Anal. Calcd. for $C_{32}H_{42}O_4$: C, 78.33; H, 8.63. Found: C, 78.21, 78.45; H, 8.44, 8.47.

Di-(4-hydroxycyclohexyl)-methane (IX).—4,4'-Dihydroxydiphenylmethane was prepared in 64% yield by Clemmensen reduction of 4,4'-dihydroxybenzophenone.[18] Ten grams was hydrogenated in 30 cc. of purified dioxane with 4 g. of 2% palladium-on-strontium carbonate for 4 hours at 165° and 1600 lb. initial pressure. The product was obtained by distillation *in vacuo* as a colorless oil which solidified on standing; yield 7.8 g. (74%), m.p. 94–95°. Crystallization from ethyl acetate gave small needles, m.p. 113.5–114.5°, cloudy melt becoming clear at 119.5°.

Anal.[12] Calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.80, 73.62; H, 11.35, 11.24.

A dibenzoate was obtained as glistening colorless sheathes from ether–methanol, m.p. 129.5–130°.

Anal.[12] Calcd. for $C_{27}H_{32}O_4$: C, 78.91; H, 7.67. Found: C, 79.06, 79.29; H, 8.08, 8.29.

α,β-Di-(4-Hydroxycyclohexyl)-ethane (X).—Five grams of 4,4'-dihydroxystilbene,[19] 20 cc. of ethanol and 2 g. of Raney nickel in a glass liner were shaken with hydrogen, initial pressure 2000 lb. at 170–180° for 2 hours. A quantitative yield of crystalline product was obtained, m.p. 134.5–139°. Further recrystallization from ethyl acetate gave colorless needles, m.p. 142.5–143.3°, clear melt at 148.5°.

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.42, 74.21; H, 11.71, 11.63.

A dibenzoate was obtained as colorless needles from ethanol, m.p. 177.3–178.8°.

Anal.[12] Calcd. for $C_{28}H_{34}O_4$: C, 77.39; H, 7.89. Found: C, 77.19, 77.28; H, 8.16, 8.02.

Di-(4-ketocyclohexyl)-methane (XI).—A cold solution of 2.1 g. of di-(4-hydroxycyclohexyl)-methane in 50 cc. of glacial acetic acid was treated with a cold solution of 2.2 g. of chromic acid in 10 cc. of water and 40 cc. of glacial acetic acid. After 18 hours at room temperature, the solution was concentrated to dryness *in vacuo* and the residue diluted with water and extracted with ether. The washed and dried ethereal solution was concentrated and the product crystallized from benzene–hexane; yield 1.25 g. (63%) colorless prismatic needles, m.p. 92.5–94°. Further purification gave colorless leaflets, m.p. 96–96.8°.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.97, 75.27; H, 9.83, 9.82.

A dioxime was obtained as colorless glistening needles from alcohol–water, m.p. 204–205.5° with previous darkening.

Anal. Calcd. for $C_{13}H_{22}O_2N_2$: C, 65.51; H, 9.31. Found: C, 65.43, 65.21; H, 9.53, 9.30.

α,β-Di-(4-ketocyclohexyl)-ethane (XII) was obtained by chromic acid oxidation of α,β-di-(4-hydroxycyclohexyl)-ethane (2.2 g.) according to the previously described procedure; yield 1.1 g. (50%), colorless flakes, m.p. 95–96.1°.

Anal.[12] Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98. Found: C, 75.01, 75.30; H, 9.98, 9.90.

A dioxime crystallized from alcohol–water in colorless needles, m.p. 212.5–214.5°.

Anal.[12] Calcd. for $C_{14}H_{24}O_2N_2$: C, 66.63; H, 9.59. Found: C, 66.96, 67.12; H, 9.80, 9.89.

GLENOLDEN, PENNA. RECEIVED SEPTEMBER 5, 1950

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[18] Available from the Dow Chemical Co., Midland, Michigan.

[19] Elbs, *J. prakt. Chem.*, [2] **47**, 60 (1893).

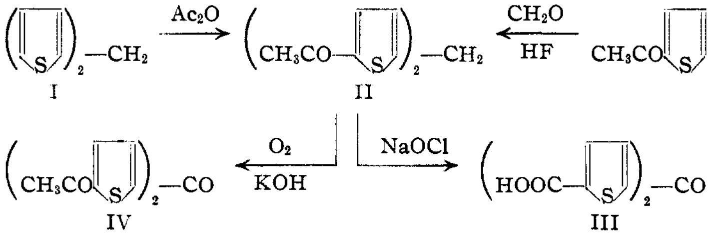
[CONTRIBUTION NO. 281 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, WILMINGTON, DELAWARE, AND CONTRIBUTION NO. 95 FROM THE JACKSON LABORATORY OF THE ORGANIC CHEMICALS DEPARTMENT, DEEPWATER, NEW JERSEY, OF E. I. DU PONT DE NEMOURS & COMPANY]

The Synthesis and Oxidation of 2,2'-Methylene-bis-(5-acetylthiophene)

BY T. L. CAIRNS, B. C. MCKUSICK AND V. WEINMAYR

The preparation of 2,2'-methylene-bis-(5-acetylthiophene) and its oxidation have been studied. Sodium hypochlorite gave 2,2'-carbonyl-bis-(5-thiophenecarboxylic acid) (III) while chromic anhydride or oxygen and alkali gave 2,2'-carbonyl-bis-(5-acetylthiophene) (IV). A new method for forming di-2-thienylmethanes from thiophenes and aldehydes, employing 48% hydrofluoric acid as condensing agent, has been developed.

In connection with work on dicarboxylic acids, it became of interest to prepare a dicarboxylic acid containing thiophene nuclei. Accordingly, di-2-thienylmethane (I) was condensed with acetic anhydride in order to form the diketone (II), which was then oxidized with sodium hypochlorite. The product of this oxidation was found to be a keto dicarboxylic acid (III) rather than the expected methylene dicarboxylic acid.



Subsequent study of the literature showed that this oxidation of a methylene group by hypohalite is not unique, for several cases are known in which a methylene group attached to an aromatic ring containing an acyl group is attacked by hypohalite.[1-3]

The observation that the methylene group of II is attacked by hypochlorite prompted a study of the action of other oxidizing agents on II. It was found that either chromic anhydride in hot acetic acid or oxygen at 25° in the presence of dilute alcoholic potassium hydroxide attacked only the methylene group of II to give a high yield of the triketone, IV. The function of the alkali in the latter oxidation probably was removal of a proton from the methylene group to give an easily oxidized anion. Such an anion, as the resonance hybrid of structures such as V and VI, might be expected to have

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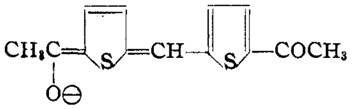
[1] Duval, *Bull. soc. chim.*, [4] **7**, 796 (1910).

[2] Schiessler and Eldred, THIS JOURNAL, **70**, 3958 (1948).

[3] It is probable that oxidation of the methylene group preceded transformation of the acetyl groups to carboxyl groups, but this was not proved. Di-2-thienylmethane was recovered unchanged when treated with sodium hypochlorite, which shows that one activating group or more must be present in the thiophene rings if the methylene group is to be attacked by hypohalite.

color, and, indeed, alkaline solutions of the diketone in ethanol or other solvents were intensely blue and remained so indefinitely as long as oxygen was excluded.[4] The intensity of the color, but not the position of λ_{max} (645 mμ), was strongly dependent on the concentration of alkali relative to that of the diketone.

V



VI

The structures assigned to the diketone (II) and triketone (IV) are logical in view of the high reactivity of the alpha-positions in thiophene toward electrophilic reagents. Verification of the structures was obtained by condensing 2-acetylthiophene with formaldehyde, whereby the diketone (II) was formed in low yield.

2,2'-Ethylidene-bis-(5-acetylthiophene), a homolog of II, was also prepared. Under the influence of alkali it too formed a deep-blue anion which was easily attacked by oxygen. The oxidation product was not identified. The blue anion showed maximum light absorption at a slightly longer wave length (λ_{max} 667 mμ) than the anion from II and it absorbed light much less intensely at the same concentration of reagents.

The di-2-thienylmethane used in this work was most conveniently prepared by a new method involving the condensation of thiophene with formaldehyde (introduced as trioxane) in the presence of 48% hydrofluoric acid at 25°. A by-product, 2,5-bis-(2-thenyl)-thiophene, was obtained by concurrent reaction of the di-2-thienylmethane with thiophene and formaldehyde. The method is fairly general for condensing aldehydes with thiophenes having a free alpha-position. It gave 39–89% yields of substituted di-2-thienylmethanes when 2-methylthiophene, 3-methylthiophene or 2-chlorothiophene was substituted for thiophene and when paraldehyde or benzaldehyde was substituted for trioxane. In assigning structures it was assumed that electrophilic reagents attack a 2-position in a thiophene ring in preference to a 3-position. The structure assigned the product from trioxane and 3-methylthiophene, bis-(3-methyl-2-thienyl)-methane, is logical in view of the fact that electrophilic reagents ordinarily attack 3-methylthiophene in the 2-position.[5,8] Benzene did not react appreciably with formaldehyde under the above conditions and furan, probably because of its great sensitivity to acids, gave only a low yield of di-2-furylmethane.

Experimental

Di-2-thienylmethane (I).—A solution of 90 g. (1.00 mole) of trioxane in 504 g. (6.00 moles) of thiophene was placed in a 1-l. copper flask equipped with a copper stirrer. The flask was immersed in an ice-bath and 200 g. of 48% hydrofluoric acid was added with stirring as follows: 25 g. at the start, 50 g. after 1.5 hours and 125 g. after 3 hours. Stirring was continued for 3 hours at 0–5° and 18 hours at 20–30°. The mixture was poured into two liters of water in a Pyrex separatory funnel (Pyrex glassware was used to minimize attack by hydrofluoric acid). The heavy oil layer was separated and taken up in ether. The ether solution was washed successively with 10% sodium hydroxide and water and dried over magnesium sulfate. Distillation gave 308 g. of crude di-2-thienylmethane, b.p. 133–135° (12 mm.), and 72 g. (14% yield) of 2,5-bis-(2-thenyl)-thiophene, b.p. 175–180° (0.4 mm.) (other data in Table I). The residue was 56 g. of dark, benzene-soluble oil, probably a mixture of thiophene–formaldehyde condensation products similar to the above and containing four or more thiophene rings. The di-2-thienylmethane solidified on standing. After recrystallization from 600 ml. of methanol, it weighed 279 g. (52% yield) and melted at 43–45°.

Other Condensations between Thiophenes and Aldehydes.—The method described for di-2-thienylmethane was successful when applied to 2-methylthiophene, 3-methylthiophene or 2-chlorothiophene in place of thiophene and with paraldehyde or benzaldehyde in place of trioxane. Di-2-furylmethane was prepared by this method, but in only 14% yield. The properties of the products obtained in this manner are summarized in Table I.

2,2'-Methylene-bis-(5-acetylthiophene) (II).[6]—A solution of 72 g. of di-2-thienylmethane in 129 g. of 95% acetic anhydride was stirred at 100° while 1.0 g. of iodine[7] in 10 ml. of ether was added over a period of 30 minutes. The solution was held at 100° for 90 minutes after the addition was complete, 25 ml. of water containing 1.1 g. of sodium bisulfite added, and the mixture cooled. The product was taken up in 200 ml. of chloroform and the extract washed successively with water and 10% sodium hydroxide, dried and distilled through a Claisen still-head of short path and wide bore. The bulk of the product distilled at 176–185° (0.1 mm.). A second distillation followed by two crystallizations from isobutyl alcohol gave 50 g. (46% yield) of colorless diketone, m.p. 124–125°. *Anal.* Calcd. for $C_{13}H_{12}O_2S_2$: C, 59.1; H, 4.6; S, 24.3. Found: C, 59.1; H, 4.6; S, 23.9.

The use of small quantities of phosphoric acid[8] or large quantities of stannic chloride in place of iodine gave lower yields of diketone.

2,2'-Carbonyl-bis-(5-thiophenecarboxylic Acid) (III).—A solution of 5.3 g. of 2,2'-methylene-bis-(5-acetylthiophene) in 25 ml. of chloroform was stirred at 60° with 150 ml. of alkaline 1.2 *M* sodium hypochlorite solution. After 56 hours there was no hypochlorite left in the mixture. The sodium salt of 2,2'-carbonyl-bis-(5-thiophenecarboxylic acid), which was insoluble in the reaction mixture, was removed by filtration and washed with chloroform. The washings were combined with the filtrate and the aqueous layer was separated from the chloroform layer and acidified; no acid precipitated. The chloroform layer was evaporated to dryness, yielding thereby 2.7 g. of starting material. The sodium salt of the acid was dissolved in hot water and the solution was filtered and acidified with hydrochloric acid, which caused the free dicarboxylic acid to precipitate. The acid was insoluble in the common organic solvents even at their boiling points, so its purification was effected by dissolving it in a slight excess of sodium carbonate solution, treating the solution with decolorizing charcoal, and reprecipitating the acid with hydrochloric acid. It weighed 1.15 g. (21% yield) after being dried. It did not melt when placed on a block at 300°. *Anal.* Calcd. for $C_{11}H_6O_5S_2$: C, 46.8; H, 2.1; S, 22.7; neut. equiv., 141. Found: C, 46.55; H, 2.15; S, 22.45; neut. equiv., 150.

Diethyl 2,2'-Carbonyl-bis-(5-thiophenecarboxylate).—Three grams of 2,2'-carbonyl-bis-(5-thiophenecarboxylic acid) was dissolved in 150 ml. of water containing 4 ml. of 29% ammonia, excess ammonia was boiled off, and the solu-

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[4] Limpricht, *Ann.*, **309**, 115 (1899), reported that *o,p'*-dibenzoyldiphenylmethane and *o,p'*-bis-(*p*-toluyl)-diphenylmethane have a deep red color in alcoholic alkali, but he did not say whether they are susceptible to subsequent attack by oxygen.

[5] King and Nord, *J. Org. Chem.*, **13**, 635 (1948); Campaigne and LeSuer, THIS JOURNAL, **70**, 415 (1948); Hartough and Dickert, *ibid.*, **71**, 3922 (1949).

[6] McKusick, U. S. Patent 2,467,439 (1949).

[7] Hartough and Kosak, THIS JOURNAL, **68**, 2639 (1946).

[8] Hartough and Kosak, *ibid.*, **69**, 3093 (1947).

Table I

Products Obtained by Condensing Thiophenes with Aldehydes in the Presence of 48% Hydrofluoric Acid

Compound[a]	Boiling point °C.	Boiling point Mm.	d^{25}_4 or m.p.	n^{25}D	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
Di-2-thienylmethane	133–135	12	43–45°[b]	....	52	$C_9H_8S_2$	180[c]	181			35.5	35.0
2,5-Bis(2-thienyl)-thiophene[d]	175–180	0.4	1.250	1.6348	14	$C_{14}H_{12}S_2$	60.8	60.7	4.4	4.5	34.8	34.6
1,1-Bis-(2-thienyl)-ethane[e]	91–94	0.9	1.168	1.5932	39	$C_{10}H_{10}S_2$	61.8	62.1	5.2	5.4		
2,5-Bis-(α-methyl-2-thienyl)-thiophene[f]	180–186	0.8	1.200	1.6150	22	$C_{16}H_{16}S_3$	63.1	63.5	5.3	5.6		
α,α'-Di-2-thienyltoluene[g]	157–160	2	72–73[h]		40	$C_{15}H_{12}S_2$					25.0	25.1
Bis-(5-methyl-2-thienyl)-methane	116–117	0.8	20[i]	1.5831	72	$C_{11}H_{12}S_2$					30.8	31.1
Bis-(3-methyl-2-thienyl)-methane	110	2	− 6°		89	$C_{11}H_{12}S_2$					30.8	30.2
Bis-(5-chloro-2-thienyl)-methane	110–112	0.1	1.404[j]	1.6140[j]	54	$C_9H_6Cl_2S_2$	43.4	44.0	2.4	2.6	28.5[k]	28.2
Di-2-furylmethane	82–84[l]	18	−26°		14	$C_9H_8O_2$	148[c]	139				

[a] Nomenclature according to "Chemical Abstracts." [b] Blicke and Burckhalter, This Journal, **64**, 477 (1942), report m.p. 45–47°. [c] Molecular weight, ebullioscopic in benzene. [d] By-product in thiophene–trioxane condensation, mol. wt.: calcd., 276; found: 253. [e] Nahke, *Ber.*, **30**, 2037 (1897). [f] By-product in thiophene–paraldehyde condensation. [g] Stirred at 50–55° after addition of hydrofluoric acid to thiophene–benzaldehyde mixture. [h] Tohl and Nahke, *Ber.*, **29**, 2205 (1896), report m.p. 75–76°. [i] Freezing point of distillate; Emerson and Patrick, *J. Org. Chem.*, 14, 790 (1949), report m.p. 38.5–39°. Ford, Prescott and Colingsworth, This Journal, **72**, 2109 (1950), report b.p. 92–94° (0.08 mm.). [j] Determined on supercooled liquid; m.p. 24–27°. [k] Chlorine analysis. [l] Gilman and Wright, This Journal, **55**, 3302 (1933), report b.p. 94° (22.5 mm.).

tion was poured into a solution of 5.4 g. (50% excess) of silver nitrate in 200 ml. of water. The silver salt which precipitated weighed 4.6 g. (87% yield).

A mixture of 1.8 g. of the silver salt and 20 ml. of ethyl iodide was refluxed for 3 hours. The ethyl iodide was removed by distillation and the residue was extracted with acetone. Removal of the acetone left 0.5 g. (37% yield) of crude diethyl ester which, after sublimation at 120–160° (0.3 mm.) and recrystallization from aqueous ethanol, was obtained as colorless platelets, m.p. 136–137°. *Anal.* Calcd. for $C_{15}H_{14}O_5S_2$: C, 53.2; H, 4.2. Found: C, 53.7; H, 4.3.

2,2'-Carbonyl-bis-(5-acetylthiophene) (IV).—To a well-stirred solution of 8.0 g. of 2,2'-methylene-bis-(5-acetylthiophene) in 1250 ml. of 95% ethanol was added 0.8 g. of 50% potassium hydroxide. The solution turned deep blue. Bubbling oxygen through the solution for half an hour caused the blue color to disappear and 8.0 g. of 2,2'-carbonyl-bis-(5-acetylthiophene) to precipitate. After two recrystallizations from acetic acid, the triketone weighed 7.3 g. (88% yield) and was in the form of pale-yellow needles melting at 262–263°. *Anal.* Calcd. for $C_{13}H_{10}O_3S_2$: C, 56.1; H, 3.6; S, 23.0; mol. wt., 278. Found: C, 56.4; H, 3.8; S, 23.1; mol. wt. (ebullioscopic in acetic acid), 239, 285, 286.

The blue color was stable in an inert atmosphere but was speedily discharged by air or oxygen. Oxygen at 25° in the absence of strong alkali had no effect on 2,2'-methylene-bis-(5-acetylthiophene). Bases weaker than sodium or potassium hydroxide, such as sodium carbonate, pyridine or ammonia, did not cause a blue color. Methanol, pyridine or dioxane were also suitable solvents for the oxidation. The absorption spectra of the diketone in the presence of alkali was determined in aqueous ethanol. As the following tabulated data show, ϵ_{max} was particularly dependent on the ratio of alkali concentration to diketone concentration but was also affected by the diketone concentration and water concentration. In contrast, λ_{max} (645 mμ) was unaffected by these variables.

Water, %	Diketone molarity	Mole ratio of NaOH to diketone	λ_{max}
1	0.0038	0.087	50
1	.0019	1.7	590
10	.0019	1.7	345
0	.0019	1.0	440
0	.0028	1.0	535
8	.00095	28	1670
14	.00095	48	2060

A solution of 0.750 g. of 2,2'-methylene-bis-(5-acetylthiophene) in 115 ml. of 95% ethanol was treated with oxygen in a closed system arranged so that the absorption of oxygen could be measured quantitatively. After the addition of 0.1 ml. of 50% potassium hydroxide, absorption of oxygen proceeded steadily for 20 minutes and then ceased simultaneously with disappearance of blue color. The volume of oxygen absorbed at 28° and a pressure of 757 mm. was 74.0 ml. The absorption expected, based on the equation $C_{13}H_{12}O_3S_2 + O_2 = C_{13}H_{10}O_4S_2 + H_2O$, is 70.4 ml.

A solution of 13.2 g. of chromic anhydride in 13 ml. of water was added to a solution of 5.0 g. of 2,2'-methylene-bis-(5-acetylthiophene) in 260 ml. of acetic acid at 90–100°. Crystals began to settle out at once. After an hour the mixture was cooled to 25°, 750 ml. of water added and the product separated by filtration. After recrystallization it weighed 3.6 g. (68% yield) and was identified as 2,2'-carbonyl-bis-(5-acetylthiophene) by a mixed melting point determination. Thus, although there was sufficient chromic anhydride to convert the starting material to 2,2'-carbonyl-bis-(5-thiophenecarboxylic acid), the acetyl groups were not appreciably attacked.

2,2'-Ethylidenebis-(5-acetylthiophene).—The diketone was prepared in the same manner as 2,2'-methylenebis-(5-acetylthiophene), starting from 1,1-bis-(2-thienyl)-ethane. It was purified by distillation (b.p. 190–220° at 0.5 mm.) followed by recrystallization from ethanol; yield 51%; m.p. 66–66.5°. *Anal.* Calcd. for $C_{14}H_{14}O_2S_2$: C, 60.4; H, 5.1; O, 11.5. Found: C, 60.7; H, 5.2; O, 11.4. **Its bis-(*p*-nitrophenylhydrazone)**, m.p. 253–254°, was purified by alternate crystallization from nitrobenzene and pyridine. *Anal.* Calcd. for $C_{26}H_{24}N_6O_4S_2$: C, 56.9; H, 4.4; N, 15.2. Found: C, 57.45; H, 4.5; N, 15.2.

Oxidation of **2,2'-Ethylidenebis-(5-acetylthiophene).**—Four grams of the diketone was dissolved in 12 ml. of ethanol. On addition of a drop of 50% potassium hydroxide, the solution became deep blue. The color was quickly discharged when oxygen was bubbled through the solution at 25°, but addition of more alkali restored it. In all, 1 to 2 ml. of 50% potassium hydroxide was used before the oxidation was complete. The behavior of this diketone differed from that of 2,2'-methylenebis-(5-acetylthiophene) in that the latter did not consume alkali during its oxidation. The absorption spectrum of a 0.0021 molar solution of the diketone in 92% ethanol in the presence of alkali was determined; λ_{max} = 667 mμ; ϵ_{max} = 59 and 388 at relative concentrations of 1.26 and 12.6 moles of sodium hydroxide per mole of diketone, respectively.

On standing, the solution deposited 3.3 g. of brown solid, m.p. 53–56°, and an additional 0.6 g. was obtained on diluting the filtrate with water. Attempts to purify the solid were unsuccessful. After sublimation at 180–200° (0.5 mm.), followed by five crystallizations from methanol, it melted at 60–82°.

Condensation of 2-Acetylthiophene with Formaldehyde.—A solution of 24 g. of trioxane in 252 g. of 2-acetylthiophene was added to 300 g. of anhydrous hydrogen fluoride at 15–

20°. The mixture was stirred at room temperature for 2 hours and poured on ice. Organic material was taken up in chloroform. The extract was washed with 10% sodium hydroxide and steam distilled. Sixty grams of 2-acetylthiophene was isolated from the distillate. Distillation of the organic material (140 g.) not volatile with steam gave 33 g. of material, b.p. 230–240° (2 mm.), which slowly solidified on standing. Five grams of this solid was dissolved in 750 ml. of 95% ethanol and 0.6 g. of 50% potassium hydroxide was added. The solution turned deep blue. When air was bubbled through the solution, the blue color was discharged with simultaneous precipitation of 0.25 g. of 2,2′-carbonylbis-(5-acetylthiophene), identified by mixed melting point. It is evident that a small amount (about 0.7% yield) of 2,2′-methylenebis(5-acetylthiophene) was formed from 2-acetylthiophene and formaldehyde. After three recrystallizations from ethanol, the solid no longer contained any 2,2′-methylenebis-(5-acetylthiophene), for it gave no blue color with alcoholic alkali. Since the solid still melted over a wide range (m.p. 120–130°), it was not investigated further.

WILMINGTON, DELAWARE RECEIVED AUGUST 10, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Rearrangements Involving 1-Pentyne, 2-Pentyne and 1,2-Pentadiene[1]

BY THOMAS L. JACOBS, RICHARD AKAWIE AND ROBERT G. COOPER[2]

The rearrangement of 1-pentyne or 2-pentyne in alcoholic potassium hydroxide at 175° gave an equilibrium mixture containing 1.3% 1-pentyne, 3.5% 1,2-pentadiene and 95.2% 2-pentyne. 1,2-Pentadiene sometimes polymerized too rapidly, but one sample gave almost the equilibrium mixture. 1,3-Pentadiene was not formed in the reaction. The rearrangement cannot involve addition and elimination of alcohol because it took place with powdered potassium hydroxide in the absence of alcohol, and because 2-ethoxy-1-pentene remained largely unchanged under the conditions of the rearrangement, and gave no alkynes or allenes.

The rearrangement of 1-alkynes to 2-alkynes by alcoholic potassium hydroxide is well known.[3–9] It occurs readily at 170° and is faster at higher alkali concentrations[3]; some 1-alkyne remains in the rearranged product.[4,5,6] A shift of the triple bond to the 3-position has not been reported.[7,8] The reverse reaction has not been observed directly, but disubstituted acetylenes can be converted to sodium derivatives of 1-alkynes by sodium[9,10,11] or sodamide[12,13,14] and 1-alkynes recovered readily from these. Allenes, which are probably intermediates in these rearrangements, yield sodium 1-alkynides with sodamide.[15] Isopropylacetylene gives a high yield of *unsym*-dimethylallene on treatment with alcoholic potassium hydroxide at 150°. The interconversion of allenes, alkynes and conjugated dienes has been studied in the vapor phase at higher temperatures over various catalysts.[16–22] and equilibrium constants have been calculated for such systems.[23,24]

In order to determine whether allenes are present among the rearrangement products in the process catalyzed by alcoholic potassium hydroxide and whether an equilibrium mixture is produced, we sought an allene–acetylene system of sufficient

TABLE I

REARRANGEMENTS IN THE SYSTEM 1-PENTYNE: 1,2-PENTADIENE: 2-PENTYNE BY 3.7–3.8 N ALCOHOLIC POTASSIUM HYDROXIDE

Starting hydrocarbon	Temp., °C.	Time, hr.	Composition of product, % 1-Pentyne	1,2-Pentadiene	2-Pentyne
1-Pentyne	175	2	37.1	3.6	59.3
		3	1.3	3.3	95.4
		4.2	1.4	3.6	95.0
		6.5	1.2	3.5	95.3
		10	1.3	3.5	95.2
		20	1.9	3.1	95.0
		18[a]	1.4	3.8	94.8
	125	8	39.0	13.4	47.6
		24	10.1	5.0	84.9
		36	10.4	4.9	84.7
		48	10.9	5.0	84.1
	175[b]	3	83.5	8.3	8.2
2-Pentyne	175	3	1.3	3.4	95.3
		7	1.1	3.5	95.4
		20	1.4	2.8	95.8
	125	24	0.8	2.0	97.2
1,2-Pentadiene	175	2.5	1.3	4.6	93.9

[a] This experiment was carried out in a steel hydrogenation bomb without liner. [b] In this experiment the concn. of alcoholic potassium hydroxide was reduced to 0.95 N. The analytical result for 1-pentyne is less reliable than in the other experiments.

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[2] Part of the material is taken from the M.S. thesis of Robert G. Cooper, 1948. A preliminary report was given at the San Francisco Meeting of the American Chemical Society, March, 1949.

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