## Summary

1. Two types of activated adsorption of hydrogen on iron synthetic ammonia catalysts have been found, type A occurring at a convenient rate at $-90°$ and above, type B at $100°$ and above.

2. Evidence has been presented to show that both types of activated adsorption are in part at least adsorptions on the surface rather than activated diffusion into cracks or solution within the lattice.

WASHINGTON, D. C. RECEIVED MAY 28, 1935

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

# Di-$p$-alkylphenyldibiphenyleneethanes. The Effect of the $p$-Alkyl Group on the Dissociation of the Ethane[1]

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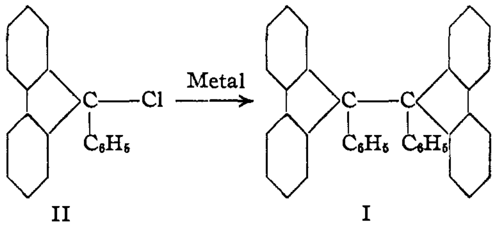
Diphenyldibiphenyleneethane (I) has been reported to be undissociated in solution at ordinary temperatures, and to be unoxidized by air until the temperature is raised to above 200°.[2] However, if the treatment of phenylbiphenylenemethyl chloride (II) with a metal is carried out in the presence of air, the hydrocarbon (I) is not obtained, but the peroxide forms in good yields.[3] Schlenk and Herzenstein[4] have also reported that the closely related hexaarylethane, in which biphenyl groups replace the simple phenyl groups in the above hydrocarbon (I), is likewise unexpectedly stable toward oxidation by air, and does not dissociate in benzene solution at room temperature. The unusual behavior of these hydrocarbons must be attributed to the extra ring system present in the biphenylene groups, since hexaphenylethane is easily oxidized in air and at room temperature in 0.08 molar solution in benzene is dissociated to the extent of 3.6%,[5] and tetraphenyldibiphenylethane is even more easily oxidized, and exists as the free radical to the extent of 10–15%.[6]



II I

In order to gain more information concerning the dibiphenyleneethanes we have prepared three homologs of diphenyldibiphenyleneethane in which the $p$-hydrogen atoms of the phenyl groups are replaced by methyl, ethyl and $n$-propyl groups, respectively. The synthesis of these compounds involved well-known reactions. Fluorenone was treated with the $p$-alkylphenylmagnesium halide after the method of Ullmann and Von Wurstemberger[7] for the preparation of phenylbiphenylenecarbinol. The $p$-tolyl compound has previously been described by Kovache.[8] The other carbinols could not be obtained in crystalline form. The carbinols were converted to chlorides by the method of Gomberg.[9] The $p$-tolyl- and $p$-ethylphenyl derivatives crystallized easily and were converted to the ethanes by treatment with copper bronze. The $p$-$n$-propylphenylbiphenylenechloromethane did not crystallize, but it did react with methyl alcohol to give the methyl ether of $p$-$n$-propylphenylbiphenylenecarbinol which crystallized readily. This methyl ether was then cleaved with sodium amalgam to give sodium $p$-$n$-propylphenylbiphenylenemethyl which was converted to the desired ethane by treatment with tetramethylethylene bromide according to the general method devised by Ziegler and Schnell.[10]

None of the new ethanes were obtained in pure crystalline form. Their solutions in benzene were light yellow to red, and all were readily oxidized by air at room temperature to give the peroxides. It is thus evident that introduction of alkyl groups into the *para* position of the phenyl group in this class of hexaarylethanes increases

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[1] For the first paper on this subject, see Copenhaver, Roy and Marvel, THIS JOURNAL, **57**, 1311 (1935).

[2] Schlenk, Herzenstein and Weickel, *Ber.*, **43**, 1753 (1910); Gomberg and Cone, *ibid.*, **39**, 2969 (1906).

[3] Gomberg and Cone, *ibid.*, **39**, 1461, 2957 (1906).

[4] Schlenk and Herzenstein, *Ann.*, **372**, 21 (1910).

[5] Ziegler and Ewald, *ibid.*, **473**, 163 (1929).

[6] Schlenk, Weickel and Herzenstein, *ibid.*, **372**, 1 (1910).

[7] Ullmann and Von Wurstemberger, *Ber.*, **37**, 73 (1904).

[8] Kovache, *Ann. chim.*, [9] **10**, 210 (1918).

[9] Gomberg, THIS JOURNAL, **26**, 1516 (1904).

[10] Ziegler and Schnell ,*Ann.*, **437**, 227 (1924).

TABLE I

*p*-ALKYLPHENYLBIPHENYLENECARBINOL ALKYL ETHERS

| *p*-R-$C_6H_4C < (C_{12}H_8)OR'$ R | R′ | M. p., °C. | Formula | Analyses, % Calcd. C | H | Found C | H |
|---|---|---|---|---|---|---|---|
| $CH_3$ | $C_2H_5$ | 123 | $C_{22}H_{20}O$ | 88.00 | 6.66 | 88.63 | 6.72 |
| $C_2H_5$ | $C_2H_5$ | 103 | $C_{23}H_{22}O$ | 87.89 | 7.00 | 87.13 | 6.74 |
| *n*-$C_3H_7$ | $CH_3$ | 82–83 | $C_{23}H_{22}O$ | 87.89 | 7.00 | 87.62 | 7.02 |
| $C_6H_{11}$ | $CH_3$ | 119–120 | $C_{26}H_{26}O$ | 88.17 | 7.34 | 87.90 | 7.39 |

TABLE II

*p*-ALKYLPHENYLBIPHENYLENEMETHYL PEROXIDES

| *p*-$RC_6H_5$-$C < (C_{12}H_8)]_2O_2$ R = | M. p., °C. | Formula | Analyses, % Calcd. C | H | Found C | H |
|---|---|---|---|---|---|---|
| $CH_3$ | 200–201 | $C_{40}H_{30}O_2$ | 88.56 | 5.53 | 88.87 | 5.60 |
| $C_2H_5$ | 186–187 | $C_{42}H_{34}O_2$ | 88.42 | 5.96 | 88.45 | 6.11 |
| *n*-$C_3H_7$ | 127–128 | $C_{44}H_{38}O_2$ | 88.29 | 6.35 | 88.06 | 6.61 |

the ease with which they are oxidized. Measurements of the degree of dissociation are in progress.

## Experimental

**_p_-Alkylphenyldiphenylenecarbinols.**—The Grignard reagents were prepared from 0.1 mole quantites of *p*-ethyl-, *p*-*n*-propyl- and *p*-cyclohexylbromobenzenes and treated with fluorenone, and the reaction mixtures worked up as described by Ullmann and Von Wurstemberger.[7] None of these carbinols were obtained as crystalline materials.

**_p_-Alkylphenyldibiphenylenechloromethanes.**—The crude carbinols prepared as described above were dissolved in 200 cc. of ether and treated with 10 g. of anhydrous calcium chloride and excess hydrogen chloride.[9] The *p*-tolyl- and *p*-ethylphenyl derivatives could be crystallized from petroleum ether and melted at 96–97° and 56–57°, respectively.

*Anal.* *p*-Tolyl derivative. Calcd. for $C_{20}H_{15}Cl$: Cl, 12.22. Found: Cl, 11.84. *p*-Ethylphenyl derivative. Calcd. for $C_{21}H_{17}Cl$: Cl, 11.60. Found: Cl, 11.56.

The *p*-*n*-propylphenyl and *p*-cyclohexylphenyl derivatives did not crystallize.

**_p_-Alkylphenylbiphenylenecarbinol Alkyl Ethers.**—The crude chlorides prepared as described above were treated with hot methyl and ethyl alcohols, and the corresponding ethers were obtained on cooling these solutions. The compounds thus prepared are listed in Table I.

**Di-_p_-alkylphenyldibiphenyleneethanes.**—The *p*-tolyl and *p*-ethylphenyl derivatives were prepared from the chlorides (5 g.) and copper bronze (15 g.) in benzene solution (80 cc.) in an atmosphere of carbon dioxide.[2] The copper bronze was then removed by filtration in an atmosphere of carbon dioxide. Both of these compounds gave yellow colored solutions. On standing, the solution of the *p*-tolyl derivative turned pink, and that of the *p*-ethylphenyl derivative became red.

The *p*-*n*-propylphenyl derivative was prepared by shaking 4 g. of the methyl ether of *p*-*n*-propylphenylbiphenylenecarbinol with 4 cc. of 40% sodium amalgam in 70 cc. of dry benzene under nitrogen for about sixty hours.[10] A red solid separated from the benzene solution during this treatment. The flask was cooled to freeze the excess amalgam, and the suspension of the red metal alkyl in benzene was decanted to another nitrogen-filled flask. To this material was added 16 cc. of a 10% solution of tetramethylethylene dibromide in dry ether. The color was completely discharged by this treatment. The sodium bromide was removed by filtration. The solution at this stage was slightly yellow, but on standing a red color developed.

The *p*-cyclohexylphenyl derivative was not prepared.

**_p_-Alkylphenylbiphenylenemethyl Peroxides.**—These solutions of the hydrocarbons in benzene were exposed to air for a short time, and then the white, crystalline peroxides were precipitated by the addition of alcohol. The red color of the solution of the *p*-*n*-propylphenyl derivative was not entirely destroyed by oxidation. The properties of the peroxides are listed in Table II.

## Summary

The di-*p*-alkylphenyldibiphenyleneethanes in which the alkyl groups are methyl, ethyl and *n*-propyl have been prepared. These ethanes are easily oxidized by air to give the corresponding peroxides at room temperature.

URBANA, ILLINOIS RECEIVED JUNE 21, 1935