action of nitrobenzene and triphenylphosphine, but only starting materials are recovered, in agreement with previous work[8] which employed triethylphosphine.

In contrast to the reactivity of *o*-dinitroso compounds, furoxans (IV) are unreactive toward tri-*n*-butylphosphine.

EXPERIMENTAL[9]

Benzofurazan. On mixing 1.36 g. (10.0 mmoles) of *o*-dinitrosobenzene and 2.86 g. (10.9 mmoles) of triphenylphosphine in 25 ml. of 95% ethanol the solution became warm and turned red. After refluxing for 30 min., steam distillation afforded 0.68 g. of benzofurazan, m.p. and mixture m.p. 52–53°,[10] insoluble in the first 200 ml. of distillate. An additional 0.13 g., m.p. 47–48°, obtained on extracting the distillate with ether and evaporation of the ether layer, gave a total of 0.81 g. (68%) of benzofurazan which absorbed in the infrared from a potassium bromide disk at [μ(%T)]: 6.14 (56.3), 6.54 (43.0), 6.89 (51.9), 6.97 (52.7), 7.26 (56.0), 7.36 (44.0), 8.75 (47.2), 9.56 (70.9), 9.82 (51.5), 9.91 (39.0), 11.41 (31.1), 11.83 (40.9), 13.24 (18.3), 13.51 (14.8), 14.37 (43.9). An authentic sample of benzofurazan, m.p. 53–54°, from *o*-dinitrosobenzene and hydroxylamine gave identical absorption except for a band in the region of 14.37 μ.

A concentrated benzene extract of the distillation residue was treated with ligroin to precipitate triphenylphosphine oxide, m.p. and mixture m.p. 156–158°,[11] 2.55 g. (91.7%). Its infrared absorption from a potassium bromide disk was identical with that obtained from a similar examination of an authentic specimen.

In an experiment with 10.0 moles of *o*-dinitrosobenzene, 21.8 mmoles of triphenylphosphine, and reflux time of 5 hr., 65% of the excess (11.8 mmoles) phosphine was recovered and triphenylphosphine oxide was obtained quantitatively.

A reaction in anhydrous petroleum ether (b.p. 60–68°) instead of 95% ethanol gave a 66% yield of triphenylphosphine oxide after 1.5 hr. at room temperature followed by heating on a steam bath for 10 min. A tarry residue with the odor of benzofurazan remained after evaporation of the filtrate.

Substitution of tri-*n*-butylphosphine for triphenylphosphine afforded benzofurazan in 62% yield after equimolar quantities of phosphine and *o*-dinitrosobenzene were refluxed in 95% ethanol under nitrogen for 1 hr. In a similar experiment benzofurazan was obtained in 58% yield from *o*-dinitrosobenzene treated with a molar excess of triethyl phosphite in refluxing ethanol under nitrogen for 12 hr.

Naphthofurazan, m.p. and mixture m.p. 77–78°,[12] was obtained in 65% yield from 1,2-dinitrosonaphthalene and tri-*n*-butylphosphine in equimolar quantities in refluxing 95% ethanol under nitrogen for 2 hr. Triphenylphosphine failed to deoxygenate 1,2-dinitrosonaphthalene in refluxing ethanol for 5.5 hr.

4,7-Diphenylfurazano[d]pyridazine, m.p. and mixture m.p. 193–195°,[13] was obtained in 36% yield from 3,6-diphenyl-4,5-dinitrosopyridazine and tri-*n*-butylphosphine (molar excess) in refluxing 95% ethanol under nitrogen for 1 hr. The crude product, isolated by filtering the reaction mixture diluted with water, was recrystallized from aqueous acetone. Equimolar quantities of reactants after 6 hr. gave lower yields of product together with recovered starting material.

Starting material was recovered and an unidentified product in low yield, m.p. 286–288° dec., and triphenylphosphine oxide (48%) were obtained on refluxing *o*-dinitrobenzene and triphenylphosphine in benzene under nitrogen for 1 hr. Nitrobenzene was unreactive toward triphenylphosphine in boiling ethanol for 18 hr. although the solution became black.

Diphenylfuroxan and bis-*p,p*′-dichlorobenzhydrylfuroxan were each unreactive toward tri-*n*-butylphosphine in boiling ethanol for 24 hr. and were recovered (90% and 57%, respectively).

CHEMISTRY DEPARTMENT
TULANE UNIVERSITY
NEW ORLEANS 18, LA.

---

(9) Melting points are uncorrected. We are indebted to Mr. R. T. O'Connor, Southern Regional Research Laboratory, New Orleans, La., for infrared data.

(10) T. Zincke and P. Schwarz, *Ann.*, **307**, 28 (1899).

(11) M. A. Greenbaum, D. B. Denney, and A. K. Hoffmann, *J. Am. Chem. Soc.*, **78**, 2563 (1956).

(12) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **111**, 612 (1917).

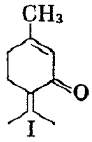
(13) E. Durio, *Gazz. chim. ital.*, **61**, 589 (1931).

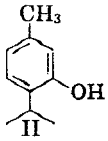
Condensation of Mesityl Oxide and Methyl Vinyl Ketone

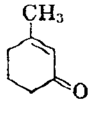
ERNST D. BERGMANN AND P. BRACHA

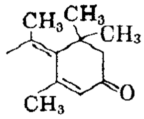
Received February 10, 1961

In a recent communication[1] we have reported that the condensation of mesityl oxide and methyl vinyl ketone in the presence of sodium *t*-pentoxide leads to piperitenone (I). Although the physical constants of the product showed some deviations from the values reported for natural piperitenone by Naves[2] and others,[3–5] we had based our conclusions on two observations which appeared to be unambiguous: the catalytic transformation to thymol (II) and the fission to acetone and 3-methylcyclohex-2-enone (III).


I


II


III


IV

Naves and Conia[6] were not able to reproduce our results and claimed that the only product formed under the conditions described was the well known[7] self-condensation product of mesityl oxide, *viz.* isoxylitone (IV). In a later communication,[8] the French authors, reported that after a private communication from Dr. Ueda,[9] they reinvesti-

---

(1) E. D. Bergmann and P. Bracha, *J. Org. Chem.*, **24**, 994 (1959).

(2) Y.-R. Naves, *Helv. Chim. Acta*, **25**, 732 (1942). Y.-R. Naves and G. Papazian, *Helv. Chim. Acta*, **25**, 1032 (1942).

(3) W. Kuhn and H. Schinz, *Helv. Chim. Acta*, **36**, 161 (1953).

(4) T. Suga, *Bull. Chem. Soc. Japan*, **31**, 569 (1958).

(5) Ch. Balant, Ch. A. Vodoz, H. Kappeler, and H. Schinz, *Helv. Chim. Acta*, **34**, 722 (1951).

(6) Y.-R. Naves and J.-M. Conia, *Bull. soc. chim. France*, 378 (1960). J.-M. Conia, and Y.-R. Naves, *Compt. rend.*, **250**, 356 (1960).

(7) J.-M. Conia, *Compt. Rend.*, **240**, 1545 (1955).

(8) Y.-R. Naves and J.-M. Conia, *Compt. rend.*, **251**, 1130 (1960).

gated the condensation of mesityl oxide and methyl vinyl ketone and concluded that the product contained, indeed, piperitenone (I) *together with* isoxylitone (IV).

We would like to clarify the situation on the basis of additional experiments carried out. While there is no doubt that piperitenone (I) is formed by the reaction in question, we concur with Naves and Conia that isoxylitone is also formed. In spite of the difference in molecular weight, I and IV can be separated only with great difficulty even in an efficient column; the boiling points reported are 92° (1.8 mm.)[2] and 90–91° (3 mm.),[8] respectively. The quantity of piperitenone (I) in the crude product and after distillation can easily be determined by the two reactions mentioned: conversion into II and III, respectively; neither of these reactions is, of course, shared by isoxylitone (IV). The ratio of I and IV in the reaction product may vary due to small differences in operating conditions. Neither the ultraviolet spectrum nor the preparation of the usual derivatives provides an easy means of differentiation between I and IV. The following figures will demonstrate this:

	Ultraviolet Spectrum	2,4-Dinitrophenylhydrazone, M.P.	Semicarbazone, M.P.
Isoxylitone (IV)	238.5 (3.36); 297 (4.12)	179; 156[a]	155–156; 180[a]
Piperitenone (I)	243 (4.10); 278 (3.90)	184–184.5; 152.5–153; 131–132	—
Our product (after distillation)	241 (3.78); 290 (3.85)	152	182

[a] J. Wiemann, B. Furth, and G. Dana, *Compt. rend.* **250**, 3674 (1960). *Cf.* also N. Bacon, S. Brewis, G. E. Usher, and E. S. Waight, *J. Chem. Soc.*, 2255 (1961).

We admit that the derivatives (dinitrophenylhydrazone, semicarbazone) obtained from our product after recrystallization, were those of isoxylitone, and it is clear that in the condensation of mesityl oxide and methyl vinyl ketone in the presence of sodium *t*-pentoxide, both piperitenone (I) and isoxylitone (IV) are formed. The thymol obtained in the palladium treatment of the product, and the acetone and 3-methylcyclohex-2-enone formed upon reaction with formic acid, have come from the piperitenone (I).

Department of Organic Chemistry
Hebrew University
Jerusalem, Israel

---

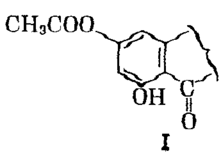
(9) *Cf.* S. Shimizu, N. Ikeda, and H. Ueda, *Bull. Agr. Chem. Soc. Japan*, **24**, 324 (1960).

Acetyl Transfer during Alkylation Reactions

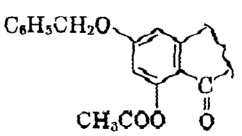
T. H. Simpson and R. S. Wright

Received February 20, 1961

The recent publication[1] on the base-catalyzed rearrangement of *p*-aroyloxyacetophenones prompts us to record our observations on acetyl transfer in phenolic compounds. In earlier communications[2,3] it was claimed that although methylation of partially acetylated phenols possessing the partial structure I proceeded normally, benzylation under similar conditions caused migration of the acetyl group with the formation of compounds of type II. The potential usefulness of these methods in the preparation of partial ethers of complex phenols prompted this more detailed study.



I



II

In our hands, benzylation of 4-acetoxy-2-hydroxyacetophenone[3] afforded, after recrystallization, only a 10% yield of impure 2-acetoxy-4-benzyloxyacetophenone. The low yield of this compound was later confirmed by chromatography of the crude reaction product. Table I lists the compounds, with their molar yields, isolated from the product of this reaction and from the corresponding methylation reaction, performed under identical conditions.

These results showed that the methylation and benzylation reactions follow similar courses and suggested that migration of acetyl and alkylation might occur independently, giving a product whose composition would be determined by the rates of alkylation of the two hydroxyl groups relative to the rate of the base-catalyzed migration.

This suggestion was supported by the results of experiments in which 4-acetoxy-2-hydroxyacetophenone was heated with potassium carbonate and acetone. On chromatography, the product was found to contain, in addition to starting material (molar yield, 38.5%), a difficulty separable mixture of resacetophenone and 2,4-diacetoxyacetophenone (35%), 2,4-diacetoxyacetophenone (6%), 2-acetoxy-4-hydroxyacetophenone (4%), together with smaller quantities (< 2%) of 4-methylumbelliferone acetate (IV), 3-acetyl-7-hydroxy-2-methylchromone and its acetate (VII a and b).

---

(1) L. Jurd, *Chem. & Ind.* (*London*), 965 (1960).

(2) L. Jurd, *Chem. & Ind.* (*London*), 1452 (1957).

(3) L. Jurd and L. A. Rolle, *J. Am. Chem. Soc.*, **80**, 5527 (1958).