were identified by boiling point,[15] and by the presence of an intense hydrogen out-of-plane bending band at 924 cm.$^{-1}$ in the infrared spectrum of the *trans* compound.

*cis* and *trans*-Propenyllithium. This procedure is representative. A solution of 4 g. of *cis*-propenyl chloride in 15 ml. of ether was stirred vigorously under nitrogen with a two-fold excess of lithium metal[16] for 3 hr.

The reaction mixture was then filtered (in a dry box under nitrogen) to remove lithium metal and some salts. The filtrate was then evaporated under vacuum, and the residue was used to prepare a mull in Nujol. This mull was placed in an infrared cell, which could then be handled in air.

A modification of this procedure eliminated the filtration above. The pieces of lithium metal were picked out by hand, and after evaporation of the volatile material, the remainder of the solid was used for the mull. The principal bands obtained and assigned to the propenyllithium were the same in either method. Some small variable bands were also obtained, and since they were not consistently present in samples prepared in different runs, they were clearly due to impurities and were not further considered. The infrared spectra were recorded on both a Beckman IR-4 and a Baird Spectrophotometer.

*trans*- and *cis*-1-Phenyl-2-butenol-1. The reaction mixture containing propenyllithium from the *trans* chloride was cooled to 5° and 2 g. of benzaldehyde was added dropwise with stirring. After stirring the mixture an additional 20 min. at 5° the solution was filtered to remove excess lithium, and a cold saturated solution of ammonium chloride was added to the filtrate. The phases were separated, and the aqueous phase was extracted with ether. The combined ether layers were dried over potassium carbonate, and the ether was evaporated. Distillation furnished 2 g. of material, b.p. 103–110° (0.25 mm.). The infrared spectrum showed a strong band at 965 cm.$^{-1}$ which is characteristic of the *trans* isomer, and it was not detectably contaminated by the *cis*, which absorbs at 980 cm.$^{-1}$

The *cis* chloride similarly yielded the *cis* alcohol, which showed strong absorption at 980 cm.$^{-1}$, and was not detectably contaminated with the *trans*.

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[15] E. H. Huntress, *Organic Chlorine Compounds*, Wiley, New York, 1948, p. 947.

[16] It was found that lithium from some batches consistently reacted very well, while that from other batches consistently failed to react. J. A. Beel, W. G. Koch, G. E. Tomasi, D. E. Hermansen, and P. Fleetwood, *J. Org. Chem.*, 24, 2036 (1959) have shown that the sodium content of the lithium can greatly affect its reactivity toward halides. The quality of the lithium used in the present work is not known.

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

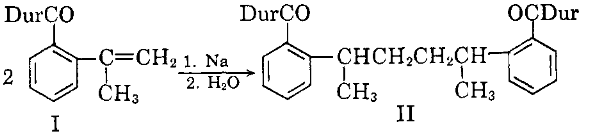
# 1,6-Reductive Coupling of Hindered *o*-Vinyl Diaryl Ketones[1]

REYNOLD C. FUSON, EARL H. HESS,[2] AND MEHM TIN MON[3]

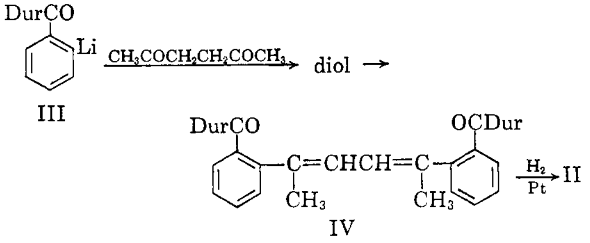
*Received July 25, 1960*

Mesityl *o*-vinylphenyl ketone, duryl *o*-vinylphenyl ketone, and duryl *o*-isopropenylphenyl ketone have been reduced with metallic sodium, the products being the corresponding butanes to be expected from 1,6-reductive coupling involving the side chain. The reductive coupling product of the isopropenyl compound was isolated in the expected two diastereoisomeric forms. These compounds were synthesized independently from *o*-duroylphenyllithium and acetonylacetone. The diol was dehydrated, and the resulting diene was hydrogenated catalytically.

1,6-Addition of Grignard reagents to hindered ketones is well known, and in the reaction of *t*-butylmagnesium chloride with duryl *o*-isopropenylphenyl ketone was shown to involve the *p*-position rather than the side chain.[4] The formation of *p,p'*-diduroylbiphenyl from duryl *p*-hydroxyphenyl ketone[5] depends on a 1,6-coupling. It has now been found that a similar coupling involving the side chain can be realized by treating hindered *o*-vinylphenyl ketones with sodium. The hexane derivatives II produced in this way from duryl *o*-isopropenylphenyl ketone (I) correspond to the two diastereoisomeric forms to be expected.



Their structure was established by an independent synthesis beginning with the condensation of *o*-duroylphenyllithium (III)[6] with acetonylacetone. The crude diol was dehydrated with dilute sulfuric acid to give 1,4-di (*o*-duroylphenyl)-1,4-dimethylbutadiene (IV). Hydrogenation of the diene produced a mixture of the two diastereoisomeric hexane derivatives. When isolated in pure form they were found, by reference to mixture melting point deter-



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[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] Socony-Vacuum Oil Company Fellow, 1954–55.

[3] Deputationist of the Government of the Union of Burma.

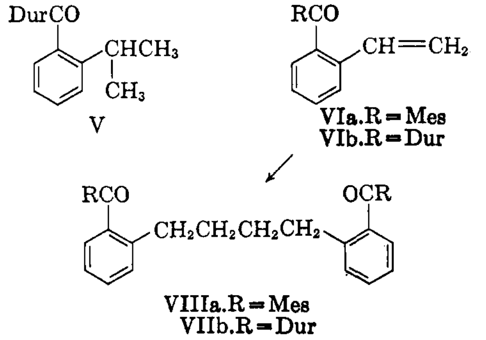
[4] R. C. Fuson, W. D. Emmons, and S. G. Smith, Jr., *J. Am. Chem. Soc.*, 77, 2503 (1955).

[5] R. C. Fuson and G. W. Parshall, *J. Am. Chem. Soc.*, 76, 5561 (1954).

[6] R. C. Fuson, W. C. Hammann, and W. E. Smith, *J. Org. Chem.*, 19, 674 (1954).

minations, and by comparison of infrared spectra to be identical to the products obtained by the sodium reduction.

In the reaction of the isopropenyl ketone I with sodium, duryl *o*-isopropylphenyl ketone (V), a 1,6-reduction product, was also isolated in a small yield. Mesityl *o*-vinylphenyl ketone (VIa) and duryl *o*-vinylphenyl ketone (VIb) were found to behave similarly. The butane derivatives were isolated each in a single form as expected.



### EXPERIMENTAL[7]

*Treatment of duryl o-isopropenylphenyl ketone with sodium.* To 1 g. of powdered metallic sodium in 100 ml. of absolute ether was added with stirring a portion of 1.4 g. (0.005 mole) of duryl *o*-isopropenylphenyl ketone (I)[8] dissolved in 50 ml. of dried benzene. After the mixture had attained a black color the rest of the ketone solution was added over 20 min. The mixture was heated under reflux, with stirring, for 6 hr. and treated with water. Chromatographic separation of the products on a column of 100 g. of alumina with large volumes of eluents yielded 267 mg. (18.9%) of duryl *o*-isopropylphenyl ketone (V), m.p. 148.5–149.5°, identified by a mixture melting point determination and comparison of the infrared spectrum[9] with that of an authentic sample. Also isolated were 55 mg. (3.9%) of the original ketone I and 340 mg. (24%) of one of the 2,5-di(*o*-duroylphenyl)hexanes II, colorless crystals from benzene-ethanol, m.p. 232–232.5°.

*Anal.*[10] Calcd. for $C_{40}H_{46}O_2$: C, 85.97; H, 8.30. Found: C, 85.90; H, 8.30.

A third product, the diastereoisomeric hexane, when recrystallized from the same solvents, melted at 211.5–212.5°, yield 400 mg. (28.5%).

*Anal.* Calcd. for $C_{40}H_{46}O_2$: C, 85.97; H, 8.30. Found: C, 85.89; H, 8.26.

The infrared spectra of the two diastereoisomeric products are nearly identical. They contain bands at 1668 cm.$^{-1}$, assignable to a carbonyl group, at 760 cm.$^{-1}$, assignable to a 1,2-disubstituted phenyl ring, and at 717 and 1485 cm.$^{-1}$, assignable to chained methylene groups.

*Condensation of o-duroylphenyllithium* (III) *with acetonylacetone.* A solution of 1 g. (0.009 mole) of freshly redistilled acetonylacetone in 15 ml. of anhydrous ether was added over 5 min. to *o*-duroylphenyllithium made at −78° from 6.34 g. (0.02 mole) of duryl *o*-bromophenyl ketone, 50 ml. of ether, and 25 ml. of 0.82*N* solution (0.02 mole) of *n*-butyllithium in ether. The cold bath was removed; the reaction mixture was allowed to warm up slowly with stirring to room temperature in the course of 1 hr. and then heated under reflux for 30 min. longer. The mixture was cooled and treated with 30 ml. of cold 5% sulfuric acid. The resultant slurry was stirred at room temperature for 10 min. The ether layer was washed and dried. Removal of ether and crystallization of the residual oil from chloroform-ethanol gave 266 mg. of 1,4-di(*o*-duroylphenyl)-1,4-dimethylbutadiene (IV), yellow crystals, m.p. 277–279°. The crystallization filtrates were concentrated and subjected to chromatography; an additional 200 mg. of the product was isolated. Its infrared spectrum has absorption bands assignable to the carbonyl groups (1675 cm.$^{-1}$), to the duryl group (818, 865, and 945 cm.$^{-1}$), and to conjugated olefinic double bonds (1635 cm.$^{-1}$). The ultraviolet spectrum[11] has two absorption maxima at 203 m$\mu$ and 250 m$\mu$ with log $\epsilon$ equal to 5.8451 and 5.7404, respectively. Duryl *o*-isopropenylphenyl ketone shows similar absorption maxima at 203 m$\mu$ and 250 m$\mu$ with log $\epsilon$ equal to 3.6324 and 3.3053, respectively.

*Hydrogenation of 1,4-di-(o-duroylphenyl)-1,4-dimethylbutadiene.* A solution of 130 mg. ($2.34 \times 10^{-4}$ mole) of the diene in 20 ml. of 1:1 chloroform-ethanol mixture was treated with hydrogen in the presence of 30 mg. of Adams catalyst at room temperature and pressure. The theoretical uptake of hydrogen (10.5 ml., $4.68 \times 10^{-4}$ mole) was complete in 1 hr. The mixture was stirred, however, for an additional 4 hr. and allowed to stand under hydrogen for 42 hr. to ensure ketonization of the product.[12] The catalyst was removed and the organic solution concentrated to give 85 mg. of colorless crystals, m.p. 182–213°. The infrared spectrum of this mixture was superimposable on those of the diastereoisomeric 2,5-di(*o*-duroylphenyl)hexanes. Chromatographic separation of 50 mg. of the mixture gave 20 mg. of the isomer melting at 232–232.5° and 18 mg. of the isomer melting at 211.5–212.5°. The identity of the compounds was established by mixture melting points and by comparison of infrared spectra.

*Treatment of mesityl o-vinylphenyl ketone with sodium.* The procedure was similar to that described for the isopropenyl compound. A solution of 2 g. of the ketone[8] in 50 ml. of sodium-dried, thiophene-free benzene was added in part to a slurry of 1 g. of freshly powdered sodium in 100 ml. of anhydrous ether which had been blanketed with dry nitrogen. The addition was accompanied with stirring, the stirrer being pushed down in order to cut fresh surfaces on sodium. A dark red color diffused throughout the solution in 3 min. The rest of the ketone solution was then added over a 15-min. interval, and the reaction mixture was heated under reflux with stirring for 6 hr. The mixture was allowed to cool slowly to 0° and treated cautiously with 50 ml. of 4% dilute hydrochloric acid; the resulting mixture was stirred under nitrogen for 20 min. The organic layer was washed and dried over anhydrous sodium sulfate. The solvent was removed by low-pressure distillation, and the residual oil was chromatographed on 120 g. of Merck acid-washed aluminum oxide. From the chromatogram 86 mg. (4.3%) of mesityl *o*-ethylphenyl ketone[8] and 1.22 g. (60.7%) of 1,4-di(*o*-mesitoylphenyl)butane (VIIa), colorless crystals from benzene-ethanol, m.p. 182–182.5°, were obtained.

*Anal.* Calcd. for $C_{36}H_{38}O_2$: C, 86.01; H, 7.62. Found: C, 85.95; H, 7.62.

The infrared spectrum of the reductive coupling product has bands assignable to a conjugated carbonyl group (1670 cm.$^{-1}$), a 1,2-disubstituted phenyl ring (760 cm.$^{-1}$), a mesityl group (852 cm.$^{-1}$), and chained methylene groups (730, 1233, and 1483 cm.$^{-1}$). The nuclear magnetic resonance spectrum[13] has values of 2.74, attributed to the phenyl hydrogen atoms, 3.26, attributed to the mesitylene hydrogen

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(7) All melting points are corrected.

(8) R. C. Fuson and M. T. Mon, *J. Org. Chem.*, **26**, 756 (1961).

(9) The infrared spectra were determined by Mr. Paul McMahon, Mrs. Mary Verkade, Miss Charlene Leubke, Mr. D. H. Johnson, and Mr. William Dalton.

(10) The microanalyses were performed by Mr. Josef Nemeth, Mrs. A. S. Bay, and Miss Jane Liu.

(11) The ultraviolet spectra were obtained from a Cary Model 14 recording spectrophotometer by Miss Cynthia Juan.

(12) R. C. Fuson and R. E. Foster, *J. Am. Chem. Soc.*, **65**, 913 (1943).

atoms, and 6.91, attributed to the methylene hydrogen atoms. The values of 7.74 and 7.98 were attributed to the hydrogen atoms on the methyl groups *para* and *ortho* to the carbonyl functions, respectively. The spectrum peaks were identified by the relative areas under their curves as compared to the number of the hydrogen atoms.

*Treatment of duryl o-vinylphenyl ketone*[8] *with sodium.* This experiment was performed in the manner just described. The products, however, offered great difficulty in purification. This might be the main reason for the relatively low yields. Duryl *o*-ethylphenyl ketone[8] was obtained in 2.2% yield and the reductive coupling product, colorless crystals from chloroform-ethanol, m.p. 242–244°, in 30.8% yield. The infrared and the nuclear magnetic resonance spectra of 1,4-di(*o*-duroylphenyl)butane (VIIb) were similar to those of its mesityl analog.

*Anal.* Calcd. for $C_{38}H_{42}O_2$: C, 85.99; H, 7.98. Found: C, 85.55; H, 8.18.

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(13) The nuclear magnetic resonance spectra were determined by Mr. O. W. Norton at 60 mc. with a Varian Model V-4300 B high-resolution spectrometer.

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

# Oxidation of Methyl-*t*-butylcarbinol with Lead Tetraacetate

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*Received March 30, 1960*

The oxidation of methyl-*t*-butylcarbinol with lead tetraacetate yields the expected ketone along with *t*-butyl acetate, isobutylene, and acetaldehyde. The relative yields of ketone and cleavage products may be varied by changing the conditions of oxidation with either the ketone or oxidative cleavage products becoming the major product. These products are consistent with an ionic mechanism.

The oxidation of benzpinacolyl alcohol with lead tetraacetate has been reported by Mosher and Neidig[1] to give 70% triphenylcarbinol as a result of oxidative cleavage. Because this represents the highest yield of such a cleavage yet reported, the reaction of the analogous aliphatic alcohol has now been carried out; methyl-*t*-butylcarbinol also yields cleavage products with lead tetraacetate under a variety of conditions.

The results of this study are summarized in Table I. Several individual reactions were carried out under the general conditions reported for the various runs. Carbon dioxide was invariably a product indicating secondary oxidations and considerable unchanged alcohol and its acetate were found. Material balances varied from 60% to nearly theoretical. With a 1:1 molar ratio of alcohol to lead tetraacetate the cleavage was 6% at 50–65° while it was almost 50% at 95–100° working in acetic acid solution. In nitrobenzene solution more esterification occurred and cleavage at 65–75° was 30%. Previous studies with this alcohol and chromic acid yielded 4% cleavage in acetic acid–water at 30°.[2]

## EXPERIMENTAL

*Preparation of reagents.* Methyl-*t*-butylcarbinol was prepared in 31% yield by the reaction of *t*-butylmagnesium chloride and acetaldehyde, and in 68% yield by the reduction of pinacolone with aluminum isopropoxide in isopropyl alcohol. Distillation of the crude alcohol through a Whitmore-Lux[3] total condensation, partial take-off column packed with a single turn glass helices, and equivalent to twenty theoretical plates, resulted in a product boiling at 120–121° at 760 mm., $n_D^{20}$ 1.4152. The procedure used for lead tetraacetate has been previously described.[4]

*Oxidation.* The data given in Table I indicate the mole quantities of alcohol, oxidizing agent, and solvent used in each experiment. In the usual case, the alcohol and oxidizing agent were mixed at room temperature with the indicated solvent in a 3-l., three-necked, round bottomed flask equipped with a thermometer, a mercury-sealed stirrer, and a reflux condenser to which was attached a Dry Ice trap, two Ascarite tubes, and a gas-collecting bottle. In Runs 1, 4, and 5, Table I, the Dry Ice trap was omitted and the acetaldehyde was absorbed by the Ascarite (with polymerization). In Run No. 2, Table I, the oxidizing agent was added, in small portions, to the stirred acetic acid–alcohol solution at reaction temperature in order to maintain a large excess of alcohol. After tetravalent lead was no longer present (negative potassium iodide test) in the reaction mixture, the product was diluted with water and steam distilled. The combined oil layers were separated, washed with bicarbonate solution, dried over anhydrous potassium carbonate, and fractionated through a column of twenty theoretical plates. In a typical experiment, from the distillation charge of 70.0 g., Run No. 1, Table I, the following cuts were obtained: I. *t*-Butyl acetate (3.8 g., 3.3%), acetanilide derivative by the method of Hardy[5] gave m.p. and mixed m.p. with an authentic sample of acetanilide, 113–115°; the ester was refluxed with hydrochloric acid (6*N*) to give *t*-butyl chloride (b.p. 54–56°, $n_D^{20}$ 1.3850), which then was converted through Grignard reagent and phenyl isocyanate to trimethylacetanilide, m.p. 127–129°. II. Pinacolone (9.2 g., 9.2%), 2,4-dinitrophenylhydrazone m.p. and mixed m.p. 126–128°. III. Unchanged carbinol (46.0 g.; 45.1%). IV. Pinacolyl acetate (5.7 g.; 4.0%), acetanilide derivative obtained by the method of Hardy[5] gave m.p. and mixed m.p. 113–114°; the ester was also hydrolyzed in basic diethylene glycol and the liberated alcohol converted to the 3,5-dinitrobenzoate ester, m.p. and mixed m.p. 105–106°. The pot residue consisted of 2.3 g. of slightly charred

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(1) W. A. Mosher and H. A. Neidig, *J. Am. Chem. Soc.*, **72**, 4452 (1950).

(2) W. A. Mosher and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2544 (1948).

(3) F. C. Whitmore and A. R. Lux, *J. Am. Chem. Soc.*, **54**, 3448 (1932).

(4) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

(5) D. V. N. Hardy, *J. Chem. Soc.*, 398 (1936).