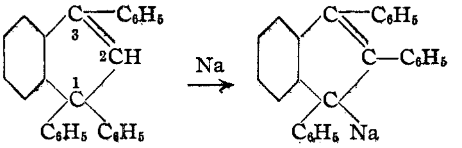
[Contribution from the School of Chemistry of the University of Minnesota]

Some Allyl Rearrangements in the Indene Series

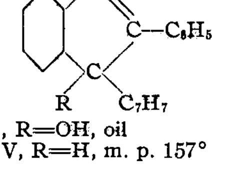
By C. Frederick Koelsch

Although the rearrangement which takes place when 1,1,3-triphenylindene is treated with sodium[1] very likely is preceded by an addition of the metal, it is not impossible that a phenyl group is directly displaced. The addition mechanism would require the sodium to be attached to carbon 3, while the displacement mechanism would require the metal to be attached to carbon 1 in the rearranged product.

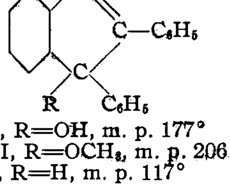


Before applying the obvious experimental test to decide between these two mechanisms, rearranging a molecule so constructed that the product will be unsymmetrical with respect to carbons 1 and 3, it is necessary to know that this product will be stable and will not consist of an equilibrium mixture of the possible isomers. Evidence brought forward in the present paper indicates that the product is such an equilibrium mixture and that this method cannot be used to differentiate between the two possible mechanisms.

The carbinol (I) obtained from 2,3-diphenylindone and *p*-tolylmagnesium bromide is different from the one (II) prepared from 2-phenyl-3-*p*-tolylindone and phenylmagnesium bromide. However, both of these carbinols give exclusively, when treated with acidified methanol, the same methyl ether (III) which is given this structure on the somewhat doubtful basis of its melting point. This ether is nearly completely insoluble in the etherifying mixture, which may account for the absence of its presumably more soluble isomer.



I, R=OH, oil
IV, R=H, m. p. 157°



II, R=OH, m. p. 177°
III, R=OCH_3, m. p. 206°
V, R=H, m. p. 117°

The ether (III) is readily cleaved by sodium amalgam. Hydrolysis of the resulting sodium compound gives a product which consists of a mixture of approximately equal amounts of the hydrocarbons (IV) and (V). These hydrocarbons, separately synthesized by methods which leave no doubt as to their structures, react with sodium by apparent substitution. Hydrolysis of the resulting sodium compounds gives in each case a mixture of approximately equal amounts of (IV) and (V). Analogously the negative ion present in a solution of the sodium compound derived from 1,2,3-triphenylindene must be quite labile, the position of its double bond being fixed only after the sodium ion has been replaced by a non-ionized hydrogen atom.

When 1,2-diphenyl-3-*p*-tolylindene (V) is boiled with potassium hydroxide in 90% alcohol, it is converted to the extent of 90% into 1-*p*-tolyl-2,3-diphenylindene (IV) which, being the more difficultly soluble isomer, separates from the solution. This result may be interpreted as evidence that even in dilute alcohol there may exist an appreciable amount of the metal salt of the indene. The solubility relation of the indenes, which does not affect the equilibrium when the rearrangement is carried out with sodium in ether, is responsible for the more complete conversion by alcoholic potash.

Experimental

1,2-Diphenyl-3-*p*-tolylindenol, II.—Fifteen grams of 2-phenyl-3-*p*-tolylindone in benzene is added to a solution of phenylmagnesium bromide containing 2.2 g. of magnesium. After standing for ten hours the mixture is worked up in the usual way; the product, crystallized from acetic acid and then from benzene–ligroin, forms fine needles that melt at 175–177°; yield, 15 g.

Anal. Calcd. for $C_{28}H_{22}O$: C, 89.8; H, 5.88. Found: C, 89.5; H, 6.0.

1-*p*-Tolyl-2,3-diphenylindenol, I.—This compound, prepared in a similar way from 2,3-diphenylindone and *p*-tolylmagnesium bromide, could not be obtained crystalline, and was converted directly into the methyl ether.

1-Methoxy-1,2-diphenyl-3-*p*-tolylindene, III. (a) **From 1,2-Diphenyl-3-*p*-tolylindenol.**—The carbinol (11.5 g.) is dissolved in 375 ml. of hot methanol, and 5 ml. of sulfuric acid is added. The ether (10.6 g.) is deposited during thirty minutes of boiling. The crude substance melts at 203–204°, and recrystallization from toluene raises this to 206–207°.

(b) **From 1-*p*-Tolyl-2,3-diphenylindenol.**—The usual procedure using the glassy indenol (I) gives a methyl ether

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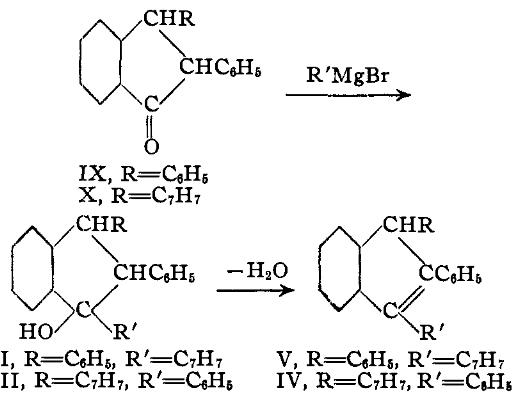
[1] Ziegler and Crössmann, *Ber.*, 62, 1768 (1929).

melting at 205–207° which a mixed melting point shows to be identical with that described under (a).

Anal. Calcd. for $C_{29}H_{24}O$: C, 89.6; H, 6.19. Found: C, 89.8; H, 6.27.

The Indenes IV and V.—These hydrocarbons are prepared in the following way



IX, $R=C_6H_5$
X, $R=C_7H_7$

XI, $R=C_6H_5$, $R'=C_7H_7$
XII, $R=C_7H_7$, $R'=C_6H_5$

V, $R=C_6H_5$, $R'=C_7H_7$
IV, $R=C_7H_7$, $R'=C_6H_5$

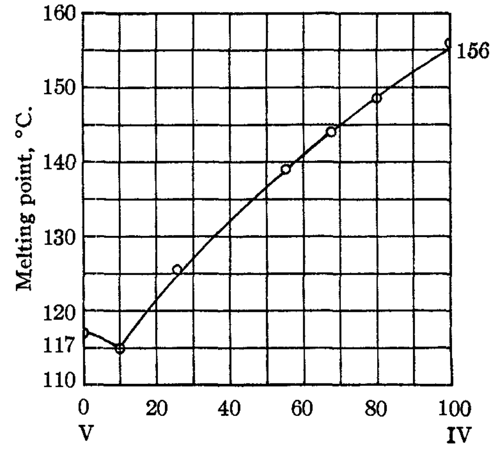


Fig. 1.—The melting points of mixtures of the isomeric indenes.

2,3-Diphenylhydrindone, IX.—Sixty grams of α,β,β-triphenylpropionic acid[2] and 45 g. of phosphorus pentachloride in 300 ml. of benzene are boiled until no more hydrogen chloride is evolved; 45 g. of aluminum chloride is added in portions and with stirring. After refluxing for thirty minutes the mixture is hydrolyzed and the benzene is removed with steam. The residue, crystallized from methanol, gives 35 g. of the hydrindone, which forms white needles that melt at 100–101°.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.7; H, 5.63. Found: C, 88.4; H, 5.67.

This ketone is converted quantitatively into diphenylindone by heating with sulfur at 250°.

2-Phenyl-3-*p*-tolylhydrindone, X.—A mixture of 15 g. of 2-phenyl-3-*p*-tolylindone, 10 g. of zinc dust and 100 ml. of acetic acid is boiled until it is colorless (twenty minutes). The ketone is isolated by pouring into water and extracting with ether. It forms a pale orange glass that cannot be crystallized, but is obtained sufficiently pure by distillation at 10 mm.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.5; H, 6.04. Found: C, 88.4; H, 6.10.

1-*p*-Tolyl-2,3-diphenylhydrindenol, XI.—To a solution of *p*-tolylmagnesium bromide containing 2.4 g. of magnesium is added 18 g. of diphenylhydrindone in ether. After thirty minutes of refluxing the mixture is decomposed with iced ammonium chloride and the solvent is removed with steam. The product crystallizes on rubbing with petroleum ether and is recrystallized from alcohol; yield, 9.4 g. of white needles that melt at 171–173°.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.3; H, 6.4. Found: C, 88.6; H, 6.4.

1,2-Diphenyl-3-*p*-tolylhydrindenol, XII.—Prepared in the same way as its isomer, using phenylmagnesium bromide and 2-phenyl-3-*p*-tolylhydrindone, this carbinol is obtained in a yield of 55% and from benzene–petroleum ether forms white needles that melt at 140–160° (stereoisomers?).

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.3; H, 6.4. Found: C, 88.8; H, 6.4.

1,2-Diphenyl-3-*p*-tolylindene, V.—The carbinol XI boiled in acetic acid containing 2% of sulfuric acid is dehydrated rapidly and quantitatively. The product forms colorless needles that melt at 116–117° when recrystallized from acetic acid.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.8; H, 6.2. Found: C, 93.4; H, 6.2.

1-*p*-Tolyl-2,3-diphenylindene, IV.—This substance is obtained quantitatively from the carbinol XII using acetic acid–sulfuric acid. It forms white needles that melt at 154–156°.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.8; H, 6.2. Found: C, 92.7; H, 6.2.

In order to estimate the composition of the indene mixtures resulting from the hydrolysis of the various sodium compounds described below, the melting points of mixtures of known composition were taken, the melting point of such a mixture being that temperature at which the last of the solid phase, observed with a lens, disappeared. The results are shown graphically in the accompanying figure.

The Sodium Reactions.—The appropriate compound (0.5 g.) dissolved or suspended in 30 ml. of ether is sealed with an excess of 40% sodium amalgam and shaken for three hours. The resulting yellow-brown solution is de-

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[2] Triphenylpropionic acid was prepared from cinnamic acid dibromide, benzene, and aluminum chloride. According to Earl and Wilson [*J. Proc. Roy. Soc. N. S. Wales*, **65**, 178 (1932)] this reaction leads to the formation of 9,10-dihydro-9-phenylphenanthrene-10-carboxylic acid, but the results obtained by these investigators could not be duplicated in this Laboratory. Since this phenanthrene derivative was earnestly wanted in connection with an investigation which has been published [Koelsch, This Journal, **56**, 480 (1934)] the conditions under which the reaction was carried out were varied in every conceivable way, including heating the intermediate aluminum complex without a solvent, bubbling oxygen through a boiling benzene solution of the complex, and using various grades of aluminum chloride. In all cases the only product was triphenylpropionic acid, obtained in quantitative yields and nearly pure before recrystallization.

canted from the amalgam and decolorized with a few drops of alcohol. The solvent is removed with steam and the residue is crystallized once from acetic acid. The results are tabulated below.

TABLE I

THE INDENE MIXTURES FROM THE SODIUM COMPOUNDS

Source of indene mixture	M. p. of indene mixture, °C.	Composition, % of 1-*p*-tolyl-2,3-diphenylindene
III through Na comp.	137	50
V through Na comp.	138	52
IV through Na comp.	140	56
a	152	90
b	137	50

[a] One-half gram of 1,2-diphenyl-3-*p*-tolylindene boiled with 15 ml. of 90% alcohol containing 5% of potassium hydroxide dissolves completely only after fifteen minutes. Then a solid separates slowly, and after an additional hour of boiling no further change can be noticed. The solution is cooled, the crystalline deposit is washed with a little alcohol and water and dried.

[b] As a check on the method, a mixture of equal parts of the two indenes was crystallized once from acetic acid. The melting point of the mixture so obtained shows that its composition was unchanged by this treatment.

Summary

1,2-Diphenyl-3-*p*-tolylindenol and 1-*p*-tolyl-2,3-diphenylindenol both yield the same methyl ether, presumably derived from the former, when treated with methanol–sulfuric acid. This ether is cleaved by sodium amalgam, and the resulting sodium compound hydrolyzes to a mixture of approximately equal parts of 1,2-diphenyl-3-*p*-tolylindene and 1-*p*-tolyl-2,3-diphenylindene. Each of these indenes reacts with sodium amalgam to give a sodium compound whose hydrolysis results in the formation of the same mixture of indenes.

1,2-Diphenyl-3-*p*-tolylindene rearranges to its less soluble isomer to the extent of 90% when boiled with dilute alcoholic potassium hydroxide.

The conclusion is drawn that the anion present in solutions of the metal salt of the indenes is labile, its structure being fixed only after it has combined with a proton.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF DELAWARE]

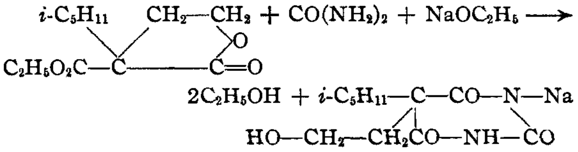
Some 5-β-Ethyl Substituted Derivatives of Barbituric Acid[1]

BY EDWARD F. ROSENBERG, RALPH F. KNEELAND AND GLENN S. SKINNER

In 1922 some work was initiated by one of us[2] which was directed toward the synthesis of 5-phenyl 5-β-ethyl substituted barbituric acids. It was desired ultimately to prepare a 5-vinyl 5-alkyl derivative. These experiments showed that the series of reactions employed go much more smoothly if the phenyl radical is replaced by ethyl. More recently Cope and McElvain[3] report failure to obtain 5-vinyl-5-ethylbarbituric acid by the condensation of vinylethylmalonic ester with urea.

In the present work these experiments have been resumed using in place of phenyl the C_4 and C_5 radicals of the paraffin series since such derivatives of barbituric acid are among the most effective hypnotics. It has been found possible to substitute ethylene bromide for ethylene chloroiodide in the condensation with both *n*-butyl- and isoamylmalonic ester with satisfactory results. The isoamyl-β-bromoethylmalonic ester, however, was largely decomposed to the lactone upon distillation unless the pressure was below 3 mm. In the case of the chloroethyl isoamyl ester a negligible amount of decomposition during the distillation was indicated by the analysis for chlorine. In our experience either benzene or ether is satisfactory as a medium. The yield fluctuates widely with the variation of the equivalent proportions of the reagents. This will be reported in more detail in a later communication.

The lactone was found to condense with urea to form 5-isoamyl-5-β-hydroxyethylbarbituric acid in 75% yield. The method should be general and will be investigated further. This condensation gives better yields if the reaction mixture is refluxed for relatively short periods of time followed by distillation of the alcohol.



$$(i\text{-}C_5H_{11})(C_2H_5O_2C)C(CH_2CH_2O)C{=}O + CO(NH_2)_2 + NaOC_2H_5 \longrightarrow 2C_2H_5OH + i\text{-}C_5H_{11}\text{—}C(HO\text{—}CH_2\text{—}CH_2)\text{—}CO\text{—}N(Na)\text{—}CO\text{—}NH\text{—}CO$$

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[1] Most of the experimental work here reported formed portions of theses presented for the degree of Master of Science in the University of Delaware by Edward F. Rosenberg, 1930, and Ralph F. Kneeland, 1933.

[2] Voorhees and Skinner, THIS JOURNAL, **47**, 1124 (1925).

[3] Cope and McElvain, *ibid.*, **54**, 4311 (1932).