was obtained. Hydrogen adsorption experiments in this Laboratory indicated that temperatures from 350 to 400° remove most of the hydrogen, but it has been reported[5] that even under these conditions the surface will still contain some hydrogen. In each experiment the dead volume of the adsorption cell was determined with helium, and then the helium was pumped off at 350° until a vacuum of 10^{-6} mm. was obtained. The gas used in the adsorption experiments contained (in volume per cent.) 98.4 carbon monoxide, 0.1 carbon dioxide, 0.7 hydrogen and 0.8 nitrogen.

Four apparent adsorption isotherms were measured at 0, 25, 65 and 108° and 280 mm. pressure. The results, plotted in Fig. 1, cover only the first 11 hours of each experiment, although in each case the adsorption was followed much longer. Even after 144 hours, the catalyst was still "adsorbing" gas at a slow but finite rate. An experiment with an unpromoted mill-scale catalyst showed essentially the same "adsorption" isotherm at 25°.

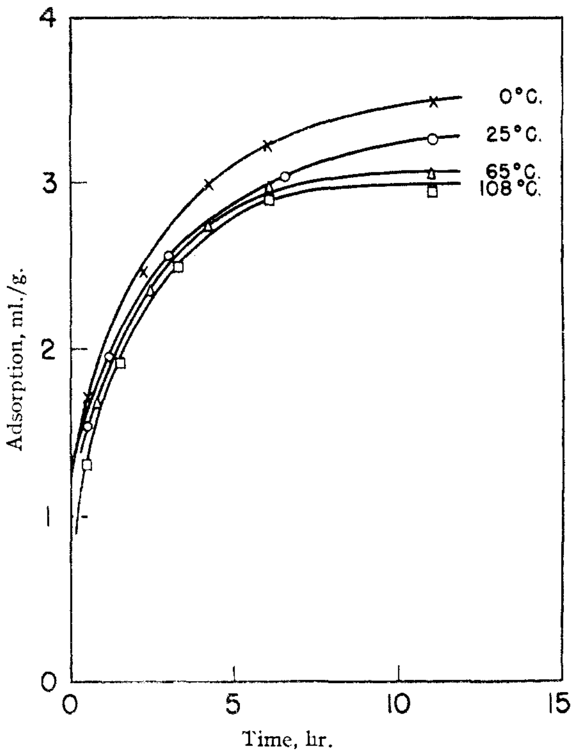

Fig. 1.—Apparent adsorption isotherms of carbon monoxide on a promoted iron catalyst.

After the measurement of each isotherm had been completed, a sample of the gas in the adsorption cell was transferred directly to the mass spectrometer for analysis. During this operation, the temperature and pressure of the cell were held constant to prevent readsorption. The gas analyses, given in Table I, unexpectedly revealed iron pentacarbonyl and large amounts of carbon dioxide. The absolute values of the iron pentacarbonyl concentrations are subject to some question, but comparisons of the concentrations at the different temperatures are believed to be valid.

TABLE I

COMPOSITION OF GAS IN ADSORPTION CELL AFTER 144 HOURS

Temp., °C.	Composition, volume per cent. $Fe(CO)_5$	CO_2	H_2	N_2	CO
0	0.05	0.1	0.3	0.6	98.9
25	.6	8.9	.7	.8	89.0
25[a]	.6	9.1	.8	.9	88.6
65	.3	12.3	.3	1.0	86.1
65[a]	.3	12.0	.1	0.9	86.7
108	<0.05	16.7	.09	1.0	82.2

[a] Duplicate adsorption experiment.

The results indicate that, at temperatures as low as 25°, carbon monoxide will react with reduced iron to form iron pentacarbonyl. The concentrations of iron pentacarbonyl in the adsorption cell after 144 hours at 0 and 25° are lower than would have been predicted from equilibrium considerations[6]; it is assumed that this is the result of a low reaction velocity. The observed pentacarbonyl concentration at 65° is ten times the calculated value for some unexplained reason. At 108° the calculated concentration is 0.0038%, which is well below the sensitivity of the mass spectrometer.

The carbon dioxide in the adsorption cell could have been produced by the iron-catalyzed conversion of carbon monoxide to carbon and carbon dioxide. However, extrapolation of the kinetic data for this reaction[7] eliminates it as the source of the carbon dioxide. It is possible that the carbon dioxide, and presumably iron carbide, were produced by the decomposition of iron pentacarbonyl[8]; kinetic or equilibrium data on this reaction are not available.

In any event, the interpretation of carbon monoxide adsorption experiments at temperatures above 25° is subject to question unless gas analyses are made to confirm the absence of chemical reactions.

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(5) J. T. Kummer and P. H. Emmett, *J. Phys. Colloid Chem.*, **55**, 337 (1951).

(6) H. Pichler and H. Walenda, *Brennstoff-Chem.*, **21**, 133 (1940).

(7) C. I. Chufarov and M. F. Antonova, *Bull. acad. sci., U. R. S. S., Classe sci. tech.*, 381 (1947).

(8) A. Mittasch, *Z. angew. Chem.*, **41**, 827 (1928).

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Reversal of 2-Ethylhex-2-enal to Butyraldehyde

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Self-condensation of butyraldehyde leads *via* the aldol[1] to 2-ethylhex-2-enal[2] (I)

$$C_2H_5CH_2CHO \longrightarrow C_2H_5CH_2CHOHCH(C_2H_5)CHO \longrightarrow C_2H_5CH_2CH{=}C(C_2H_5)CHO \quad (I)$$

In an attempt to condense (I) with fluorene by azeotropic distillation in presence of freshly fused potassium hydroxide,[3] a hydrocarbon of m.p. 55°

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(1) V. Grignard and co-workers, *Bull. soc. chim. France*, [4] **37**, 425 (1925); *Compt. rend.*, **177**, 300 (1923); *Ann. chim.*, [10] **2**, 282 (1924); [10] **9**, 5 (1928); Ch. Weizmann and S. F. Garrard, *J. Chem. Soc.*, **117**, 324 (1920).

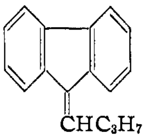
(2) V. Grignard and A. Vesterman, *Bull. soc. chim. France*, [4] **37**, 425 (1925).

(3) D. Lavie and E. Bergmann, *ibid.*, 250 (1951).

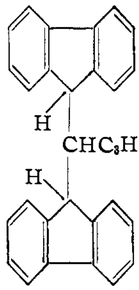
was obtained which had an unexpectedly low boiling point. It was identified as 9-butylidenefluorene[3a] by comparing with a sample prepared from 9-butylfluorenol by dehydrating with a mixture of concentrated hydrochloric and glacial acetic acids.

A second product of the reaction was a hydrocarbon $C_{30}H_{26}$ of m.p. 186–187°, which exhibited the spectrum of fluorene[4] (Fig. 1). It is assumed that this compound is 1,1-di-(9′-fluorenyl)-butane (III) and that it had been formed by a Michael reaction between 9-butylidenefluorene and excess fluorene. Such a reaction has been observed in the case of dibiphenylene ethylene and benzylidenefluorene[5]; it is made possible by the polar character of the semicyclic double bond in fulvenes and their benzologs.[3,6] As the central carbon atom of the fluorene system constitutes the negative end of these dipoles, it is likely that II adds fluorene to form III.

Whilst it was known that aldols[7] and ketols[8] revert to the constituent carbonyl compounds from which they are formed, no such reversion appears to be known generally for the α,β-unsaturated aldehydes and ketones which result from the dehydration of these aldols and ketols.[9] It must, therefore, be assumed, that either 2-ethylhex-2-enal (I) or its condensation product with fluorene, primarily formed, undergo hydration at the original α,β-double bond, followed by formation of two moles of butyraldehyde or one mole each of 9-butylidenefluorene (II) and butyraldehyde, respectively.



II



III

Experimental

9-Butylidenefluorene (II) (a) From 2-Ethylhex-2-enal (I).—A mixture of fluorene (33.2 g., 0.20 mole) and 2-ethylhex-2-enal (27 g., 0.21 mole) was refluxed azeotropically and with stirring for 6 hours with toluene (100 cc.) in the presence of freshly fused and powdered potassium hydroxide (14 g., 0.25 mole). A small amount (0.7 cc.) of water was liberated. The dark mixture was treated with water and the toluene layer separated, washed with dilute sulfuric acid and water and dried. High-vacuum distillation yielded fluorene (in the fraction b.p. 105–110° (0.08 mm., 11 g.) and a main fraction, b.p. 135–150° (0.08 mm.) (22 g.), which soon started to crystallize. By crystallization from hexane at low temperature, the crystalline part was isolated; yield 5 g. The m.p. (52°) was raised to 55° by recrystallization from alcohol. A second crop of 5 g. was obtained by evaporating the hexane mother liquor, dissolving the residue in alcohol and cooling the solution to −20°; the crystals formed were freed from adherent oil by washing with ice-cold alcohol.

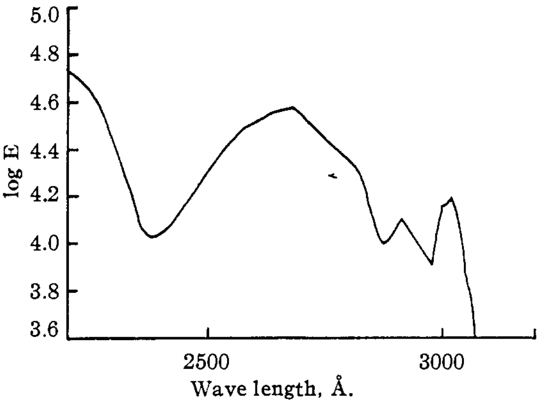


Fig. 1.—Absorption spectrum of the presumed 1,1-di-(9-fluorenyl)-butane in dioxane.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3; mol. wt., 220. Found: C, 92.8; H, 7.4; mol. wt., 213 (Rast), 220 (benzene).

(b) A solution of fluorenone (8 g.) in ether (100 cc.) was added to the Grignard solution prepared from butyl bromide (6.4 g.) and magnesium (1.3 g.) in ether (75 cc.). The reaction product was refluxed for 30 minutes and decomposed by means of ice and ammonium chloride. The residue of the ether solution crystallized spontaneously (7 g., 66%). Recrystallization from alcohol gave **9-butylfluorenol**, m.p. 129–131°.[10]

Concentrated hydrochloric acid (2.5 cc.) was added to a boiling solution of 9-butylfluorenol (1 g.) in glacial acetic acid (12.5 cc.). The crystals formed on cooling were filtered, washed with water and alcohol and recrystallized from heptane; m.p. 55°. The products of the two syntheses (a) and (b) did not depress the melting points of each other.

9-Butylidenefluorene (III) is autoxidized easily, turning gradually yellow and soft and developing the odor of butyraldehyde.[11] No deterioration was observed in a sample kept under nitrogen for four months.

9-Butylidenefluorene dibromide was prepared in carbon tetrachloride and recrystallized from alcohol; m.p. 93–94°.

Anal. Calcd. for $C_{17}H_{16}Br_2$: Br, 42.1. Found: Br, 42.5.

1,1-Di-(9′-fluorenyl)-butane (III).—The residue of the distillation of the reaction product from fluorene and (I) (10 g.) was triturated with warm petroleum ether, which left a white powder (2.3 g.) undissolved, m.p. 183–186°. After recrystallization from heptane, it had m.p. 186–187°.

Anal. Calcd. for $C_{30}H_{26}$: C, 93.3; H, 6.7; mol. wt., 386. Found: C, 93.2; H, 6.3; mol. wt., 378 (benzene).

[3a] Schultz and Smullin, This Journal, **62**, 2904 (1940).

[4] W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (*London*), **A158**, 634 (1937).

[5] L. A. Pinck and G. E. Hilbert, This Journal, **68**, 2014, 2739 (1946): the structure of the condensation product with benzylidenefluorene has been determined by E. Bergmann and D. Lavie, *ibid.*, **74**, in press (1952).

[6] A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, 1097 (1950) (also for previous literature); E. Bergmann and E. Fischer, *ibid.*, 1084 (1950).

[7] See, *e.g.*, for acetaldol: Beilstein, 2nd Suppl., Vol. I, p. 868.

[8] See, *e.g.*, H. Hammarsten, *Ann.*, **421**, 293 (1920).

[9] L. Claisen (*Ber.*, **7**, 1168 (1879)) and C. Harries (*ibid.*, **32**, 1326 (1899)) have described the reversion of mesityl oxide to acetone by boiling dilute sulfuric acid and alkali, respectively.

[10] W. Schlenk, Jr., *Ber.*, **64**, 742 (1931).

[11] Compare, for 9-ethylidenefluorene: M. Daufresne, *Bull. soc. chim. France*, [4] **1**, 1233 (1907).

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Synthesis of Acetylcycloheptene

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In connection with experiments directed toward the synthesis of tricyclic compounds containing seven-membered rings, acetylcycloheptene (I) has been prepared by the condensation of cycloheptene and acetyl chloride in carbon disulfide in the pres-