[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Stobbe Condensation with Sodium Hydride[1]

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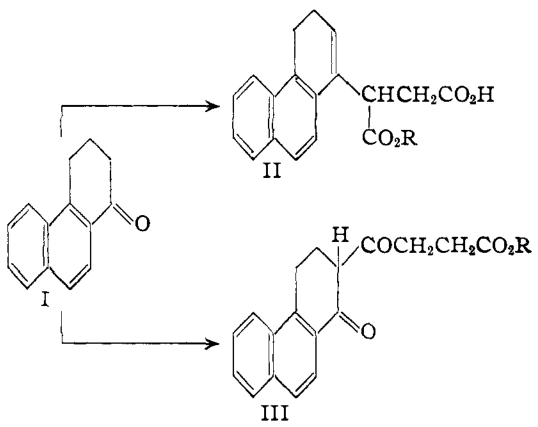
In a preliminary communication[3] the reaction of two representative ketones, benzophenone and acetophenone, with diethyl succinate in the presence of sodium hydride was shown to proceed by a Stobbe condensation giving the expected half-esters in excellent yield. In the present work we are reporting an extension of this study with particular emphasis on the use of di-*t*-butyl succinate as the ester component.

Excellent yields (92, 89.5, 91, 89 and 97%, respectively) of the crude half-esters were obtained from the condensation of acetophenone, 3-acetylphenanthrene, 2-propionyl-6-methoxynaphthalene, 1-keto-1,2,3,4-tetrahydrophenanthrene and benzophenone with diethyl succinate in the presence of sodium hydride; however, the yields were only fair (64 and 73%) with *p,p'*-dimethoxybenzophenone and 1-tetralone and poor (19%) with the more strongly enolizable ketone, desoxybenzoin. The condensation of 1-keto-1,2,3,4-tetrahydrophenanthrene and 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene with dimethyl succinate gave the expected half-esters in 81.5 and 41% yields, respectively.

The condensation of 1-keto-1,2,3,4-tetrahydrophenanthrene (I) with diethyl and with dimethyl succinate afforded, in addition to the expected half-esters II (R = C_2H_5 and CH_3), low yields (3 and 7%, respectively) of ethyl and methyl β-(1-keto-1,2,3,4-tetrahydro-2-phenanthroyl)-propionate (III) (R = C_2H_5 and CH_3) arising from an acetoacetic ester type of condensation of the ester with the ketone. This is, to our knowledge, the first conclusive demonstration of this type of behavior of a succinic ester with a ketone.[4] Evidence for the structure III was provided by analysis, color reaction with ferric chloride, and hydrolysis with dilute potassium hydroxide at room temperature to the free acid III (R = H) which was further cleaved on longer treatment to regenerate the ketone I.



The condensation of di-*t*-butyl succinate with several ketones in the presence of sodium hydride was also investigated. Since the rate of self-condensation of the *t*-butyl ester is considerably lower than that of the ethyl and methyl esters, the use of a large excess of the ester was unnecessary, and, in addition, the extent of condensation could be followed conveniently in most cases by measuring the amount of hydrogen evolved during the reaction. The yields of half-ester obtained by such condensation with benzophenone, *p,p'*-dimethoxybenzophenone, 1-keto-1,2,3,4-tetrahydrophenanthrene and 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene were 98, 91, 93 and 86%, respectively, and the amount of hydrogen evolved during the reaction in each case was in fair agreement with the calculated value. With 1-tetralone, however, the yield was only 72% and with desoxybenzoin very poor (11%), the amount of hydrogen evolved from the condensation with these ketones being considerably higher than expected from the yield of half-ester isolated. This may be attributed in part to enolization, particularly in the latter case.

The condensation of di-*t*-butyl succinate with acetophenone gave, in addition to a 56–64% yield of the half-ester, a 19–34% yield of 1,6-dibenzoyl-2,5-diketohexane, $C_6H_5COCH_2COCH_2CH_2COCH_2COC_6H_5$, resulting from an acetoacetic ester type of condensation of two moles of acetophenone with one of the ester. The structure of the tetraketone was confirmed by hydrolysis with aqueous sodium hydroxide to acetophenone and benzoic acid in yields of 50 and 27%, respectively.

The condensation of 1-keto-2-methyl-2-cyano-1,2,3,4-tetrahydrophenanthrene with diethyl, dimethyl and di-*t*-butyl succinates[5] in the presence of sodium hydride gave only low yields of the corresponding 15-carbalkoxy-14,15-dehydro-17-equilenones (IV). When di-*t*-butyl succinate was used, the amount of hydrogen evolved did not

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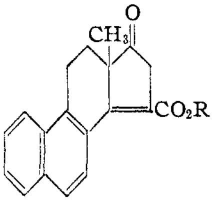
[3] Daub and Johnson, THIS JOURNAL, **70**, 418 (1948).

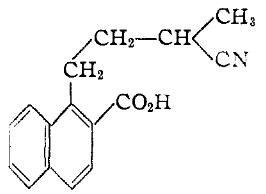
[4] Robinson and Seijo, *J. Chem. Soc.*, 582 (1941), have reported that a compound believed to be methyl γ-keto-γ-(1-keto-2-cyclohexyl)-butyrate was probably formed as a side-product from the condensation of dimethyl succinate with cyclohexanone; however, the compound was not isolated, and its presence was not proved conclusively, since a positive ferric chloride test could have been due to self-condensation products of the succinate.

[5] *Cf.* Johnson, Petersen and Gutsche, THIS JOURNAL, **69**, 2942 (1947).

coincide with the yield of keto ester. This discrepancy was apparently due to side reactions producing alkali-soluble materials, part of which was shown to be α-methyl-γ-(2-carboxy-1-naphthyl)-butyronitrile (V) formed by cleavage of the starting cyano ketone. A similar side-product was previously isolated from the potassium *t*-butoxide-catalyzed condensation of 1-keto-2-methyl-2-cyano-7-methoxy-1,2,3,4-tetrahydrophenanthrene with dimethyl succinate.[5]



IV



V

A new method was developed for the preparation of di-*t*-butyl succinate for use in this study. The procedure of Backer and Homan,[6] *via* succinyl chloride, is reported to give the ester in only 31% yield and in our hands the pure material was obtained in even lower yield. Max W. Miller and Henry Jeffay of this Laboratory have shown that diphenyl succinate—which can be prepared in 77% yield in a single operation by modification and simplification of the procedure of Rasinski[7]—undergoes smooth ester-exchange on treatment with potassium or sodium *t*-butoxide in *t*-butyl alcohol to give the pure crystalline di-*t*-butyl ester in 85% yield. The combined reactions thus permit the preparation of the di-*t*-butyl ester in 65% over-all yield from succinic acid.

Experimental[8]

General Procedure for Ketones.—The following procedure represents a modification of the previously reported method.[3] The reactions were carried out in a 125-ml. round-bottomed flask, equipped with a sealed (rubber slip sleeve) Hershberg wire stirrer, a side-arm capped with a ground-glass stopper (for addition of reagents), and a condenser connected through a calcium chloride tube either to a mercury trap or to a eudiometer (preceded by a Dry Ice trap) depending upon whether the volume of gas evolved was to be measured. The system was flame-dried, filled with dry nitrogen, and the flask charged with the amounts of sodium hydride,[9] succinate and ketone indicated in Table I. When gas measurements were to be made, the benzene (see Table I) was added at this point; otherwise enough solvent was usually introduced as needed to keep the reaction mixture from becoming too viscous. In order to start the reaction a small amount of the alcohol (0.25 mole per mole of ketone) corresponding to the succinate was added. When gas measurements were made, the amount of alcohol was measured carefully and appropriate corrections were applied for the hydrogen produced by its interaction with sodium hydride. An alternate procedure, obviating the necessity of this correction, was to introduce only the sodium hydride, benzene and alcohol; then, after no more gas was evolved, to add the ketone and succinate.

The reaction flask was maintained at the specified temperature and stirring continued for the time indicated (see Table I) or until gas evolution had become very slow. The rate of evolution was generally quite rapid, and finally decreased as the reaction neared completion.

At the end of the reaction period the mixture was cooled and acidified by the cautious addition of glacial acetic acid. Water and ether were then added, and the products isolated in the conventional manner. Sodium carbonate (5%) solution of 1 *N* ammonium hydroxide was used for the extraction of the half-ester, and 5% potassium hydroxide for the removal of less acidic side products (see below). The melting points of the crude solid half-esters are given in Table I. When oily products were obtained, they were dried in ether solution over anhydrous sodium sulfate, and after removal of the ether, dried to constant weight by heating at 100° *in vacuo*.

Procedure for Cyano Ketones.—This procedure is typified by the following description for the condensation of 1-keto-2-cyano-2-methyl-1,2,3,4-tetrahydrophenanthrene with di-*t*-butyl succinate at 80°.

The condensation was carried out as described above in the procedure for ketones with the quantities indicated in Table I. At the end of the reaction period, water was added cautiously to decompose the excess sodium hydride. Ether was added and the aqueous layer with suspended solid separated. The organic layer was washed with 5% potassium hydroxide solution, 5% hydrochloric acid and finally with water. These washings were then combined with the original aqueous slurry, 80 ml. of concentrated hydrochloric acid added and the mixture shaken with ether until the slurry dissolved. The aqueous layer was separated, and the ether layer washed with 5% hydrochloric acid. An ammonia analysis[5] of the combined acid solutions indicated a yield of 40%.

Extraction of the second ether layer with 5% sodium bicarbonate removed 0.49 g. of acidic oil which was purified by evaporative distillation at 160° (0.05 mm.). The distillate amounted to 0.132 g. of crude **α-methyl-γ-(2-carboxy-1-naphthyl)-butyronitrile (V)** which was obtained as colorless needles, m. p. 130–131° after repeated recrystallization from petroleum ether (b. p. 90–100°).

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97; neut. equiv., 253. Found: C, 75.58; H, 6.01; neut. equiv., 251.

The ether solution was then washed with 5% potassium hydroxide solution, which removed 0.2 g. of orange semi-solid material, then with water followed by saturated sodium chloride solution, and finally dried over anhydrous sodium sulfate. The red oily residue left on evaporation of the ether was crystallized from alcohol, and thus 0.359 g. (21% yield) of **15-carbo-*t*-butoxy-14,15-dehydro-17-equilenone** (IV, R = t-C_4H_9), was obtained as orange needles, m. p. 153.3–154.3°. Repeated recrystallization from alcohol gave almost colorless needles, m. p. 154.5–155.5°.

Anal. Calcd. for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.41; H, 7.03.

1,6-Dibenzoyl-2,5-diketohexane.—After extraction of the half-ester, produced in the condensation of acetophenone with di-*t*-butyl succinate at 50° (see Table I), the ether layer was washed with 5% potassium hydroxide solution. Acidification of these alkaline extracts with hydrochloric acid afforded 0.820 g. of crude 1,6-dibenzoyl-2,5-diketohexane as a pale yellow solid, m. p. about 70–80° uncor., which gave a deep red color with alcoholic ferric chloride solution. Recrystallization from alcohol gave 0.391 g. of fine colorless needles, m. p. 92–95°. Repeated recrystallizations from methanol gave material with the m. p. 92–92.5°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.60; H, 5.77.

Hydrolysis of 1,6-Dibenzoyl-2,5-diketohexane.—A 0.402-g. sample of the tetraketone was dissolved in 100 ml. of 20% sodium hydroxide solution and warmed on the steam-bath for one-half hour. After thirty hours at room

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[6] Backer and Homan, *Rec. trav. chim.*, **58**, 1048 (1939).

[7] Rasinski, *J. prakt. Chem.*, [2] **26**, 63 (1882).

[8] All melting points are corrected unless otherwise specified.

[9] Obtained from the Electrochemicals Department, E. I. du Pont de Nemours and Company.

TABLE I

STOBBE CONDENSATIONS WITH SODIUM HYDRIDE

Ketone, (g.)		Succinate, (g.)	NaH, g.	C_6H_6, ml.	Time, hours	Temp., °C.	Yield of half-esters, %	M. p., °C.	Hydrogen evolved	
									Ml.[a]	% of theory[a]
Acetophenone	(6.0)	Diethyl (26.13)	3.6	50	1	25	92[b]	[c]	...	...
	(1.8)	Di-*t*-butyl (4.34)	0.99	30	8	50	57.5[d]	[e]	630	94
	(1.8)	Di-*t*-butyl (6.9)	0.99	30	3	50	64[f]	[e]	653	97
	(1.8)	Di-*t*-butyl (4.34)	0.99	30	19	21	56.5[g]	[e]	595	88.5
Benzophenone	(9.11)	Diethyl (26.13)	2.4	25	8	25	97	124.5–125.5[h]	...	...
	(3.64)	Di-*t*-butyl (5.76)	1.32	40	3.5	50	98	164–167[i]	815	91
	(2.73)	Di-*t*-butyl (4.34)	0.99	30	5.5	50	96	165.5–167.5[i]	624	93
p,p'-Dimethoxybenzophenone[10]	(2.42)	Diethyl (5.23)	0.96	25	22.5	25	64	[j]	...	...
	(2.42)	Diethyl (5.23)	1.2	35	9.5	25–50	64	[j]	...	...
	(2.42)	Di-*t*-butyl (2.88)	0.66	20	11	50	91	101–103.5[k]	417	93
Desoxybenzoin	(2.95)	Diethyl (7.84)	1.2	30	5	25	19	[j]	...	...
	(2.95)	Di-*t*-butyl (4.34)	0.99	30	11	50	11	[j]	545	81
	(2.95)	Di-*t*-butyl (10.4)	0.99	5	4	50	11	[j]	672	100
1-Tetralone[11]	(2.19)	Diethyl (7.84)	1.2	30	3–3.5	25	70–73	82–86[l]	...	...
	(2.19)	Di-*t*-butyl (4.34)	0.99	30	8.5	50	72	[m]	548	81.5
2-Propionyl-6-methoxynaphthalene[12]	(4.28)	Diethyl (10.46)	1.2	30	2	25	91	[n]	...	...
3-Acetylphenanthrene[13]	(3.3)	Diethyl (7.84)	1.2	25	1.5	25	89.5	[o]	...	...
1-Keto-1,2,3,4-tetrahydrophenanthrene[14]	(7.85)	Diethyl (20.92)	2.16	20	1	25	89[p]	140.7–146.2[q]	...	...
	(3.92)	Diethyl (10.46)	1.08	5	1.5	0	86	120–150.2[q]	...	...
	(3.92)	Dimethyl (8.8)	1.08	10	2.25	25	81.5	143.2–151.2[r]	...	...
	(2.94)	Di-*t*-butyl (4.34)	0.99	30	5.5	50	93	126.5–134.5[s]	597	89
	(2.94)	Di-*t*-butyl (4.34)	0.99	30	7	50	87	128.5–134.5[s]	572	85
1-Keto-2-methyl-1,2,3,4-tetrahydrophenanthrene[15]	(4.2)	Dimethyl (8.8)	1.08	30	11.5	25	41	134–145[t]	...	...
	(4.2)	Dimethyl (8.8)	1.32	35	5	50	34.5	140.5–146.5[t]	...	...
	(3.16)	Di-*t*-butyl (4.34)	0.99	30	20.5	50	86	95–113[u]	575	85.5
1-Keto-2-cyano-2-methyl-1,2,3,4-tetrahydrophenanthrene[5]	(0.588)	Diethyl (4.36)	1.44	20	23	24	24.5[v,w]	Not isolated	...	...
	(0.588)	Dimethyl (3.7)	1.44	20	21	50	57[v,w] 46[x]	132–140[y]	...	...
	(1.176)	Di-*t*-butyl (2.3)	0.68	20	11	50	29[v,w]	Not isolated	202	60[z]
	(1.176)	Di-*t*-butyl (2.3)	0.58	20	8.5	80	40[v,w] 21[x]	153.3–154.3	358	106[z]

[a] Corrected to standard conditions. Theory is based upon two moles of hydrogen evolved per mole of starting ketone. [b] Partial separation of isomers was accomplished by crystallization of crude half-ester mixture from petroleum ether.[3] [c] Oily mixture of isomers, neut. equiv. 261 (calcd. 248). [d] A 34% yield of 1,6-dibenzoyl-2,5-diketohexane, m. p. 70–80° uncor. was also obtained as a side-product (see experimental part). [e] Oily mixture of isomers, neut. equiv. 242–250 (calcd. 276). [f] A 19% yield of 1,6-dibenzoyl-2,5-diketohexane was obtained as a side-product. [g] The 1,6-dibenzoyl-2,5-diketohexane isolated amounted to 27% of theory, m. p. 72.5–80°. [h] Reported m. p. 124.5–125.5°.[16] [i] Reported m. p. 167–168°.[17] [j] Oily acidic product. [k] Recrystallization of the crude product from a 50% alcohol–water mixture gave a higher melting polymorphic form as colorless needles, m. p. 127–128.5° (reported,[18] m. p. 126.2–127.6°). [l] Reported m. p. 89.6–90.4°.[19] [m] Oily product, neut. equiv. 292 (calcd. 302). [n] See Johnson and Graber[12] for the nature of this product. [o] Oily mixture of isomers, neut. equiv., 348.5 (calcd. 348). [p] A 5% yield of β-(1-keto-1,2,3,4-tetrahydro-2-phenanthroyl)-propionic acid, m. p. 170.5–175.5°, was obtained as a side-product. [q] Reported m. p. 148.2–149.3°.[20] [r] Recrystallization of the crude product from methanol gave an analytical sample of **β-carbomethoxy-β-(3,4-dihydro-1-phenanthryl)-propionic acid** as colorless rods, m. p. 153.5–154.5°. *Anal.* Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.47; H, 5.43. [s] Repeated recrystallization of the crude product from a petroleum ether (b. p. 90–100°)–ethyl acetate mixture gave an analytical sample of **β-carbo-*t*-butoxy-β-(3,4-dihydro-1-phenanthryl)-propionic acid** as colorless prisms, m. p. 138.2–139.2°. *Anal.* Calcd. for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 74.99; H, 7.01. [t] Reported for crude product using potassium *t*-butoxide as the catalyst, m. p. 119–143°; one isomer obtained pure, m. p. 159–160.5°.[21] [u] Repeated recrystallization of the crude half-ester from a petroleum ether (b. p. 60–68°)–ethyl acetate mixture gave an analytical sample of **β-carbo-*t*-butoxy-β-(1,2,3,4-tetrahydro-2-methyl-1-phenanthrylidene)-propionic acid** as colorless needles, m. p. 132.8–133.8°. *Anal.* Calcd. for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.32; H, 7.20. [v] The product is a 15-carbalkoxy-14,15-dehydro-17-equilenone. [w] Yield of keto ester based on am-

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(10) Schnackenberg and Scholl, *Ber.*, **36**, 654 (1903).

(11) "Org. Syntheses," **20**, 94 (1940).

(12) Johnson and Graber, THIS JOURNAL, **72**, Feb. (1950).

(13) Mosettig and van de Kamp, *ibid.*, **52**, 3704 (1930).

(14) Wilds, *ibid.*, **64**, 1421 (1942).

(15) Wilds and Beck, *ibid.*, **66**, 1688 (1944).

(16) Stobbe, *Ann.*, **308**, 89 (1899).

(17) Johnson, Petersen and Schneider, THIS JOURNAL, **69**, 74 (1947).

(18) Johnson and Miller, *ibid.*, **72**, 511 (1950).

(19) Johnson, Johnson and Petersen, *ibid.*, **67**, 1360 (1945).

(20) Johnson and Petersen, *ibid.*, **67**, 1366 (1945).

(21) Johnson, Stromberg and Petersen, *ibid.*, **71**, 1384 (1949).

monia analysis of acid wash liquors. [x] Actual yield of keto ester isolated. [y] Pure keto ester **IV** (R = CH_3), m. p. 158–159°.[22] ***Anal.*** Calcd. for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.77; H, 6.34. [z] Theory is based upon three moles of hydrogen evolved per mole of starting ketone.

temperature the solution was extracted with ether, and the combined ether solutions washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. The oil which remained on evaporation of the ether was heated with excess semicarbazide hydrochloride in alcoholic solution containing pyridine. Evaporation of the alcohol followed by the dilution with water afforded 0.220 g. of acetophenone semicarbazone, m. p. 199–200°, undepressed upon admixture with an authentic sample.

The alkaline solution remaining after removal of the neutral material was acidified with hydrochloric acid and extracted twice with ether. The combined ether solutions were extracted with 5% sodium bicarbonate solution and the acidified bicarbonate extracts were extracted with ether. The ether solution was dried over anhydrous sodium sulfate, filtered and evaporated. Sublimation of the residue at atmospheric pressure gave 0.081 g. of benzoic acid, m. p. 119–121°, undepressed upon admixture with an authentic sample.

Ethyl and Methyl β-(1-Keto-1,2,3,4-tetrahydro-2-phenanthroyl)-propionate (III, R = C_2H_5 and CH_3).—The ether solution remaining after extraction of the half-ester II (R = C_2H_5) in the condensation of 1-keto-1,2,3,4-tetrahydrophenanthrene with diethyl succinate at 0° (see Table I), was washed with water, saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After removal of the solvent and excess diethyl succinate (reduced pressure), the residue was subjected to evaporative distillation. The fraction distilling at 100–140° (0.05–0.2 mm.), consisted of a mixture of starting ketone and diethyl 1,4-diketocyclohexane-2,5-dicarboxylate. The distillation was continued at 180–200° (0.1 mm.) and the oily distillate recrystallized from alcohol to give 0.19 g. (3% yield) of yellow plates, m. p. 62–64°. Recrystallization from petroleum ether (b. p. 60–68°) raised the m. p. to 63.5–64.2°.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.15; H, 6.11.

The above product gave a green color with alcoholic ferric chloride, and on treatment at room temperature with 10% potassium hydroxide solution was hydrolyzed to the **free acid** III (R = H), m. p. 173–175.5°. After repeated recrystallization from alcohol it was obtained as yellow needles, m. p. 176.8–179°, giving a green color with alcoholic ferric chloride.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.78; H, 5.25.

When a solution of the ester or the acid in 10% potassium hydroxide solution was allowed to stand for several days, crystals of 1-keto-1,2,3,4-tetrahydrophenanthrene separated. The ketone thus obtained melted at 94.5–95.5° alone or when mixed with an authentic specimen.

The methyl ester III (R = CH_3) was isolated from the condensation of I with dimethyl succinate at room temperature (Table I) just as described above for the ethyl ester. The fraction which distilled evaporatively at 180–200° (0.05 mm.) gave after crystallization from methanol, 0.458 g. (7% yield) of yellow needles, m. p. 92–93°, giving a green color with ferric chloride. Recrystallization raised the m. p. to 92.5–94°.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.44; H, 5.87.

Di-*t*-butyl Succinate.—Diphenyl succinate was prepared by the following modification of the procedure of Rasinski.[7] A mixture of 118 g. of succinic acid, 188 g. of phenol and 138 g. of phosphorus oxychloride was heated under reflux in a 2-liter flask on the steam-bath. After one and one-quarter hours, 500 ml. of benzene was added and refluxing continued for another hour. The hot benzene solution was then decanted from the red sirupy phosphoric acid residues and filtered. The residues were treated with two 100-ml. portions of benzene by decantation and filtration, and the combined benzene solution concentrated to about 600 ml. On cooling 181 g. of colorless diphenyl succinate separated, m. p. after washing with ether, 120–121° (reported m. p. 119°).[7] An additional 28 g., m. p. 118–120°, was obtained from the filtrate after washing with dilute potassium hydroxide, making the total yield 77%.

To a solution of 19.6 g. of potassium in 350 ml. of dry *t*-butyl alcohol was added 67.6 g. of diphenyl succinate. The mixture became warm and turned deep red in color. After refluxing for one hour on the steam-bath, the mixture was diluted with water, and most of the alcohol removed by concentration at reduced pressure. The oily ester was taken up in ether, washed with 2% sodium hydroxide, followed by saturated salt solution, and dried over anhydrous potassium carbonate. Distillation of the residue gave 48.8 g. (85% yield) of colorless ester, b. p. 109–110° (9 mm.), m. p. 36–37° (reported,[6] 36°).

Summary

The use of sodium hydride as a condensing agent in the Stobbe condensation of representative alkyl, diaryl, cyclic and α-cyano ketones with succinic esters has been described. When di-*t*-butyl succinate was employed it was possible in a number of cases to follow the condensation by observing the amount of hydrogen evolved.

The condensation of 1-keto-1,2,3,4-tetrahydrophenanthrene with dimethyl and with diethyl succinate has been shown to give, in addition to the expected half-ester, a low yield of methyl and ethyl β-(1-keto-1,2,3,4-tetrahydro-2-phenanthroyl)-propionate.

Acetophenone condensed with di-*t*-butyl succinate to give in addition to a mixture of half-esters, a side-product shown to be 1,6-dibenzoyl-2,5-diketohexane, resulting from an acetoacetic ester type of condensation of two moles of acetophenone with one of the ester.

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(22) Johnson and Shelberg, unpublished observation.