCOCH_3$) and 1700 cm^{-1} ($COCH_3$); n.m.r. ($CDCl_3$) τ 2.42 (s, 1, 3-*H*), 3.13 (s, 1, 6-*H*), 7.50 (s, 3, $COCH_3$), 7.69 (s, 3, CH_3), and 7.73 (s, 3, CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 206 (6, M) 164 (62, *M* − CH_2CO), 149 (100), 91 (16), 43 (35).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.78; H, 6.80.

*2-Acetyl-2′,4,4′,5,6′-pentamethylbiphenyl (**14**)*

Boron trifluoride etherate (1 cm^3) was diluted with ether (3 cm^3); the solution was added dropwise to a solution of diene **1** (2 g, 7.9 mmol) and mesitylene (5 cm^3) in methylene chloride (3 cm^3) and the mixture left to stand for 4 h. After work-up, chromatography on silica gel and elution with ether–pentane gave mesitylene in the 5% ether fraction, the biphenyl (1.47 g, 5.5 mmol) in the early 20% ether fractions and a mixture of 3,4-dimethyl-2- and 3,4-dimethyl-5-nitroacetophenone (300 mg, 1.6 mmol) in the later 20% ether fractions. After recrystallization from ethanol, 2-acetyl-2′,4,4′,5,6′-pentamethylbiphenyl had m.p. 74°; i.r. (Nujol) 1675 (C=O) 1610, 1275, 1220, 890, and 860 cm^{-1}; n.m.r. ($CDCl_3$) τ 2.44 (s, 1, 3-*H*), 3.11 (m, 3, 3′-*H*, 5′-*H*, and 6-*H*); 7.74 (s, 9, 4-CH_3, 4′-CH_3, and 5-CH_3) 8.10 (s, 9, 2′-CH_3, 6′-CH_3, and $COCH_3$); mass spectrum (70 eV) *m/e* (relative intensity) 266 (56, M) 251 (100, *M* − CH_3) 193 (78), 178 (43), 152 (54), 132 (47), 118 (100), 115 (49), 103 (55), 89 (67), 44 (71).

Anal. Calcd. for $C_{18}H_{22}O$: C, 85.67; H, 8.23. Found: C, 85.84; H, 8.23.

*2-Acetyl-4′-methoxy-4,5-dimethylbiphenyl (**15**)*

A solution of boron trifluoride etherate (1 cm^3) in ether

(5 cm^3) was added to a mixture of diene **1** (2 g, 7.9 mmol) and anisole (5 cm^3) at 0°. The mixture turned bright blue. After work-up and chromatography on silica gel, elution with 10% ether–pentane washed down excess anisole. Elution with 20% ether–pentane gave 2-acetyl-4′-methoxy-4,5-dimethylbiphenyl (230 mg, 0.9 mmol); n.m.r. ($CDCl_3$) τ 2.64 (s, 1, 3-*H*), 2.73 (d, 2, J = 8 Hz, 3′-*H* and 5′-*H*), 2.83 (s, 1, 6-*H*), 3.05 (d, 1, J = 8 Hz, 2′-*H* and 6′-*H*), 6.18 (s, 3, OCH_3), 7.68 (s, 6, 4-CH_3 and 5-CH_3), 8.00 (s, 3, $COCH_3$); mass spectrum (70 eV) *m/e* (relative intensity) 254.141 (19, M_r ($^{12}C_{17}{}^{1}H_{18}{}^{16}O_2$) 254.131), 149, (100), 132 (82), 104 (58), 83 (69), 77 (70), 43 (95.) Further elution with 20% ether–pentane gave 3,4-dimethyl-6-nitroacetophenone (700 mg, 3.6 mmol) and 3,4-dimethyl-2-nitroacetophenone (240 mg, 1.2 mmol).

Reaction of Diene 1 with Boron Trifluoride

Diene **1** (1.5 g, 5.0 mmol) was added to boron trifluoride etherate (1.5 cm^3). A vigorous reaction ensued. After work-up followed by chromatography on silica gel and elution with 20% ether–pentane there was obtained 3,4-dimethylacetophenone (245 mg, 1.7 mmol), 3,4-dimethyl-5-nitroacetophenone (245 mg, 1.3 mmol), and 3,4-dimethyl-2-nitroacetophenone (550 mg, 2.8 mmol). The identity of the products was confirmed by comparison of R_f values on thin-layer chromatography with those of authentic samples and by n.m.r.

Reaction of Diene 1 with 78% Sulfuric Acid

Diene **1** (500 mg) was stirred overnight with 78% (by weight) sulfuric acid. The n.m.r. of the product obtained after work-up showed 35% 3,4-dimethylacetophenone, 48% 3,4-dimethyl-2-nitroacetophenone, and 16% 3,4-dimethyl-5-nitroacetophenone. The identity of the components was confirmed by t.l.c.

Other Rearomatization Reactions of Diene 1

In each case diene **1** (100 mg) was reacted with the appropriate reagent in an n.m.r. tube and the products determined by n.m.r. and confirmed by t.l.c. Reaction with 50% sulfuric acid in acetic acid gave 23% 3,4-dimethylacetophenone, 61% of 3,4-dimethyl-2-nitro-, and 16% of 3,4-dimethyl-5-nitroacetophenone. Reaction with 5% sulfuric acid in acetic acid gave only 2-acetyl-4,5-dimethylphenyl acetate as did reaction with neat trifluoroacetic acid and reaction with neat acetic acid. Reaction with acetic acid was slow at ambient temperature ($t_{1/2} \sim 10$ days) and epimerization of the mixture in which **1*b*** predominated to a mixture in which **1*a*** was the major diastereoisomer occurred. At 120° elimination to the acetate was complete in 10 min. The rate of rearomatization was measured in 65% (by weight) trifluoroacetic acid – 35% [$^2H_4$]acetic acid mixture and at a probe temperature of 35°, by integrating over the upfield part of the diene region of the n.m.r. spectrum at measured time intervals. A plot of log(integral) against time was linear leading to a first-order rate constant of 4.0×10^{-4} s^{-1}.

Nitration of 3,4-Dimethylbenzophenone

A solution of nitric acid (8 cm^3, 0.2 mol) in acetic anhydride at −70° was added to a stirred solution of the ketone (20 g, 0.10 mol) in acetic anhydride (20 cm^3) also at −70°. The temperature of the reaction mixture was allowed to rise to 5° and held at this temperature overnight. Diene adduct **2** (9.7 g, 30 mmol) crystallized from the reaction mixture and was filtered off. The filtrate was worked up in the normal manner to yield a semicrystalline product from which more adduct **2** (4.3 g, 14 mmol) was filtered off after the addition of ether (50 cm^3). The residue (15.8 g) obtained after evaporation of the ether from the filtrate was chromatographed on deactivated alumina at −25°. Elution with ether–pentane gave 3,4-dimethylbenzophenone (0.5 g, 2 mmol) in the 20–30% ether fractions, 3,4-dimethyl-5-nitrobenzophenone (1 g, 4 mmol) in the 40–50% ether fractions, a mixture 3,4-dimethyl-2-nitro- and 3,4-dimethyl-6-nitrobenzophenone (2.5 g, 10 mmol) in the third 50% ether fraction, a mixture of 2- and 6-nitro isomers (0.7 g, 3 mmol) and diene adduct **2** (4.2 g, 13 mmol) in the 60–70% ether fractions from which the adduct **2** crystallized. In other nitration reactions 3,5-dinitro-*o*-xylene was isolated from early column fractions: n.m.r. ($CDCl_3$) τ 1.53 (d, 1, J = 2 Hz, 4-*H*), 1.75 (d, 1, J = 2 Hz, 6-*H*), 7.50 (s, 6, 1-CH_3 and 2-CH_3). Chromatography of the diene fractions at −45° gave the individual diastereoisomers **2*a*** and ***b***. *Trans* adduct **2*a*** was formed in larger amount (3:1) than *cis* adduct **2*b***. At higher temperatures adduct **2*a*** decomposed on the column and 2-benzoyl-4,5-dimethylphenyl acetate, eluted in the early column fractions, and 2-benzoyl-4,5-dimethylphenol, eluted with methanol, were formed. Adducts constituted 65–75% of the reaction product before work-up.

trans-2-Benzoyl-4,5-dimethyl-4-nitro-1,4-dihydrophenyl acetate (**2*a***) was recrystallized from chloroform–pentane, m.p. 118°; u.v. (CH_3OH) 255 nm (ε 1330 m^2 mol^{-1}); i.r. (Nujol) 1740 and 1250 ($OCOCH_3$), 1660 (C=O), 1560 (NO_2), 730 cm^{-1}; n.m.r. (220 MHz, $CDCl_3$) τ 2.22 (d, 2, J = 8 Hz, 2′-*H* and 6′-*H*), 2.38 (t, 1, J = 8 Hz, 4′-*H*), 2.51 (t, 2, J = 8 Hz, 3′-*H* and 5′-*H*), 3.46 (d, 1, 3-*H*), 3.60 (m, 1, 1-*H*), 3.90 (m, 1, 6-*H*), 8.01 (s, 3, $OCOCH_3$), 8.04 (s, 3, 4-CH_3), 8.10 (t, 3, 5-CH_3), J_{13} = 1.38, J_{16} = 3.60, $J_{1,5-CH_3}$ = 1.43, $J_{6,5-CH_3}$ = 1.43 Hz.

Anal. Calcd. for $C_{17}H_{17}NO_5$(M_r 315): C, 64.75; H, 5.43; N, 4.44. Found (307): C, 64.74; H, 5.29; N, 4.43.

cis-2-Benzoyl-4, 5-dimethyl-4-nitro-1,4-dihydrophenyl acetate (**2*b***) was recrystallized from chloroform–pentane, m.p. 128–130° (dec.); u.v. (CH_3OH) 252 nm (ε 1140 m^2 mol^{-1}); i.r. (Nujol) 1735 and 1250 ($OCOCH_3$), 1660 (C=O), 1560 (NO_2), 730 cm^{-1}; n.m.r. (220 MHz, $CDCl_3$) τ 2.11 (d, 2, J = 8 Hz, 2′-*H*, 6′-*H*), 2.37 (t, 1, J = 8 Hz, 4′-*H*), 2.50 (t, 2, J = 8 Hz, 3′-*H* and 5′-*H*), 3.54 (d, 1, 3-*H*), 3.68 (m, 1, 1-*H*), 3.93 (m, 1, 6-*H*), 7.99 (s, 3, $OCOCH_3$), 8.10 (t, 3, 5-CH_3), 8.26 (s, 3, 4-CH_3), J_{13} = 1.41, J_{16} = 3.21, $J_{1,5-CH_3}$ = 1.46, $J_{6,5-CH_3}$ = 1.43 Hz; in the 60 MHz spectrum irradiation of the methyl triplet collapsed the multiple t at 3.07 to a doublet of doublets and that at 3.95 to a doublet. The decoupled spectrum was simulated and refined to give coupling constants and chemical shifts for the hexadiene ring protons. These coupling constants together with the estimated coupling constants to the methyl group were then used to simulate the undecoupled 220 MHz spectrum and the simulation refined to give the listed coupling constants and chemical shifts.

Anal. Calcd. for $C_{17}H_{17}NO_5$ (M_r 315): C, 64.75; H, 5.43; N, 4.44. Found (306): C, 64.72; H, 5.16; N, 4.33.

The arguments for the structure of **2** are similar to those for the structure **1** and are likewise supported by the similar effects of shift reagent. The assignment of **2*a*** as the *trans* and **2*b*** as the *cis* adduct follows from the more rapid downfield shift of the 4-methyl peak in the former.

Nitro Compounds

The three nitro substitution products were obtained from the nitration mixture after chromatography and crystallization. The 2-nitro and 5-nitro isomers were also isolated from rearomatization reactions.

3,4-Dimethyl-2-nitrobenzophenone had m.p. 103–104°; i.r. (Nujol) 1680 (C=O), 1545 and 1375 cm^{-1} (NO_2); n.m.r. ($CDCl_3$) τ 2.20 (m, 2, 2′-*H* and 6′-*H*), 2.39 (m, 1, 4′-*H*), 2.53 (m, 2, 3′-*H* and 5′-*H*), 2.63 (d, 2, 6-*H*), 2.71 (d, 2, 5-*H*), 7.57 (s, 3, 3-CH_3), 7.69 (s, 3, 4-CH_3), J_{56} = 7.9, $J_{2'3'}$ = 8.1, $J_{2'4'}$ = 1.3, $J_{2'5'}$ = 0.6, $J_{2'6'}$ = 1.6, $J_{3'4'}$ = 7.5, $J_{3'5'}$ = 1.4 Hz; addition of the shift reagent to this isomer shifted the quartet of lines of the 2′-*H* and 6′-*H* down to τ 1.15 and the doublet (J = 8 Hz) of the 6-H to 1.65. Only three protons were moved substantially downfield confirming the identification as the 2-nitro isomer since there are only three protons *ortho* to the carbonyl group where the europium is expected to complex. Mass spectrum (70 eV) *m/e* (relative intensity) 255 (19, M), 238 (3, M − OH), 178 (23, M − C_6H_5), 165 (17), 162 (35), 149 (10), 132 (9), 105 (100), 77 (36).

3,4-Dimethyl-5-nitrobenzophenone had m.p. 64–69°; i.r. (Nujol) 1660 (C=O), 1540 and 1365 cm^{-1} (NO_2); n.m.r. ($CDCl_3$) 2.04 (d, 1, J = 2 Hz, 6-*H*), 2.19 (d, 1, J = 2 Hz, 2-*H*), 2.24 (q, 2, J = 2 Hz and J = 8 Hz, 2′-*H* and 6′*H*), 2.45 (m, 3, 3′-*H*, 4′-*H*, and 5′-*H*), 7.57 (s, 6, 3-CH_3 and 4-CH_3); addition of the shift reagent moved four aromatic protons to much lower field (τ 1.2). There are four protons *ortho* to the carbonyl group in the 5-nitro isomer and thus the identification of this isomer is confirmed. Mass spectrum (70 eV) *m/e* (relative intensity) 255 (80, M), 238 (80, M − OH), 105 (100), 77 (100).

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.31; H, 5.04; N, 5.29.

3,4-Dimethyl-6-nitrobenzophenone had m.p. 80°; i.r. (Nujol) 1680 (C=O), 1530 and 1360 cm^{-1} (NO_2); n.m.r. ($CDCl_3$) τ 2.02 (s, 1, 5-*H*), 2.26 (q, 2, J = 2 Hz and J = 8 Hz, 2′-*H* and 6′-*H*), 2.53 (m, 3, 3′-*H*, 4′-*H* and 5′-*H*), 2.79 (s, 1, 2-*H*), 7.60 (s, 3, CH_3), 7.64 (s, 3, CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 255.083 (30, M_r ($^{12}C_{15}{}^{1}H_{13}{}^{14}N^{16}O_3$) 255.090), 178 (47, M − C_6H_5), 165 (23), 162 (100), 132 (25), 105 (94), 77 (50).

The structures of the three nitro substitution products are readily assigned from their n.m.r. spectra. In each case the aromatic region exhibits the complex multiplets from the protons of the benzoyl ring in addition to the peaks of the nitro-substituted ring, the patterns for which are similar to the dimethylnitroacetophenone analogs. 3,4-Dimethyl-2-nitrobenzophenone exhibits the AB quartet with an 8 Hz coupling of the two *ortho* protons of the substituted ring at higher field than the multiplets of the phenyl ring. The 5-nitro isomer exhibits for the *meta* protons of the substituted ring an AB quartet with a 2 Hz coupling of which the low field doublet (6-H) is at lower field than the phenyl ring multiplets, and the higher field doublet (2-H) overlaps the phenyl ring part of the spectrum. The 6-nitro isomer exhibits two singlets for the *para* protons of the substituted ring, one of which (5-H) lies at lower field and the other (2-H) at higher field than the phenyl ring multiplets.

2-Benzoyl-4,5-dimethylphenol and 2-Benzoyl-4,5-dimethylphenyl Acetate

Diene **2** was treated with a concentrated solution of sodium methoxide as described above for diene **1**. After work-up, 2-benzoyl-4,5-diemthylphenol was obtained, m.p. 112–113.5° (lit. (12) m.p. 111–112°); i.r. (Nujol) 1635 cm^{-1} (C=O); n.m.r. ($CDCl_3$) τ 2.44 (m, 5, C_6H_5), 2.72 (s, 1, 3-*H*), 3.15 (s, 1, 6-*H*), 7.75 (s, 3, 5-CH_3), 7.87 (s, 3, 4-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 226 (7, M), 225 (8, M − H), 149 (25, M − C_6H_5), 120 (10), 105 (30), 93 (14), 91 (50), 77 (100).

The phenol was acetylated with acetic anhydride containing sulfuric acid to give 2-benzoyl-4,5-dimethylphenyl acetate, m.p. 69–70°; i.r. (Nujol) 1720 ($OCOCH_3$), 1670 (C=O), 1285, 1210, 1180, 735, and 705 cm^{-1}; n.m.r. ($CDCl_3$) τ 2.2 (m, 2, 2′-*H* and 6′-*H*), 2.45 (m, 3, 3′-*H*, 4′-*H*, and 5′-*H*), 2.65 (s, 1, 3-*H*), 3.01 (s, 1, 6-*H*), 7.65 (s, 3, 5-CH_3), 7.71 (s, 3, 4-CH_3), 8.08 (s, 3, $OCOCH_3$); mass spectrum *m/e* 268 (M).

*2-Benzoyl-2′,4,4′,5,6′-pentamethylbiphenyl (**16**)*

A solution of diene **2** (2 g, 6.3 mmol) and mesitylene in methylene chloride was treated with boron trifluoride etherate as described for diene **1**. After work-up, chromatography on silica gel and elution with pentane and 15% ether–pentane gave mesitylene in the pentane fractions, the biphenyl (1.8 g, 5.5 mmol) in the early ether–pentane fractions followed by 3,4-dimethyl-2- and 3,4-dimethyl-5-nitrobenzophenone (90 mg, 0.4 mmol). After recrystallization from ethanol 2-benzoyl-2′,4,4′,5,6′-pentamethylbiphenyl had m.p. 98–99.5°; i.r. (Nujol) 1675 (C=O), 1265, 900 and 725 cm^{-1}; n.m.r. ($CDCl_3$) τ 2.7 (m, 5, C_6H_5), 2.72 (s, 1, 3-*H*), 3.02 (s, 1, 6-*H*), 3.26 (s, 2, 3′-*H* and 5′-*H*), 7.71 (s, 6, 4-CH_3 and 5-CH_3), 7.81 (s, 3, 4′-CH_3) 8.03 (s, 6, 2′-CH_3 and 6′-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 328 (20, M) 313 (58, M − CH_3), 251 (100, M − C_6H_5), 132 (100), 105 (60), 77 (50), 43 (78).

Anal. Calcd. for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.70; H, 7.23.

Reaction of Diene 2 with Trifluoroacetic Acid

Trifluoroacetic acid (2.5 cm^3) was added dropwise to a stirred solution of diene **2** (1 g) in chloroform (10 cm^3). Brown fumes of NO_2 were given off. After work-up, 2-benzoyl-4,5-dimethylphenyl acetate was obtained, identified by n.m.r. and t.l.c.

Reaction of Diene 2 with Acetic Acid

A solution of diene **2** (0.5 g) in acetic acid (5 cm^3) was heated under reflux for 30 min. Brown fumes of NO_2 were given off. After work-up, 2-benzoyl-4,5-dimethylphenyl acetate was obtained. When the reaction was carried out at ambient temperature it took 14 days to go to completion.

Thermolysis of Diene 2

A solution of diene **2** (0.5 g) in toluene (10 cm^3) was heated under reflux. Brown fumes of NO_2 were given off. The toluene was distilled off and the residue was characterized as 2-benzoyl-4,5-dimethylphenyl acetate by n.m.r. and t.l.c.

Reaction of Diene 2 with Boron Trifluoride Etherate

Diene **2** (3 g, 9.5 mmol) was added to boron trifluoride etherate (3 cm^3). A vigorous reaction ensued. After work-up and chromatography on silica gel and elution with 20% ether–pentane, 3,4-dimethylbenzophenone (640 mg, 3 mmol), 3,4-dimethyl-5-nitrobenzophenone (580 mg, 2.3 mmol), and 3,4-dimethyl-2-nitrobenzophenone (770 mg, 3.0 mmol) were obtained.

Reaction of Diene 2 with 78% Sulfuric Acid

Diene **2** (0.5 g, 1.6 mmol) was stirred with 78% sulfuric acid (2 cm^3) overnight. After work-up and chromatography on silica gel, 3,4-dimethylbenzophenone (112 mg, 0.5 mmol), 3,4-dimethyl-5-nitrobenzophenone (100 mg, 0.4 mmol), and 3,4-dimethyl-2-nitrobenzophenone (120 mg, 0.5 mmol) were obtained.

Reaction of Diene 2 with Mesitylene in Acetic Acid Containing Sulfuric Acid

A solution of sulfuric acid (1.35 cm^3) in acetic acid (2.5 cm^3) was added dropwise to a solution of diene **2** (2 g, 6.3 mmol) in mesitylene (10 cm^3). After stirring for 1.5 h the mixture was neutralized and worked-up. Chromatography on silica gel and elution with pentane removed the excess mesitylene. Elution with 20% ether–pentane gave 2-benzoyl-2′,4,4′,5,6′-pentamethylbiphenyl (810 mg, 2.5 mmol) and a mixture of 3,4-dimethyl-2-nitro- and 3,4-dimethyl-5-nitro-benzophenone (640 mg, 2.5 mmol).

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