nection in the case of other vinyl compounds.

One new aliphatic phosphonic acid, 2,4,4-tri-methyl-1-pentenephosphonic acid, was prepared from commercial di-isobutylene.

Experimental

The procedure used was essentially that of Bergmann and Bondi. The experimental data and the constants of the new compounds are given in the preceding table.

Attempted Ring Closure of 2-Phenylstyrene-β-phosphonic Acid.—2-Phenylstyrene-β-phosphonic acid (1.0 g.) was heated for twenty-five minutes with 0.2 g. of sulfur at 230–240°. The brisk evolution of hydrogen sulfide was essentially complete in twenty minutes. The cooled mass was extracted with dilute sodium hydroxide and the alkaline extract was added slowly to warm dilute hydrochloric acid to give 0.2 g. of the dehydrogenation product, which formed tiny colorless flakes and decomposed at 160–162°. Pyrolysis of this material yielded a small amount of yellowish liquid which could not be induced to crystallize and which failed to exhibit the typical fluorescence of phenanthrene in ultraviolet light. Although the product does not appear to be the desired phenanthrene derivative, further investigation of its nature was prevented by the meager yields.

Reaction of Styrene, Phosphorus Trichloride and Chlorine.—A solution of 52.1 g. (0.5 mole) of styrene in 500 cc. of dry benzene was treated with 68.7 g. (0.5 mole) of phosphorus trichloride. Dry chlorine was introduced into the solution with vigorous stirring and cooling by

means of an ice-bath. After five hours, the mixture assumed a yellowish color due to the presence of free chlorine. At this point the mixture was in the form of a creamy suspension of the styrene–phosphorus pentachloride adduct. The mixture was hydrolyzed with 200 grams of ice, after which the spontaneous evaporation of the benzene layer gave 32.9 g. (35.7%) of β-styrenephosphonic acid, m. p. 140–144°. The filtrate deposited 43.4 g. (49.6%) of styrene dichloride, as a heavy oil, b. p. 105–120° at 10.5 mm., $n^{25}D$ 1.5553.

β-Styrenephosphonic acid was readily purified by slow addition of its solution in dilute sodium hydroxide to warm dilute hydrochloric acid with stirring. Recrystallization from hot water gave the product in the form of lustrous colorless plates, m. p. 154.5–155°. The addition of hydrochloric acid to a solution of the styrenephosphonic acid in dilute sodium hydroxide, however, yields a poorly soluble acid sodium salt which forms colorless plates which melt indefinitely at 224–227°.

Summary

Ten new unsaturated phosphonic acids were prepared by the addition of phosphorus pentachloride to the corresponding olefins.

The addition of phosphorus pentachloride and of chlorine to styrene was shown to be competitive.
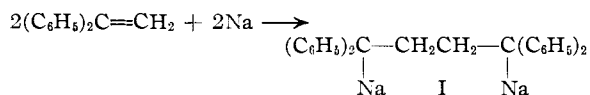

The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. III. Mechanism of the Dimerizing Addition of Sodium to Olefins[1,2]

By Stanley Wawzonek and Joyce Wang Fan[3]

Certain types of olefins when treated with alkali metals add and dimerize in a similar manner to that shown for 1,1-diphenylethylene.

$$2(C_6H_5)_2C{=}CH_2 + 2Na \longrightarrow$$
$$(C_6H_5)_2C{-}CH_2CH_2{-}C(C_6H_5)_2$$
$$\underset{Na}{|} \quad I \quad \underset{Na}{|}$$

Two mechanisms have been proposed for the formation of the dimer (I). Ziegler and co-workers[4] have suggested that the reaction follows normal 1,2-addition with the resulting organo-alkali compound adding to another molecule of

$$(C_6H_5)_2C{=}CH_2 \xrightarrow{2Na} (C_6H_5)_2C{-}CH_2 \xrightarrow{(C_6H_5)_2C{=}CH_2} I$$
$$\underset{Na}{|}\underset{Na}{|}$$
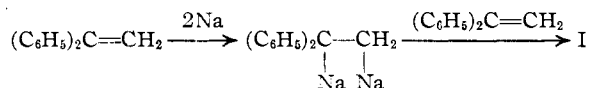
olefin. Schlenk and Bergmann[5] have proposed free radical formation as the initial step followed by polymerization.

(1) Paper II, Wawzonek and Laitinen, This Journal, **64**, 2365 (1942).

(2) Presented before the Division of Organic Chemistry of the American Chemical Society at the Chicago meeting, September, 1946.

(3) Abstracted from a thesis by Joyce Wang Fan, presented to the Graduate College of the State University of Iowa, in partial fulfillment of the requirements for the Ph.D. degree, June, 1946.
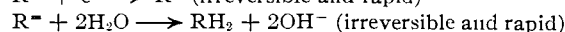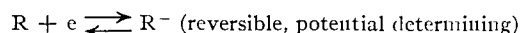
(4) Ziegler, Colonius and Schafer, *Ann.*, **473**, 36 (1929).

(5) Schlenk and Bergmann, *ibid.*, **463**, 1 (1928).

$$2(C_6H_5)_2C{=}CH_2 \xrightarrow{2Na} 2(C_6H_5)_2C{-}CH_2{}^- \longrightarrow I$$
$$\underset{Na}{|}$$
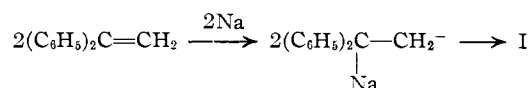
Chemical evidence offered up to the present time has not been able to distinguish between these mechanisms.[6]

The behavior of unsaturated hydrocarbons at the dropping mercury electrode has been found in previous work[1] to resemble that observed with alkali metals. Both are sources of electrons with the dropping mercury electrode having the advantage of being a controlled source. Therefore the mechanisms of reduction at each should be comparable. Work[7] with 1,1-diphenylethylene has indicated the following mechanism for its electroreduction.

$R + e \rightleftarrows R^-$ (reversible, potential determining)

$R^- + e \longrightarrow R^=$ (irreversible and rapid)

$R^= + 2H_2O \longrightarrow RH_2 + 2OH^-$ (irreversible and rapid)

This mechanism is in essential agreement with Ziegler's hypothesis. The second electron adds before the free radical can dimerize. The resulting products at the dropping mercury electrode differ from those obtained with sodium in this respect.

(6) Wooster, *Chem. Rev.*, **11**, 1 (1932).

(7) Laitinen and Wawzonek, This Journal, **64**, 1765 (1942).

The bivalent anion formed reacts preferentially with the water present rather than with another molecule of the olefin. The result at the dropping mercury electrode is a wave involving two electrons.

To determine whether this mechanism is a general one, other unsaturated hydrocarbons which undergo dimerization with alkali metals have been studied at the dropping mercury electrode. The results obtained are presented in this paper.

Results

The behavior of various olefins and related compounds was studied in a 0.175 M tetrabutylammonium iodide–75% dioxane solution. Olefins which do not dimerize were included to aid in ascertaining the number of electrons involved in the reductions. No concentration is given for triphenylmethyl since its method of preparation offered sources of error. A summary of the observed half-wave potentials and individual diffusion current constants is given in Table I.

TABLE I

HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS OF VARIOUS COMPOUNDS IN 0.175 M TETRABUTYLAMMONIUM IODIDE, 75% DIOXANE

Compound	$\pi_{1/2}$ vs. S. C. E., volts	i_d micro-amperes	C, milli-moles/liter	$i_d/Cm^{2/3}t^{1/6}$
Stilbene	−2.14	4.70	1.13	5.20
1,1-Diphenylethylene	−2.22	5.88	1.55	4.74
	−2.17[a]	3.47[a]	0.96[a]	4.54[a]
Dimethylfulvene	−1.89	5.78	1.50	4.81
	−1.85[a]	3.82[a]	0.97[a]	4.92[a]
Diphenylfulvene	−1.57	3.72	1.00	4.65
Dimethylbenzofulvene	−1.98	5.00	1.20	5.20
	−1.94[a]	3.43[a]	0.87[a]	4.92[a]
Diphenylbenzofulvene	−1.61	2.94	1.00	4.38[b]
	−2.74	2.84		4.23[b]
Benzalfluorene	−1.67	2.84	1.00	4.23[b]
	−2.65	5.83		8.69[b]
	−1.67[a]	3.04[a]	0.84[a]	4.52[a]
	−2.69[a]	3.82[a]		4.69[a]
Furfuralfluorene	−1.62	3.03	.92	4.11[b]
	−2.62	3.33		4.52[b]
	−1.66[a]	3.18[a]	1.00[a]	4.74[a]
	−2.63[a]	7.05[a]		10.50[a]
Biphenylenediphenylethylene	−1.63	2.99	1.00	4.46[b]
	−2.64	10.49		15.63[b]
9-Benzhydrylfluorene	−2.64	6.22	1.00	7.77
Cinnamylidenefluorene	−1.46	1.47	1.00	2.19[b]
	−1.62	1.76		2.62[b]
	−1.91	1.67		2.48[b]
	−2.66	5.39		8.03[b]
	−1.43[a]	1.76[a]	0.96[a]	2.29[a]
	−1.61[a]	1.67[a]		2.18[a]
	−1.90[a]	1.57[a]		2.05[a]
	−2.66[a]	1.47[a]		1.91[a]
γ-Phenylpropylidenefluorene	−1.87	2.94	1.00	3.67
	−2.67	3.72		4.65
1-Fluorenyl-2-benzylethylene	−2.63	4.51	1.00	5.63
Fluoranthene	−1.79	1.76	1.09	2.40[b]
	−2.11	2.55		3.49[b]
	−2.62	6.81		9.31[b]
	−1.72[a]	1.96[a]	0.90[a]	2.72[a]
	−2.08[a]	2.79[a]		3.87[a]
	−2.63[a]	2.64[a]		3.66[a]
Dibiphenyleneethylene	−1.04	1.57	0.99	2.35[b]
	−1.39	1.42		2.13[b]
	−2.42	2.01		3.02[b]
	−2.67	10.78		16.09[b]
	−0.99[a]	1.67[a]	0.89[a]	2.35[a]
	−1.37[a]	1.37[a]		1.93[a]
	−2.41[a]	2.35[a]		3.30[a]
	−2.67[a]	6.47[a]		9.09[a]
9,9'-Difluorenyl	−2.40	3.28	1.04	3.94
	−2.69	7.99		9.60
Triphenylmethyl	−1.05	1.76		
	−1.72	2.94		
	−2.00	4.50		

[a] In 0.175 M tetrabutylammonium iodide, 0.052 M tetrabutylammonium hydroxide, 75% dioxane. [b] Capillary number one. All other values were obtained with capillary number two.

Discussion of Results

A comparison of the diffusion current constants, $i_d/Cm^{2/3}t^{1/6}$, obtained, indicates that two electrons are involved in the first reduction wave of all the compounds with the exception of cinnamylidenefluorene, fluoranthene and dibiphenyleneethylene. Accordingly 1,1-diphenylethylene (4.74), dimethylfulvene (4.81), and dimethylbenzofulvene (5.20) have similar diffusion current constants to those of stilbene (5.20), diphenylfulvene (4.65) and diphenylbenzofulvene (4.38), compounds which undergo normal 1,2-addition. Benzalfluorene (4.52) and furfuralfluorene (4.11) in turn have diffusion current constants approximately equal to that of biphenylenediphenylethylene (4.46) which undergoes 1,2-addition. The half-wave potentials obtained for these waves indicate that the same double bonds are involved in these reductions as in the addition of sodium. Thus compounds with similar structures have approximately the same half-wave potentials. Dimethylfulvene (−1.89 v.) is reduced at approximately the same value as dimethylbenzofulvene (−1.98 v.), while diphenylfulvene (−1.57 v.) approximates diphenylbenzofulvene (−1.61 v.). The second wave at −2.74 v. for diphenylbenzofulvene is no doubt due to the reduction of the double bond in the resulting indene, since a similar behavior has been observed with indene.[1] The reduction of dimethylfulvene is the first example of a reduction of an olefin which is void of aromatic groups. In the fluorene series the appearance of a wave at approximately −1.63 v.

for all the compounds points to the reduction of the 9,10-double bond. A second wave at approximately —2.64 v. which is characteristic of the fluorene ring system[1] is obtained in every case. This type of reduction is substantiated further by the half-wave potential (—2.64 v.) obtained for 9-benzhydrylfluorene, the reduction product of biphenylenediphenylethylene. The high diffusion current constant of 15.63 microamperes/millimole/liter/mg.$^{2/3}$sec.$^{-1/2}$ obtained for the second wave of biphenylenediphenylethylene is abnormal and points to the use of more than the required two electrons. 9-Benzhydrylfluorene, the reduction product involved, gave a diffusion current constant (7.77) which is higher than the usual value for the reduction of a fluorene ring. This behavior is difficult to explain, and is possibly complicated by an interaction of the 9-benzhydrylfluorene with decomposition products of the buffer formed in this region.
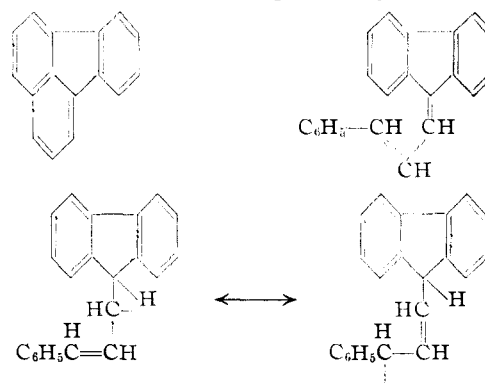
The above results point to a similar mechanism of electroreduction for, or of the addition of sodium to, dimethylfulvene, dimethylbenzofulvene, benzalfluorene and furfuralfluorene, as has been proposed for 1,1-diphenylethylene.

Cinnamylidenefluorene, fluoranthene and dibiphenylene-ethylene gave diffusion current constants which point to a different type of reduction.

Cinnamylidenefluorene gave four waves with diffusion current constants of 2.19, 2.62, 2.48 and 8.03 microamperes/millimoles/liter/mg.$^{2/3}$sec.$^{-1/2}$, respectively. The first three values point to one-electron reduction steps since γ-phenylpropylidenefluorene, which has a similar molecular weight and adds two electrons, gave a wave with a diffusion current constant of 3.67. The only apparent explanation at the present time for this behavior is that one electron adds to cinnamylidenefluorene and the radical formed dimerizes faster than it can add a second electron. This type of reduction would be in agreement with Schlenk's postulation.[5] The nature of the reduction products is not known as yet. The dimer (m. p. 259°) reported by Thiele[8] proved to be too insoluble to give a reduction wave. This property seemingly eliminates it as a product in the electroreduction of cinnamylidenefluorene. Attempts to prepare other dimers that have been reported,[5] failed. γ-Phenylpropylidenefluorene and 1-fluorenyl-2-benzylethylene formed by the addition of two electrons gave little information as to the course of the reduction. The fourth wave observed with cinnamylidenefluorene at —2.66 v. is involved in the reduction of the fluorene ring.

Fluoranthene gave three waves with diffusion current constants of 2.40, 3.49 and 9.31 microamperes/millimoles/liter/mg.$^{2/3}$sec.$^{-1/2}$, respectively. The first wave, in analogy to cinnamylidenefluorene, points to a one-electron reduction. The mechanism of reduction in this step must be similar to that in the first step of cinnamylidenefluo-

rene. This similarity is not surprising, since both compounds involve a conjugate system. Addition of one electron would give a free radical which could stabilize itself toward further reduction by means of resonance. The possibility of dimeriza-

tion at two points complicates the prediction of the structure of the reduction products. The third wave at —2.62 v. for fluoranthene is the characteristic reduction value observed for the fluorene ring. The nature of the reduction products is being investigated further for both fluoranthene and cinnamylidenefluorene.

Dibiphenylene-ethylene gave four waves with diffusion current constants of 2.35, 2.13, 3.02 and 16.09 microamperes/millimoles/liter/mg.$^{2/3}$sec.$^{-1/2}$, respectively. The first two waves point to two one-electron reductions. The product formed is 9,9'-difluorenyl, since the last two waves at —2.42 and —2.67 v. obtained are identical with those obtained for this compound. These results indicate that one electron adds to dibiphenylene-ethylene to give a free radical, which probably due to steric reasons, cannot dimerize. A second electron then adds at a more negative potential to give 9,9'-difluorenyl. The first reduction wave at —1.04 v. suggests that dibiphenylene-ethylene may be a diradical since this value is similar to that observed with the first wave of triphenylmethyl at —1.05 v. The color and chemical behavior[9] of dibiphenylene-ethylene substantiates such a structure.

The half-wave potentials obtained for the compounds in alkaline solution differed only slightly from those in neutral solution. Such a behavior indicates that the radical anion reacts predominantly with water and not with hydrogen ions.

$$R^- + H_2O \longrightarrow RH + OH^- \qquad (a)$$
$$R^- + H^+ \longrightarrow RH \qquad (b)$$
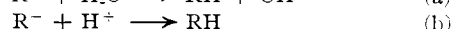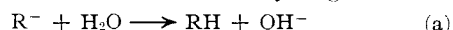
Reaction (a) would not be measurably affected by a change in the pH of the solution. No explanation is apparent for the decrease in the diffusion current constants for the waves at —2.63 in the alkaline buffer.

Logarithmic analyses of the first reduction wave of 1,1-diphenylethylene, cinnamylidenefluorene, fluoranthene and dibiphenylene-ethylene

(8) Thiele and Henle, Ann., 347, 303 (1906).

(9) Wittig and Lange, ibid., 536, 266 (1938).

gave straight lines in each case. The slopes of the lines were 0.079, 0.0481, 0.55 and 0.0604 v., respectively. These results are in essential agreement with the theoretical slope of 0.059 v. (25°) for a reversible potential-determining reaction involving one electron.

Experimental

The current–voltage curves were determined manually by means of a Fisher Elecdropode after removing dissolved air in the usual way with tank nitrogen. All measurements were made in a thermostat at 25 ± 0.1°. The dropping mercury electrodes used had the following characteristics. Capillary no. 1 at a pressure of 64.5 cm. of mercury, had a drop time of 4.1 seconds in 0.1 N potassium chloride (open circuit). The value of m was 1.47 mg. sec.$^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 0.669 mg.$^{2/3}$-sec.$^{-1/2}$. Capillary no. 2 at a pressure of mercury of 64.5 cm., had a drop time of 3.9 seconds in 0.1 N potassium chloride (open circuit). The value of m was 1.84 mg.-sec.$^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 0.800 mg.$^{2/3}$-sec.$^{-1/2}$.

Experiments were carried out in the same manner as has been described in previous work.[7]

Materials.—The solutions used had the following compositions and anode potentials[10]: 0.175 M tetrabutyl-ammonium iodide, 75% dioxane, anode potential −0.485 volt; 0.175 M tetrabutylammonium iodide, 0.052 M tetrabutylammonium hydroxide, 75% dioxane, anode potential, −0.590 volt. Stilbene, 1,1-diphenylethylene and fluoranthene were obtained from stock. Dimethyl-fulvene,[11] diphenylfulvene,[11] dimethylbenzofulvene,[12] diphenylbenzofulvene,[12] benzalfluorene,[8] furfuralfluorene,[8] 9,9'-difluorenyl,[8] biphenylenediphenylethylene,[5] 9-benz-hydrylfluorene,[5] cinnamylidenefluorene,[13] γ-phenylpro-

pylidenefluorene,[14] 1-fluorenyl-2-benzylethylene[14] and di-biphenyene-ethylene[15] were prepared by appropriate methods given in the literature.

Triphenylmethyl was prepared in the following manner. To an air-free, dry solution of dioxane containing a few cc. of mercury, triphenylmethyl chloride was added. The resulting mixture was shaken vigorously for fifteen minutes. The yellow solution of triphenylmethyl thus formed was added to an air-free solution of tetrabutylammonium iodide in water. These two substances were present in such amounts that the resulting solution was 0.175 M tetrabutylammonium iodide in 75% dioxane. After each analysis air was introduced into the solution and the solution analyzed. The introduction of air caused the yellow color of the free radical to disappear and formed free iodine. Analysis of the resulting solution indicated that the first and third waves originally observed had disappeared. This behavior points conclusively to the presence of triphenylmethyl in solution. The second wave is probably due to the presence of the peroxide. A similar behavior was observed using solid triphenylmethyl prepared by the method of Conant.[16]

Summary

A polarographic study has been made of olefins which dimerize when treated with sodium.

Most of the compounds investigated were found to dimerize according to the mechanism proposed by Ziegler.

Fluoranthene and cinnamylidenefluorene were found to dimerize according to the mechanism proposed by Schlenk.

Dibiphenylene-ethylene was found to behave like a diradical.

(10) Values given in previous work[7] are in error, but the final half-wave potentials are correct.

(11) Thiele, Ber., **33**, 672 (1900).

(12) Thiele and Merck, Ann., **415**, 266 (1918).

(13) Whitby and Katz, THIS JOURNAL, **50**, 1168 (1928).

(14) Kuhn and Winterstein, Helv. Chim. Acta, **11**, 123 (1928).

(15) Schmidt and Wagner, Ber., **43**, 1796 (1910).

(16) Conant, Small and Taylor, THIS JOURNAL, **47**, 1959 (1925).

Nitroölefins by the Vapor Phase Catalytic Cleavage of Esters of Nitro Alcohols

BY MARVIN H. GOLD

In the course of certain investigations in these laboratories, it became necessary to produce kilogram lots of several α,β-unsaturated nitroölefins. Since these were relatively large laboratory preparations, a simple and efficient process of preparation was required.

A number of methods appear in the literature for the preparation of the lower molecular weight nitroölefins. Thus, nitroethylene[1] was first made by dehydrating 2-nitroethanol with sodium bisulfate or phosphorus pentoxide. Similarly 1-chloro-1-nitroethylene[2] was synthesized by heating 2-chloro-2-nitroethanol with phosphorus pentoxide at 170°. The same authors also treated 2-chloro-2-nitroethyl nitrate with sodium bicarbonate in refluxing ether to give the chloro nitroethylene. Schmidt and Rutz[3] used this latter principle in

preparing nitroölefins and chloro nitroölefins. They synthesized a number of these compounds, from the nitropropenes through to the nitroöctenes. Their reactions were conducted by refluxing the acetate esters of the nitro alcohols with an ether suspension of potassium bicarbonate. This reaction operated efficiently but the yields of lower molecular weight nitroölefins were sharply decreased by polymerization. Other means of preparation have been described. Thus Haitinger[4] showed that the action of nitric acid on tertiary alcohols gave rise to branched chain nitroölefins. This work was amplified by Bouveault and Wahl[5] who show that highly branched olefins are nitrated under anhydrous conditions to give branched nitroölefins. The authors[6] also prepared

(1) Wieland and Sakellarios, Ber., **52B**, 898 (1919); **53B**, 201 (1920).

(2) Wilkendorf and Trenal, ibid., **57B**, 306 (1924).

(3) Schmidt and Rutz, ibid., **61B**, 2142 (1928).

(4) Haitinger, Ann., **193**, 366 (1878).

(5) Bouveault and Wahl, Bull. soc. chim., [3] **25**, 910 (1901); [3] **29**, 517 (1903).

(6) Bouveault and Wahl, Comp. rend., **134**, 1227 (1902); Bull. soc. chim., [3] **29**, 643 (1903).