terial (1.05 g.), which, upon recrystallization from benzene–ethyl alcohol, yielded 1-phenyl-3-(4-biphenyl)-cyclohexane.[3]

**Preparation of *m*-Phenyl-(4-biphenyl)-benzene (V).**—Dehydrogenation of each diene, IV and VII, gave the same results. 1-Phenyl-3-(4-biphenyl)-cyclohexadiene-1,3 (1.5 g.) dissolved in 7 ml. of *p*-cymene was refluxed briskly in the presence of 0.5 g. of palladium–charcoal (5%) for four hours. Benzene was added and the catalyst removed by filtration. Removal of most of the benzene and addition of ethyl alcohol precipitated 1.0 g. of solid which on recrystallization from benzene–alcohol yielded *m*-phenyl-(4-biphenyl)-benzene.[3]

**Preparation of 1,3-Di-(4-biphenyl)-cyclohexadiene-1,3 (VIII).**—A slurry of finely divided 3-(4-biphenyl)-$\Delta^2$-cyclohexenone (II) (5.9 g.) in 100 ml. of ether was added to a solution of *p*-biphenyllithium in 125 ml. of ether prepared from 0.8 g. of lithium and 15.7 g. of *p*-bromobiphenyl. This mixture was refluxed for an hour at the end of which time a small amount of ethyl alcohol was added to destroy the remaining unreacted lithium. The lithium complex was hydrolyzed with dilute sulfuric acid and the solution subjected to steam distillation to remove some of the impurities. The solid residue, filtered, dried, powdered and crystallized from 500 ml. of toluene, weighed 11 g. and melted at 265–269°. *Anal.* Calcd. for $C_{30}H_{24}$: C, 93.70; H, 6.29. Found: C, 93.40, 93.75; H, 6.39, 6.34.

**Hydrogenation of 1,3-Di-(4-biphenyl)-cyclohexadiene-1,3.**—Finely divided 1,3-di-(4-biphenyl)-cyclohexadiene-1,3 (1.0 g.) in 50 ml. of toluene with Raney nickel absorbed 140 ml. of hydrogen (106% for two ethylenic links) at atmospheric pressure and room temperature in approximately forty minutes. At the end of the hydrogenation all the organic solid had dissolved. After filtration of the catalyst, addition of a small amount of ethyl alcohol precipitated a high melting solid (0.05 g.) which melted at 312° after recrystallization from toluene–ethyl alcohol and was not further studied. *Anal.* Found: C, 94.28, 94.41; H, 6.08, 6.02. Addition of more ethyl alcohol precipitated 0.75 g. of 1,3-di-(4-biphenyl)-cyclohexane which melted at 145–145.5° after recrystallization from toluene–ethyl alcohol. *Anal.* Calcd. for $C_{30}H_{28}$: C, 92.74; H, 7.26. Found: C, 92.86, 92.96; H, 7.33, 7.34.

**Preparation of *m*-Di-(4-biphenyl)-benzene (IX).**—1,3-Di-(4-biphenyl)-cyclohexadiene-1,3 (1.0 g.) dissolved in 10 ml. of phenetole to which had been added 0.3 g. of palladium-charcoal (5%) was refluxed for three hours. This mixture was then introduced into 300 ml. of boiling toluene, filtered while nearly at the boiling temperature and cooled. *m*-Di-(4-biphenyl)-benzene (0.8 g.) precipitated which upon recrystallization from toluene melted at 264–266°. *Anal.* Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.23, 94.42; H, 5.88, 5.96. This substance gave no depression with the precursor diene in a mixed melting point determination.

## Summary

1. The utility of the ethyl enol ether of dihydroresorcinol for the preparation of some *m*-diarylbenzenes is shown.

2. The preparation of *m*-phenyl-(4-biphenyl)-benzene and *m*-di-(4-biphenyl)-benzene is reported.

COLLEGE PARK, MARYLAND RECEIVED APRIL 15, 1948

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# The Reaction of Allylsodium with 2-Bromooöctane[1]

BY R. L. LETSINGER AND JAMES G. TRAYNHAM

In a previous publication[2] it was shown that benzylsodium couples readily with secondary bromides to give high yields of the Wurtz product. Since allylsodium is near benzylsodium in reactivity, one might expect it to behave similarly. In this paper we show that allylsodium does in fact react with 2-bromooöctane to give a 71% yield of 4-methyl-1-decene.

The allylsodium used in this work was prepared by the cleavage of diallyl ether with sodium metal.[3] That allylsodium was present in this cleavage mixture was shown by isolation of vinylacetic acid from the carbonated product. When fine sodium sand, high speed stirring, and a creased flask were employed, a 77% yield of vinylacetic acid was obtained.[4] The presence of the other expected product of the cleavage reaction, sodium alloxide, was demonstrated by the preparation of the 3,5-dinitrobenzoate derivative of allyl alcohol.

The reaction of the allylsodium–sodium alloxide mixture with 2-bromooöctane proceeded smoothly to give 4-methyl-1-decene. Hydrogenation of this olefin yielded 4-methyldecane.

We investigated the product of the Wurtz reaction carefully to determine whether it might be contaminated with allyl 1-methylheptyl ether. This ether could have been formed by a reaction of 2-bromooöctane with the sodium alloxide present. Both 4-methyl-1-decene and allyl 1-methylheptyl ether, since neither had been previously reported, were synthesized independently: the olefin from allyl bromide and 1-methylheptylmagnesium bromide, and the ether from allyl bromide and sodium 1-methylheptoxide. The physical constants of these compounds are given in Table I, and the infrared absorption spectra are given in Fig. 1. The spectra of the Wurtz product and 4-methyl-1-decene prepared by the Grignard reaction are identical, whereas allyl 1-methylheptyl ether shows strong absorption in a region of low absorption for the olefin. It is apparent from these data that the 4-methyl-1-decene prepared by this Wurtz reaction was entirely free of contamination by allyl

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[1] This investigation was supported by a grant from the Abbott Fund of Northwestern University.

[2] Letsinger, THIS JOURNAL, **70**, 406 (1948).

[3] The fact that diallyl ether can be cleaved by sodium to give allylsodium was previously observed by Morton, Magat and Letsinger, unpublished wok.

[4] Cleavage could also be accomplished under less favorable conditions, such as with sodium pellets, a low speed Hershberg stirrer, and a conventional flask; however, the yield of allylsodium was lower.

1-methylheptyl ether within the accuracy of our measurements.

TABLE I

A COMPARISON OF PHYSICAL CONSTANTS

| | $n^{25}_{\mathrm{D}}$ | $d^{25}_{4}$ |
|---|---|---|
| 4-Methyl-1-decene from Wurtz reaction | 1.4241 | 0.7474 |
| 4-Methyl-1-decene from Grignard reaction | 1.4241 | .7476 |
| Allyl 1-methylheptyl ether | 1.4270 | .8015[a] |

[a] This value is for $d^{20}_{4}$.

## Experimental

**Cleavage of Diallyl Ether: (a) Vinylacetic Acid.**—Sodium sand (5.8 g., 0.25 g. at.) was prepared in octane in a 500-cc. creased flask under a nitrogen atmosphere. The octane was then replaced with hexane (b. p. 60–70°), and a solution of diallyl ether (14.7 g., 0.15 mole) in an equal volume of hexane was added over a period of one hour. The temperature was maintained at 35° and high speed stirring (5000 r. p. m.) was used throughout the reaction. Cleavage of the ether began soon after the addition was started, as evidenced by the evolution of heat and formation of a fine, white suspension. The final mixture was pure white and moderately viscous. After another thirty minutes of stirring, the mixture was siphoned onto Dry Ice. Water (200 cc.) was then added and vinylacetic acid was separated by conventional procedure; wt. 8.3 g. (77% based on sodium); b. p. 61–62° (6 mm.), $n^{23}_{\mathrm{D}}$ 1.4220, $d^{25}_{4}$ 0.9984.

(b) **Allyl 3,5-Dinitrobenzoate.**—A similar reaction was carried out with 5.8 g. (0.25 g. at.) sodium and 12.3 g. (0.125 mole) diallyl ether. After the reaction mixture had been carbonated, 100 cc. of water was added. The aqueous layer was then mixed with an equal volume of 35% sodium hydroxide solution and cooled to 0°. A solution of 5.0 g. (0.0217 mole) 3,5-dinitrobenzoyl chloride in 10 cc. of ligroin and 35 cc. of benzene was added, and the mixture was alternately shaken and cooled in an ice-bath for thirty minutes. An ether extraction then yielded 2.5 g. (49% based on the chloride) of crude ester[5] melting at 42.5–43.5°. Fine white needles, m. p. 46–47°, were obtained on recrystallization from an alcohol-water mixture.

**4-Methyl-1-decene by Wurtz Reaction.**—Allylsodium was prepared as in the previous reactions from sodium (11.7 g., 0.52 g. at.) and diallyl ether (24.5 g., 0.25 mole). A solution of 2-bromoöctane (29.0 g., 0.15 mole) in an equal volume of hexane was then added dropwise, with stirring, over a period of thirty minutes. The temperature of the reaction was maintained at 0°. Stirring was continued for an hour at 0° after the addition had been completed, and for another twenty minutes while the mixture warmed to room temperature. After the mixture had stood overnight, it was stirred for an hour and then carbonated. Water was then added, and the organic layer separated, dried over calcium chloride, and distilled. The weight of 4-methyl-1-decene collected at 71–72° (12 mm.) was 16.4 g. (71% based on 2-bromoöctane); $n^{25}_{\mathrm{D}}$ 1.4241, $d^{25}_{4}$ 0.7474.

*Anal.* (by M. Hines). Calcd. for $C_{11}H_{22}$: C, 85.62; H, 14.38. Found: C, 85.71; H, 14.52.

**4-Methyldecane.**—The olefin from the Wurtz reaction was reduced with hydrogen (32 p. s. i.) over a platinum catalyst in methanol; b. p. product 71–72° (12 mm.), $n^{25}_{\mathrm{D}}$ 1.4156. This material was washed with concentrated sulfuric acid to remove any ether impurity should it be present, and redistilled: $n^{25}_{\mathrm{D}}$ 1.4156; $d^{25}_{4}$ 0.7379; $M_{\mathrm{R}}$ 52.69; calcd. $M_{\mathrm{R}}$ 52.53.

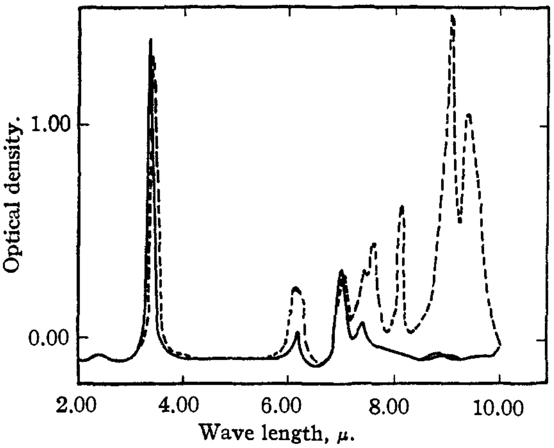

Fig. 1.—Infrared absorption spectra, 20% solution in $CHCl_3$, 0.1 mm. cell: solid line, 4-methyl-1-decene by both Wurtz reaction and by Grignard reactions; dotted line, allyl 1-methylheptyl ether. (Spectra data obtained by Kenneth Waldock.)

**4-Methyl-1-decene by Grignard Reaction.**—1-Methylheptylmagnesium bromide was prepared from 8.5 g. (0.35 g. at.) of magnesium and 29.0 g. (0.15 mole) of 2-bromoöctane with 100 cc. of absolute ether as solvent. The Grignard was siphoned from the excess magnesium into another flask and cooled to 15°. Allyl bromide (24.2 g., 0.20 mole) in 25 cc. of ether was then added dropwise with stirring over a forty-minute period. The mixture was stirred for another ninety minutes, allowed to stand overnight, and decomposed with a saturated ammonium chloride solution. Distillation of the organic layer gave 7.5 g. of material which boiled at 63–66° (9 mm.), but gave a positive Beilstein test. From the density ($d^{20}_{4}$ 0.7884) it was estimated that about 11% of the material was 2-bromoöctane. On this basis the actual yield of the olefin was about 6.3 g. or 29%. The bromoöctane was removed by heating the material with sodium at 100° for seven hours. Distillation then yielded the pure 4-methyl-1-decene; b. p. 60° (8 mm.); $n^{25}_{\mathrm{D}}$ 1.4241; $d^{25}_{4}$ 0.7476.

**Allyl 1-Methylheptyl Ether.**—Sodium 1-methylheptoxide was prepared by heating 15.0 g. (0.65 g. at.) sodium and 65.1 g. (0.50 mole) 2-octanol in 150 cc. of dry toluene at reflux temperature for approximately sixteen hours. Most of the sodium was consumed. The toluene solution was then transferred to a 500-cc. 3-necked flask fitted with a condenser, stirrer and dropping funnel. While the solution was heated on the steam-bath, 72.5 g. (0.60 mole) of allyl bromide was added over a twenty-five-minute period with stirring. Toluene (100 cc.) was added to keep the mixture fluid, and stirring continued for two hours. The mixture was then left standing for three days.

At the end of this time 400 cc. of water was added to the mixture. The organic material (the combined organic layer and ether extract of the aqueous layer) was then dried and distilled; 67.6 g. of material was obtained which boiled at 75–79° (10–12 mm.). It evolved bubbles with sodium, indicating the presence of unreacted 2-octanol. Since the ether itself, however, was found to react with sodium at room temperature, the alcohol was removed by the use of lithium rather than sodium. Addition of lithium metal to the mixture resulted in sufficient heat to cause boiling; however, the ether did not appear to undergo cleavage. The main fraction obtained on distillation boiled at 77° (8 mm.). It was redistilled over lithium; b. p. 77° (8 mm.); $n^{25}_{\mathrm{D}}$ 1.4270; $d^{20}_{4}$ 0.8015.

*Anal.* (by M. Hines). Calcd. for $C_{11}H_{22}O$: C, 77.59; H, 13.26. Found: C, 77.78; H, 12.84.

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(5) The procedure used here to prepare a derivative of allyl alcohol in an aqueous solution is essentially that of Lipscomb and Baker, THIS JOURNAL, **64**, 179 (1942), the principal difference being that we employed sodium vinylacetate rather than sodium acetate as a buffer. With a molar ratio of allyl alcohol to 3,5-dinitrobenzoyl chloride of about four to one, Lipscomb and Baker obtained a 42% yield of crude ester melting at 40–41°.

## Summary

An allylsodium–sodium alloxide mixture was obtained by cleaving diallyl ether with sodium metal. This mixture reacted with 2-bromooctane to give a high yield of 4-methyl-1-decene.

For comparative purposes, 4-methyl-1-decene was also synthesized by a Grignard reaction, and allyl 1-methylheptyl ether was prepared by a Williamson reaction.

EVANSTON, ILLINOIS RECEIVED MAY 29, 1948

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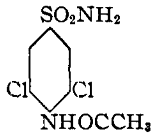
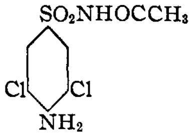
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

# Acetylation of 3,5-Dichlorosulfanilamide

BY MARGARET K. SEIKEL

Preliminary attempts to acetylate 3,5-dichlorosulfanilamide, I,[1] led to a mixture of products. Specific conditions, therefore, have been developed by which each of the four possible acetyl derivatives, II, III, IV and V can be obtained directly from the parent compound in good yields.[2] These four derivatives have been identified,[3] and the hydrolysis of each in different media has been studied in respect to products and speed.


II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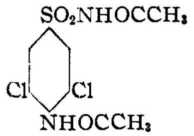
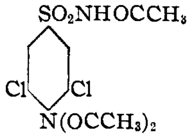

IV


V

The acetylation of 3,5-dichlorosulfanilamide and the properties of its acetyl derivatives are in general in agreement with material in the literature. The presence of the two chlorine atoms ortho to the amino nitrogen distinguishes I from sulfanilamide because of the resultant decrease in basicity. Sulfanilamide is soluble in acid while I separates even from hot concentrated hydrochloric acid solution.[1] Only three acetyl derivatives of sulfanilamide have been reported,[4] the $N^4$-acetyl,[5] the $N^1$-acetyl,[6] and the $N^1$, $N^4$-diacetyl.[6a,6b,7] Unsuccessful preliminary attempts were made in the present work to obtain a triacetyl derivative by the method used to triacetylate I. Such negative results check work on diacetylation of substituted anilines, in which the presence of diortho substituents was shown to favor diacetylation markedly.[8]

The markedly greater effect which the sulfuric acid catalyst has on the speed of monoacetylation *versus* that of diacetylation of an amino nitrogen with diortho substituents by acetic anhydride mentioned by Smith and Orton[9] was noticed and evidence obtained on the dependence of the rate of monoacetylation on the amount of acid. Smaller amounts of sulfuric acid were used than have generally been reported.[9,10] The use of an acetic acid solution to retard diacetylation of the amino group[9,10a] was confirmed in studying the preparation of IV.

Differential acetylation of the amino group and the amido group in I by acetic anhydride has been accomplished and distinguishes I from sulfanilamide and its non-diortho substituted derivatives. First, this was attained by controlling the amount of sulfuric acid used. The amino group acetylated at room temperature with low concentrations of sulfuric acid (0.001 ml. per 0.5 ml. of acetic anhydride) while the amido groups remained for the most part unacetylated even in the presence of excess anhydride. With higher concentrations (0.01 ml. per 0.5 ml. of anhydride) both acetylated. It is felt that the local heating effect of rapid monoacetylation may have promoted the diacetylation. Secondly, reactions in basic media (aqueous alkali or pyridine) led first to acetylation of the amido group. Sodium hydroxide solutions have been used in acetylation of amines containing acid groups,[11] but no preparations of N-acetylsulfonamides employing hydroxide solutions have been discovered. Acetic anhydride in pyridine solution has been used in recent years for acetylating the $N^1$-nitrogen of sulfanilamide and its deriva-

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[1] Seikel, THIS JOURNAL, **62**, 1214 (1940), and "Organic Syntheses," **24**, 47 (1944).

[2] During the work each of the five compounds has been obtained from and converted into all of the others with the exception of II to and from III and III from V.

[3] Their structures are proven by the fact that only III contains a diazotizable amino group, by strongly acidic imidic hydrogen in III, IV and V, by their logical conversion into one another on hydrolysis or further acetylation, by the fact that IV can yield two different monoacetyl derivatives (II and III) on hydrolysis, by the relatively great instability of the third acetyl group in V, and by the fact that V may be reprecipitated unchanged from a bicarbonate solution.

[4] The references given do not presume to be complete.

[5] Gelmo, *J. prakt. Chem.*, [2] **77**, 371 (1908); Scudi, THIS JOURNAL, **59**, 1481 (1937); Miller, Rock and Moore, *ibid.*, **61**, 1199 (1939).

[6] (a) Crossley, Northey and Hultquist, *ibid.*, **61**, 2950 (1939); (b) Huang-Minlon and Lo, *J. Chinese Chem. Soc.*, **9**, 61 (1942); (c) Braz, *J. Applied Chem.* (*U. S. S. R.*), **17**, 508 (1944), *C. A.*, **41**, 4061 (1945).

[7] Scudi, *Ind. Eng. Chem., Anal. Ed.*, **10**, 347 (1938).

[8] Ulffers and von Janson, *Ber.*, **27**, 93 (1894); Sudborough, *J. Chem. Soc.*, **79**, 533 (1901); Raiford, Taft and Lankelma, THIS JOURNAL, **46**, 2051 (1924); Hodgson, *J. Soc. Dyers and Colourists*, **46**, 187 (1930); Dubsky, *Chem. Z.*, **36**, 677, 697 (1912).

[9] Smith and Orton, *J. Chem. Soc.*, **93**, 1242 (1908).

[10] (a) Blanksma, *Chem. Weekblad*, **6**, 717 (1909); (b) Skraup, *Monatsh.*, **19**, 458 (1898); (c) Chattaway and Irving, *J. Chem. Soc.*, 143 (1933).

[11] For example, Chattaway, *ibid.*, 2495 (1931).