obtained with *m*-tolyltriethylsilane. In this compound (but not in the ortho or para isomers) the directive influence of both the methyl and triethylsilyl groups (assuming the latter is ortho–para directing) reinforce one another which may account for the higher yield of product.

Experimental

***o*-Tolyltriethylsilane.**—A solution of *o*-tolyllithium prepared from 83.5 g. (0.5 mole) of *o*-bromotoluene and 7.0 g. (1 g. atom) of lithium was added to 83.6 g. of triethylchlorosilane (90% pure). The mixture was stirred until a negative Color Test I was obtained, then poured onto ice. The ether layer was separated, dried and evaporated. The residue was distilled through a Claisen head to give 76 g. (74%) of *o*-tolyltriethylsilane, b.p. 71–72° at 0.5 mm., d^{20}_4 0.906, n^{20}_{D} 1.5132, MR_{calcd} 68.6, MR_{found} 68.5.

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.6. Found: Si, 13.4.

***m*-Tolyltriethylsilane**: prepared from *m*-tolyllithium and triethylchlorosilane in 0.5-mole quantity as described above: yield 74 g. (72%), b.p. 63–64° at 0.5 mm., d^{20}_4 0.8905, n^{20}_{D} 1.5030, MR_{calcd} 68.6, MR_{found} 68.5.

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.6. Found: Si, 13.6.

***p*-Tolyltriethylsilane**: prepared from *p*-tolyllithium and triethylchlorosilane in 0.5-mole quantity as described for the ortho isomer: yield 65 g. (65%), b.p. 68–69° at 0.5 mm., d^{20}_4 0.888, n^{20}_{D} 1.5025, MR_{calcd} 68.6, MR_{found} 68.5.

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.6. Found: Si, 13.3.

2-Methyl-5-nitrophenyltriethylsilane.—To a nitrating mixture from 32.7 g. (0.27 equiv.) of copper nitrate trihydrate and 175 cc. of acetic anhydride was added 46 g. (0.223 mole) of *o*-tolyltriethylsilane, keeping the temperature at 30° during the addition. The mixture was then heated to 40° for 8 hours. It was then hydrolyzed by pouring onto cracked ice and was neutralized with ammonium hydroxide. The mixture was then extracted with four 200-cc. portions of ether and the extracts were combined. The ethereal solution was dried and evaporated, and the residual oil fractionated in a Todd column to give 8 g. (27%) of triethylsilanol and a small amount of *o*-nitrotoluene. A fraction boiling between 129–142° at 3 mm. was collected and a portion of this solidified. This solid when crystallized from pentane amounted to 8 g. and melted 40–41°.

Anal. Calcd. for $C_{13}H_{21}O_2NSi$: Si, 11.1. Found: Si, 11.0.

The total yield of mononitrosilanes in this run was 28 g. (50%).

2-Methyl-5-aminophenyltriethylsilane.—A mixture of 8.3 g. (0.033 mole) of 2-methyl-5-nitrophenyltriethylsilane in 50 cc. of ethanol was reduced in a Parr low-pressure hydrogenator with a Raney nickel catalyst. The product was distilled through a Claisen head at 123° at 2.5 mm. A yield of 7 g. (94%) was obtained, n^{20}_{D} 1.5430, d^{20}_4 0.9570, MR_{calcd} 73.0, MR_{found} 72.9.

Anal. Calcd. for $C_{13}H_{23}NSi$: Si, 12.7. Found: Si, 13.0.

The acetyl derivative melted at 105° after crystallization from 90–100° petroleum ether.

Anal. Calcd. for $C_{15}H_{25}ONSi$: Si, 10.6. Found: Si, 10.5.

Structure Proof of 2-Methyl-5-aminophenyltriethylsilane.—Hydrogen chloride was passed through a solution of 6.4 g. (0.029 mole) of the amine in 100 cc. of ethanol for 4 hours. The solution was evaporated and the residue was dissolved in water. Solid potassium hydroxide was added until the solution was basic and the mixture was then extracted with ether. The ether extract was evaporated and the acetyl derivative of the residue was prepared in the usual manner. There was obtained 1.3 g. (30%) of *p*-acetotoluide (mixed m.p.) melting at 151–153°.

Nitration of *m*-Tolyltriethylsilane.—The reaction was carried out as described above for the ortho isomer. Distillation through a Todd column gave 1.3 g. of triethylsilanol, 3.7 g. (12%) of *m*-nitrotoluene and 41 g. (74%) of mononitrated silanes. A cut (18.6 g.) boiling at 135–136° at 1 mm. was collected. The refractive index (n^{20}_{D}) varied from 1.5299 to 1.5307. The density of the cut with an index of refraction of 1.5303 was 1.029; MR_{calcd} 74.9, MR_{found} 75.4.

Anal. Calcd. for $C_{13}H_{21}O_2NSi$: Si, 11.1. Found: Si, 11.0.

Reduction of Nitrated *m*-Tolyltriethylsilanes.—The cut boiling at 135–136° at 1 mm. was reduced catalytically in the same fashion as described above and the product was distilled through a Todd column. Two cuts were collected, the one (A) boiling at 110–126° at 3 mm. with n^{20}_{D} varying from 1.5362–1.5383, and the other (B) 126–130° at 3 mm. with n^{20}_{D} varying from 1.5382–1.5385; d^{20}_4 0.944.

Anal. (Cut B) Calcd. for $C_{13}H_{23}NSi$: Si, 12.7. Found: Si, 13.1.

Cut (A) gave a mixture of acetylated amines from which 2-acetamino-5-methylphenyltriethylsilane melting at 124–125° was obtained after two crystallizations from 90–100° petroleum ether.

Anal. Calcd. for $C_{15}H_{25}ONSi$: Si, 10.6. Found: Si, 10.8.

Cleavage of the above compound with hydrogen chloride gave 30% *p*-acetotoluide. Cut (B) gave only one acetyl derivative melting at 66–67°. This was shown (see below) to be 3-methyl-4-acetaminophenyltriethylsilane.

Anal. Calcd. for $C_{15}H_{25}ONSi$: Si, 10.6. Found: Si, 10.9.

Structure Proof of 3-Methyl-4-aminophenyltriethylsilane.—Seven grams (0.27 mole) of iodine was added to 3.0 g. (0.014 mole) of the aminosilane obtained from cut (B) above. The solution immediately became very hot and tar formation was noted. The mixture was heated on a steam-bath for 3 hours, hydrolyzed and extracted with ether. The ether extract was washed with thiosulfate and evaporated. The acetyl derivative was prepared from the residue in the usual manner. Recrystallized from petroleum ether, it melted at 167–168° and did not depress the melting point of authentic 5-iodo-2-acetaminotoluene.[3]

4-Methyl-3-nitrophenyltriethylsilane.—Nitration of *p*-tolyltriethylsilane was accomplished as described for the ortho isomer. Distillation through a Todd column gave 8.7 g. of triethylsilanol, 10.7 g. (26%) of solid *p*-nitrotoluene and 46 g. (60%) of material boiling at 140° at 1 mm., n^{20}_{D} 1.5268, d^{20}_4 1.0277, MR_{calcd} 74.9, MR_{found} 75.1.

Anal. Calcd. for $C_{13}H_{21}O_2NSi$: Si, 11.1. Found: Si, 10.7.

4-Methyl-3-aminophenyltriethylsilane.—The amine was prepared in 95% yield from the nitro compound by catalytic reduction as described above. The boiling point was 109° at 0.5 mm., n^{20}_{D} 1.5350, d^{20}_4 0.944, MR_{calcd} 73.0, MR_{found} 73.0.

Anal. Calcd. for $C_{13}H_{23}NSi$: Si, 12.6. Found: Si, 12.9.

The acetyl derivative melted at 65–66°.

Anal. Calcd. for $C_{15}H_{25}ONSi$: Si, 10.6. Found: Si, 10.8.

When the free amine was treated with hydrogen chloride as described above a 68% yield of *o*-acetotoluide was obtained melting at 109–110°. This did not depress the melting point of an authentic sample.

---

[3] H. L. Wheeler and L. M. Liddle, *Am. Chem. J.*, **42**, 502 (1909).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

The Reaction of Phenyllithium with Diphenylketene[1]

BY JOHN A. BEEL AND EDWARD VEJVODA

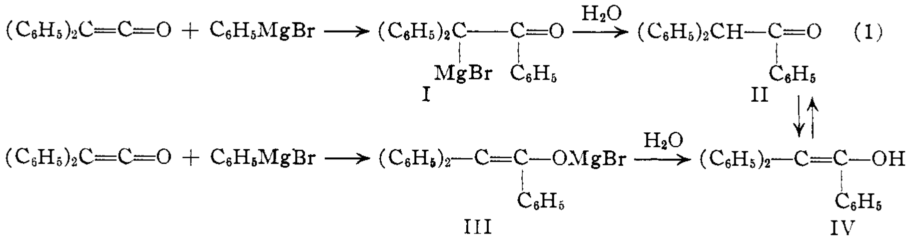
RECEIVED AUGUST 14, 1953

The addition of Grignard reagents to diphenylketene was first investigated by Staudinger[2] who suggested that the reaction proceeded *via* addition to the ethylenic double bond. In the reaction between phenylmagnesium bromide and diphenylketene, Staudinger obtained diphenylacetophenone (II) (equation 1) which tautomerized to form triphenylvinyl alcohol (IV).

---

[1] This paper was presented in part before the Colorado-Wyoming Academy of Science, Denver, Colorado, April 27, 1951.

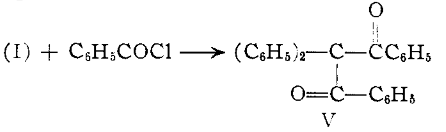
[2] H. Staudinger, *Ann.*, **356**, 122 (1907).



$$(C_6H_5)_2C{=}C{=}O + C_6H_5MgBr \longrightarrow \underset{\text{I}}{(C_6H_5)_2\underset{\substack{|\\ MgBr}}{C}-\underset{\substack{|\\ C_6H_5}}{C}{=}O} \xrightarrow{H_2O} \underset{\text{II}}{(C_6H_5)_2CH-\underset{\substack{|\\ C_6H_5}}{C}{=}O} \quad (1)$$

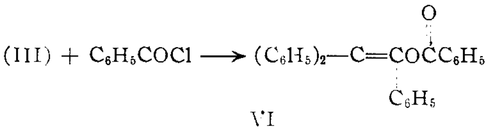
$$(C_6H_5)_2C{=}C{=}O + C_6H_5MgBr \longrightarrow \underset{\text{III}}{(C_6H_5)_2-C{=}\underset{\substack{|\\ C_6H_5}}{C}-OMgBr} \xrightarrow{H_2O} \underset{\text{IV}}{(C_6H_5)_2-C{=}\underset{\substack{|\\ C_6H_5}}{C}-OH} \quad (2)$$

Because Grignard reagents do not normally add to the ethylenic bond,[3] Gilman and Heckert[4] suggested that the addition was to the carbonyl grouping (equation 2). As the same compound would result in either case, no clue to the mode of addition was provided. To ascertain the type of addition, benzoyl chloride was added to the adduct of phenylmagnesium bromide and diphenylketene before hydrolyzing. If the Grignard addition were ethylenic, a β-diketone, diphenyldibenzoylmethane (V), would result (equation 3). On the other hand, if the Grignard added to the carbonyl double bond, an ester, triphenylvinyl benzoate (VI), would result (equation 4).



$$(I) + C_6H_5COCl \longrightarrow (C_6H_5)_2-\underset{\substack{|\\ O{=}C-C_6H_5}}{C}-\overset{\substack{O\\ \|}}{C}C_6H_5 \quad (3)$$

V



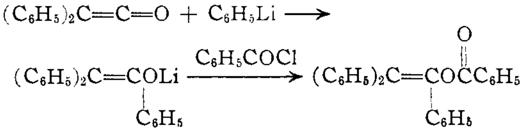
$$(III) + C_6H_5COCl \longrightarrow (C_6H_5)_2-C{=}\underset{\substack{|\\ C_6H_5}}{C}O\overset{\substack{O\\ \|}}{C}C_6H_5 \quad (4)$$

VI

The identification of triphenylvinyl benzoate (VI) established that the addition is to the carbonyl grouping.

In general organolithium compounds are more reactive toward ethylenic addition than Grignard reagents.[5,6] Consequently, it was of interest to see whether ethylenic addition by phenyllithium to diphenylketene is possible. This reaction was carried out using benzoyl chloride to prove the type of addition. Triphenylvinyl benzoate (VI), identified by mixed melting point with that synthesized by the method of Biltz,[7] was isolated. The saponification of VI with alcoholic potassium hydroxide gave benzoic acid and triphenylvinyl alcohol.[7]

The identification of the ester VI indicates that phenyllithium follows the Grignard pattern and adds to the carbonyl linkage in diphenylketene (reaction 5).



$$(C_6H_5)_2C{=}C{=}O + C_6H_5Li \longrightarrow$$

$$(C_6H_5)_2C{=}\underset{\substack{|\\ C_6H_5}}{C}OLi \xrightarrow{C_6H_5COCl} (C_6H_5)_2C{=}\underset{\substack{|\\ C_6H_5}}{C}O\overset{\substack{O\\ \|}}{C}C_6H_5 \quad (5)$$

VI

It was found that lowering the temperature of the reaction to −80° increased the yield of the ester somewhat. Also the order of addition affected the yield, which was highest (86.4%) when diphenylketene was added to the phenyllithium. The reverse procedure gave a lower yield of the ester and at higher temperatures produced two other compounds. At 0° compound A, melting at 250°, was formed, while the reaction at 20° produced compound B, melting at 175°.

The saponification of compound A in alcoholic potassium hydroxide resulted in diphenylmethane and diphenylacetic acid. A large depression shown by a mixed melting point determination with compound A and the dimer of diphenylketene[8] eliminated the possibility that compound A might be the dimer of diphenylketene. The carbon–hydrogen analyses[9] and the molecular weight determinations suggest the single addition of the phenyllithium to the dimer of diphenylketene and the subsequent reaction with the benzoyl chloride.

The treatment of compound B with alcoholic potassium hydroxide resulted in the identification of benzoic acid by mixed melting point determination and the identification of diphenylmethane from its nitro derivative. From the analytical data[9] (carbon–hydrogen analyses and molecular weight) compound B could possibly be a nine-molecule polymerization product of diphenylketene.

Experimental

Addition of Phenyllithium to Diphenylketene at −80°.—An ethereal solution of 5.4 g. (0.028 mole) of diphenylketene[10] was placed in a dry three-neck flask fitted with a dropping bottle, mechanical stirrer and a reflux condenser. The temperature of −80° was maintained by a Dry Ice–acetone-bath while the entire system was kept under an atmosphere of nitrogen.

With constant stirring 0.030 mole of phenyllithium[11] was slowly added to the ethereal solution of diphenylketene. The first addition of phenyllithium produced a red-brown color which darkened upon the complete addition of phenyllithium. Approximately 15 to 20 minutes after the complete addition of phenyllithium, the reaction turned a yellow-white, and a flocculent white precipitate became evident. At this point the organometallic Color Test I[12] was positive.

An ethereal solution of 4.5 g. (0.032 mole) of benzoyl chloride was slowly introduced into the reaction flask. The reaction color turned from a yellow-white to a milk-white upon completion of the benzoyl chloride addition. The reaction was further stirred for another 15 minutes and then permitted to attain room temperature.

On standing, a flocculent white precipitate settled out, and the ether layer acquired an orange color. The reaction was hydrolyzed with 50 ml. of water, and 4.1 g. of a precipitate, melting at 148–149°, was recovered. The filtrate was

---

[3] H. Gilman, "Organic Chemistry," Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 515.

[4] H. Gilman and L. C. Heckert, THIS JOURNAL, **42**, 1010 (1920).

[5] H. Gilman and R. H. Kirby, *ibid.*, **63**, 2046 (1941).

[6] R. C. Fuson, H. A. De Wald and R. Gaertner, *J. Org. Chem.*, **16**, 21 (1951).

[7] H. Biltz, *Ber.*, **32**, 655 (1899).

[8] H. Staudinger, *ibid.*, **44**, 530 (1911).

[9] All analyses and molecular weight determinations were done by the Clark Microanalytical Laboratory, Urbana, Ill.

[10] L. I. Smith and H. H. Hoehn, *Org. Syntheses*, **20**, 47 (1940).

[11] H. Gilman, E. A. Zoellner and W. M. Selby, THIS JOURNAL, **54**, 1957 (1932).

[12] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

placed in a separatory funnel, and the ether layer was separated and dried over sodium sulfate. After removing the ether a dark yellow oil remained. Recrystallization from alcohol of both the residue from the ether layer and the original precipitate yielded 4.1 g. (43.6%) of triphenylvinyl benzoate, melting at 151°, undepressed on mixture with triphenylvinyl benzoate synthesized by the method of Biltz.[7] The recrystallization liquors from the ester were concentrated to yield 0.4 g. (5.9%) of triphenylvinyl alcohol, identified by mixed melting point with an authentic specimen.[7]

Addition of Phenyllithium to Diphenylketene at 0°.—The same technique was followed as in the $-80°$ addition using 0.034 mole of phenyllithium and 6.2 g. (0.032 mole) of diphenylketene[10] followed by the addition of 5.3 g. (0.038 mole) of benzoyl chloride. The temperature of 0° was maintained by an ice–salt-bath. The reaction showed the same color changes as the reaction at $-80°$, was hydrolyzed, and a yellow precipitate was isolated. The precipitate was recrystallized from toluene yielding 2.30 g. of a substance melting at 258° (compound A). After separation from the water layer, the ether was distilled away, and 0.9 g.(8.3%) of triphenylvinyl benzoate was obtained upon recrystallization. The mother liquors were condensed to yield 2.9 g. (36.8%) of triphenylvinyl alcohol.

Compound A.—The compound was dissolved in methyl alcohol and refluxed 48 hours with 10% alcoholic potassium hydroxide solution. A compound melting at 146° was obtained from the water layer and identified as diphenylacetic acid by a mixed melting point determination. Diphenylmethane, m.p. 24–26°, was recovered from the ether layer and identified as its nitro derivative.

The polymer of diphenylketene,[11] m.p. 244–245°, showed a melting point depression of thirty degrees with compound A. The analytical data for compound A suggest the single addition of phenyllithium to the dimer of diphenylketene followed by the usual reaction with benzoyl chloride to give a compound with a formula of $C_{41}H_{30}O_3$.

Anal. Calcd. for $C_{41}H_{30}O_3$: C, 86.29; H, 5.29; mol. wt., 571. Found: C, 87.45, 87.21; H, 5.14, 5.36; mol. wt., 608, 647.

Addition of Phenyllithium to Diphenylketene at 20°.—The procedure described above was repeated with 0.036 mole of phenyllithium and 0.034 mole of diphenylketene at a bath temperature of 20° with subsequent addition of benzoyl chloride. After hydrolysis the ether was removed by distillation. On recrystallization from alcohol the residue yielded 4.6 g. of a substance melting at 175° (compound B).

Compound B.—The compound was refluxed in a 10% alcoholic potassium hydroxide solution for 24 hours. From the saponification mixture, benzoic acid and diphenylmethane were isolated and identified.

The analytical data indicate that compound B may possibly be a nine-molecule polymerization product of diphenylketene, $(C_{14}H_{10}O)_9$.

Anal. Calcd. for $(C_{14}H_{10}O)_9$: C, 86.57; H, 5.19; mol. wt., 1748. Found: C, 86.65, 86.57; H, 5.38, 5.22; mol. wt., 1773, 1808.

Addition of Diphenylketene to Phenyllithium at 20°.—To a solution of 0.06 mole of phenyllithium in ether was added 11.0 g. (0.057 mole) of diphenylketene in ether. Approximately one-half hour after the addition was complete 8.5 g. (0.07 mole) of benzoyl chloride was added to the mixture. On working up in the manner described above an 86.4% yield of triphenylvinyl benzoate (m.p. 151°) was obtained.

DEPARTMENT OF CHEMISTRY
COLORADO STATE COLLEGE OF EDUCATION
GREELEY, COLORADO

Note on the Theory of the Kinetics of Polarographic Electrode Processes

BY R. BRDIČKA AND J. KOUTECKÝ

RECEIVED JUNE 29, 1953

In the last few years increased attention is being paid to polarographic electrode processes involving various reactions the rate of which, jointly with the diffusion of reactants, controls the resulting depolarization current. The contributions to this problem concern on the one hand reactions occurring in the solution surrounding the electrode, and on the other hand processes related to the electron exchange with the depolarizer. Since the investigations of this problem are being developed in different laboratories and its original treatment is not always adequately referred to, interpreted or known, we wish to present here some comments on this subject.

In the first attempt[1-3] to define the kinetic component of the total limiting current, the concept of a reaction layer around the electrode was introduced. Instead of considering the transfer of the reactants from the bulk to the electrode, their concentrations at the surface of the electrode were expressed with the Ilkovič diffusion formula. This simplified treatment of the problem was completed by Wiesner[4] with a statistical estimate of the effective thickness of the reaction layer made on the basis of the Einstein–Smoluchowski law.

The first treatment of the problem using a system of differential equations with appropriate boundary conditions describing the diffusion to a plane electrode and considering the reversible formation of the depolarizer in the solution, was worked out by Koutecký and Brdička.[5] The results were extended with certain approximations to the dropping electrode and tabulated data were furnished for an easy evaluation of the rate constants due to ionic recombination of weak acids from the limiting currents observed. Small but distinct deviations of the theoretical results from the experimental data were ascertained concerning the variation of the limiting currents with the pH and the drop time,[6] the theoretical curve being somewhat steeper than the experimental one. It was shown at the same time that the Wiesner statistical definition of the thickness of the reaction layer represents a reliable estimate, provided that the rates of recombination are high enough.

After extending this mode of procedure to various general schemes of electrode processes among which the problem of the regeneration of the depolarizer during the depolarization process was also discussed,[7] a more accurate treatment of the rate-controlled currents was recently presented by Koutecký[8,9] in which the growth of the dropping electrode against the electrolyte was taken into account. With this essential improvement the theoretical results fully agree with the experimental

---

(1) K. Wiesner, *Z. Elektrochem.*, **49**, 164 (1943).

(2) R. Brdička and K. Wiesner, *Věstník Král. České Společnosti Nauk, Třída Mat. Přiro.*, No. 18 (1943); *Collection Czechoslov. Chem. Communs.*, **12**, 39 (1947).

(3) R. Brdička and K. Wiesner, *ibid.*, **12**, 138 (1947).

(4) K. Wiesner, *Chem. Listy*, **41**, 6 (1947).

(5) J. Koutecký and R. Brdička, *Collection Czechoslov. Chem. Communs.*, **12**, 237 (1947).

(6) V. Hanuš, *Proc. Intern. Polarog. Congr. Prague*, Part I, 803 (1951).

(7) J. Koutecký, *ibid.*, Part I, 826 (1951); *Chem. Listy*, **46**, 193 (1952); *Collection Czechoslov. Chem. Communs.*, **18**, 183 (1953).

(8) J. Koutecký, *Chem. Listy*, **47**, 9 (1953); *Collection Czechoslov. Chem. Communs.*, **18**, 311 (1953).

(9) J. Koutecký, *Chem. Listy*, **47**, 323 (1953); *Collection Czechoslov. Chem. Communs.*, **18**, 597 (1953).