(ϵ=26230); 203(ϵ=30590); NMR δ 7.82 (aromatic protons, m) 0.69 (18-CH$_3$), 1.11 (19-CH$_3$).

3-Aza-A-homo-4α-androsten-4,17-dione[17,16-β]indole (V). To a solution of 1.204 g of I (*9*) in 35 mL of ethanol, 0.454 g of phenylhydrazine was added. The mixture was heated under reflux for 5 h. Then, water was added and the resulting precipitate was collected by filtration to give phenylhydrazone IV with 95% yield. Recrystalization from chloroform–methanol gave IV, mp 174–176 °C.

A solution of 1.2 g of phenylhydrazone IV in 25 mL of glacial acetic acid was refluxed for 24 h. The reaction mixture was poured into ice water and extracted with chloroform. The organic layer was washed with water and dried over sodium sulfate. After evaporation of the solvent the residue was crystallized from chloroform–methanol to give 40% yield of V: mp >300 °C; IR ν_{max} 3360 (NH), 1635 (NHCO), 1600 (C=C), 740 cm^{-1} (aromatic ring); UV λ_{max} 228(ϵ=41.800); NMR δ 10.72 (NH), 7.48 (NHCO) 7.10 (aromatic protons m), 5.54 (C=CH), 0.75 (18-CH$_3$), 1.12 (19-CH$_3$).

13α-Amino-13,17-seco-5α-androstan-17-oic-13,17-lactam[3,2-β]indole **(Va).** To a solution of 1.20 g of Ia (*10*) in 25 mL of glacial acetic acid was added excess of phenylhydrazine. The mixture was heated under reflux for 24 h. After work up as for V and recrystallization from methanol, indole Va was obtained in 55% yield: mp >300 °C, ν_{max} 3400 (NH), 1640 (NHCO), 735 cm^{-1} (aromatic ring); UV λ_{max} 228(ϵ=11560); NMR δ 10.4 (NH), 7.10 (aromatic protons, m), 0,75 (18-CH$_3$), 1.12 (19-CH$_3$).

2′-Methylthiazolo[5′,4′:16,17]-3-aza-A-homo-4α-androsten-4,17-dione (VI). Bromoketone II (380 mg) and thioacetamide (150 mg) were added in 10 mL dimethylformamide and the mixture was heated under reflux for 2 h. Then, it was poured into ice water and the precipitate collected by filtration to give crude compound VI. This precipitate was chromatographed on a silica gel column prepared with chloroform. Elution with chloroform–methanol (98:2) gave 250 mg of VI which was recrystallized from CH$_3$COOC$_2$H$_5$: mp 264–266 °C; IR ν_{max} 3250 (NH), 1650, 1630 (NHCO), 1150 cm^{-1}; NMR δ 7.50 (NHCO), 5.52 (CH=C), 2.60 (CH$_3$–C–S), 0.9 (18-CH$_3$), 1.16 (19-CH$_3$).

2′Methylthiazolo[5′,4′:2,3]-13α-amino-13,17-seco-5α-androstan-17-oic-13,17-lactam (VIa). Under the same reaction conditions of VI, thiazole VIa in 40% yield was obtained, using as starting material bromoketone IIa. Recrystallization from CH$_3$COOC$_2$H$_5$–CHCl$_3$ gave VI: mp 289–291 °V; ν_{max} 3190, 3040 (NH), 1650 (CO), 1170 cm^{-1}; NMR δ 7.19 (NHCO), 2.48 (CH$_3$–C–S), 0.70 (18-CH$_3$), 1.08 (19-CH$_3$).

Registry No. I, 20986-87-2; Ia, 71178-08-0; II, 105431-58-1; IIa, 105431-60-5; III, 105431-59-2; IIIa, 105431-61-6; IV, 105431-62-7; V, 105431-63-8; Va, 105431-64-9; VI, 105431-65-0; VIa, 105431-66-1; *o*-phenylenediamine, 95-54-5; phenylhydrazine, 100-63-0; thioacetamide, 62-55-5.

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The Stobbe Condensation. 6. Reaction of Aryl Aldehydes with Dimethyl Adipate

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Aromatic aldehydes (Ia–h) were condensed with dimethyl adipate in the presence of sodium hydride to give the corresponding half-esters (IIIa–h). Saponification of these esters produced the dibasic acids (Va–b). The structures of all products were substantiated by chemical and spectral methods.

The Stobbe condensation with succinic esters was the subject of several studies (*1–3*). Other ester components were successfully used (*4–8*). The present work deals with the extension of the Stobbe condensation of aromatic aldehydes with a new ester component. Thus benzaldehyde and some of its derivatives as well as furan-2-carboxaldehyde and 1-naphthaldehyde were condensed with dimethyl adipate by using sodium hydride as a base, to produce the half-esters IIIa–h. The latter might have the (*E*) configuration, rather than the (*Z*) configuration (IV), due to the preferential formation of the intermediate lactone A which is free from steric and polar interactions (*9*) (Scheme I).

Table I. Melting Points and Yields of Compounds III and V

compd	mp, °C	yield, %	compd	mp, °C	yield, %
IIIa	oil	70	Va	96	95
b	165	78	b	170	97
c	oil	72	c	125	94
d	170	80	d	232	96
e	oil	75	e	150	91
f	oil	68	f	96	88
g	oil	65	g	140	93
h	100	72	h	115	90

Hydrolysis of the above half-esters gave the corresponding dibasic acids (Va–h).

The structures of the compounds III and V were evident from their spectral and chemical data (*10*, *11*) (Tables I and II). The infrared spectra of III show absorption bands in the

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Table II. Spectrometric Data of Compounds III and V

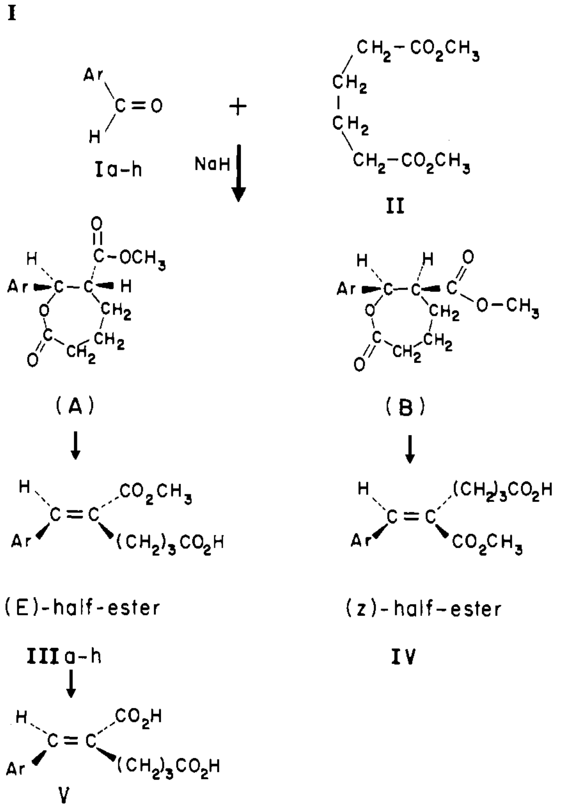
	MS		UV (ethanol)			
compd	*m/e*	% of base peak	λ_{max}, nm	ϵ_{max}	δ, ppm	NMR($CDCl_3$) assign
IIIa	248	0.16	203	9300	1.0–3.70	m, 6, $CH_2CH_2CH_2$
	91	100	226	12230	3.87	s, 3, CO_2CH_3
	129	22.39	273	3790	7.77–8.0	m, 5, Ar–H
	115	37.49			8.33	d, 1, =CH
					9.73	s, 1, CO_2H
IIIb	278	0.01	207	43980	1.40–3.0	m, 6, $CH_2CH_2CH_2$
	18	100	251	40720	3.98	s, 3, CO_2CH_3
					4.00	s, 3, OCH_3
					7.0–8.5	m, 5, Ar–H+, =CH
					9.67	br, 1, CO_2H
IIIc	262	0.94	205	19265	1.0–2.60	m, 6, $CH_2CH_2CH_2$
	18	100	228	13485	3.60	s, 3, CH_3
	91	54.56	279	9250	3.81	s, 3, CO_2CH_3
	115	9.29			7.15–8.25	m, 5, Ar–H+, =CH
					10.34	s, 1, CO_2H
IIId	327	34.58	205	31215	1.20–2.73	m, 6, $CH_2CH_2CH_2$
	266	100	239	28745	3.93	s, 3, CO_2CH_3
	326	38.75	275	3380	7.53–8.0	m, 5, Ar–H+, =CH
	296	86.66			9.30	br, 1, CO_2H
IIIe	327	0.67	265	7430	1.40–2.3	m, 6, $CH_2CH_2CH_2$
	332	0.61			3.60	s, 3, CO_2CH_3
	17	100			7.0–7.73	m, 5, Ar–H+, =CH
	18	100			9.80	br, 1, CO_2H
IIIf			213	20135	1.69–2.33	m, 6, $CH_2CH_2CH_2$
			265	8500	3.63	s, 3, CO_2CH_3
					7.40–8.2	m, 5, Ar–H+, =CH
					11.0	br, 1, CO_2H
IIIg	238	0.58	215	3415	1.35–2.80	m, 6, $CH_2CH_2CH_2$
	59	100	305	14940	3.60	s, 3, CO_2CH_3
	115	1.94			6.35–7.78	m, 4, Ar–H+, =CH
					9.9	br, 1, CO_2H
IIIh	298	5.57	225	17250	1.60–2.2	m, 6, $CH_2CH_2CH_2$
	127	100	285	18400	3.50	s, 3, CO_2CH_3
	115	46.69	295	17250	7.43–8.20	m, 8, Ar–H+, =CH
					9.93	s, 1, CO_2H
Va	234	1.03	204	11995	1.60–2.75	m, 6, $CH_2CH_2CH_2$
	129	100	225	14920	7.0	m, 5, Ar–H
	115	75.14	270	5265	7.33	s, 1, =CH
	91	40			9.80	s, 2, CO_2H
Vb	264	14.70	206	12750	1.20–3.40	m, 6, $CH_2CH_2CH_2$
	144	100	252	10395	3.74	s, 3, CO_2CH_3
	115	17.04			6.80–8.20	m, 5, Ar–H+, =CH
					9.31	br, 2, CO_2H
Vc	248	10.78	205	20010	1.40–2.60	m, 6, $CH_2CH_2CH_2$
	159	100	236	12400	2.40	s, 3, CH_3
	115	20.86	275	7610	7.33–7.60	m, 4, Ar–H
					7.82	s, 1, =CH
					8.53	s, 2, CO_2H
Vd	313	3.14	240	25880	1.40–2.63	m, 6, $CH_2CH_2CH_2$
	315	2.68	275	2360		
	50	100			7.30–8.33	m, 5, Ar–H+, =CH
	224	47.87			8.66	br, 2, CO_2H
Ve			260	5870	1.73–2.60	m, 6, $CH_2CH_2CH_2$
					7.40–8.25	m, 5, Ar–H+, =CH
					9.33	s, 2, CO_2H
Vf			205	49000	2.0–2.80	m, 6, $CH_2CH_2CH_2$
			275	5370	7.60–8.27	m, 5, Ar–H+, =CH
					10.40	s, 2, CO_2H
Vg	224	3.07	205	11775	1.80–3.20	m, 6, $CH_2CH_2CH_2$
	54	100	297	14240	6.80–7.87	m, 4, Ar–H+, =CH
					8.33	br, 2, CO_2H
Vh	284	8.86	225	17530	1.80–2.60	m, 6, $CH_2CH_2CH_2$
	127	100	284	17190	7.60–8.93	m, 8, Ar–H+, =CH
	179	30.57	294	15700	9.68	br, 2, CO_2H

ranges 1675–1740 cm^{-1} and 2940–3050 cm^{-1} attributed to $\nu_{C=O}$ and OH groups, respectively. The acids V show also absorptions in the regions 1670–1710 cm^{-1} ($\nu_{C=O}$) and 2860–3040 cm^{-1} (ν_{OH}).

Experimental Section

Microanalyses were performed by Prof. H. Malissa and G. Reuter, Analytisches Laboratorium, West Germany, and are provided for review. Infrared spectra (KBr) and electronic spectra (ethanol) were measured on Perkin-Elmer 580B and Pye Unicam SP 8000 spectrophotometers, respectively. NMR spectra were recorded in deuteriochloroform with tetramethylsilane as external standard on Varian T60A and Jeol JNM-MH 100 spectrometers. The mass spectra were carried out with Varian MAT 311A. Melting points were determined with a Bock-Monoscop M (thermal microscope). The purity of the products was tested with a Perkin Elmer Sigma 1B gas chromatograph equipped with a Sigma 10 Data station, and a

Scheme I



Compound	Ar	Compound	Ar	Compound	Ar
I,III,Va	C_6H_5	I,III,Vd	p-Br-C_6H_4	I,III,Vg	C_4H_3O
b	p-OCH_3-C_6H_4	e	O-Br-C_6H_4	h	$C_{10}H_7$
c	p-CH_3-C_6H_4	f	m-Cl-C_6H_4		

flame ionization detector was employed for purity analysis. The samples were treated with TMCS prior to GLC analysis.

Preparation of the Half-Esters IIIa–h. The dimethyl adipate (0.12 mol), aldehyde (0.1 mol), and sodium hydride (0.15 mol) are stirred in excess dry benzene with occasional cooling to prevent rise of temperature above 40 °C (few drops of methanol are added to initiate the reaction) the reaction mixture was left overnight by room temperature and then worked up as previously reported (*5*). The residue was crystallized from *n*-hexane or cyclohexane to produce 5-methoxycarbonyl-6-(aryl)-hex-5-enoic acids (IIIa–h).

Saponification of the Half-Esters IIIa–h. The half-ester (2 g) was refluxed with 15% aqueous alcoholic potassium hydroxide solution (15 g KOH, 50 mL H_2O, and 50 mL methanol) for 4 h. The alcohol was distilled off, and the cold alkaline solution was acidified with cold dilute HCl. The resulting dibasic acid was taken in ether, washed with cold distilled water, and dried (Na_2SO_4) and the ether was removed. Crystallization of the acids with *n*-hexane gave 5-carboxy-6-(aryl)-hex-5-enoic acids (Va–h).

Registry No. Ia, 100-52-7; Ib, 123-11-5; Ic, 104-87-0; Id, 1122-91-4; Ie, 6630-33-7; If, 587-04-2; Ig, 98-01-1; Ih, 66-77-3; IIIa, 105064-44-6; IIIb, 105064-45-7; IIIc, 105064-46-8; IIId, 105064-47-9; IIIe, 105064-48-0; IIIf, 105064-49-1; IIIg, 105064-50-4; IIIh, 105064-51-5; Va, 105064-52-6; Vb, 105064-53-7; Vc, 105064-54-8; Vd, 105064-55-9; Ve, 105064-56-0; Vf, 105064-57-1; Vg, 105064-58-2; Vh, 105064-59-3; dimethyl adipate, 627-93-0.

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Reactions of Dibenzoylacetylene with *N*-Alkylnitrones, Heteroaromatic *N*-Oxides, and Diazo and Azoxy Compounds

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Dibenzoylacetylene affords 4-oxazolines, enamines, and pyrazoles by reaction with *N*-alkylnitrones, heteroaromatic *N*-oxides, and aryl diazo compounds, respectively. However, azoxy compounds did not react with dibenzoylacetylene.

We have recently reported (*1*) that the reaction of dibenzoylacetylene (**1**) with *N*-arylnitrones follows a different path from those with other alkynes (*2*). 3-Anilino-1,4-diphenylbutane-1,2,4-trione and the corresponding aldehydes were obtained from the reaction of **1** with those *N*-arylnitrones (*1*). These results prompted us to extend this reaction to *N*-alkylnitrones **2a,b** and other 1,3-dipolar heteroaromatic *N*-oxides **5a,b**, **8**, and **10**, and diazo **12a–c** and azoxy **14a,b** compounds (see Experimental Section), to investigate the behavior of this alkyne **1** toward these 1,3-dipoles.

The reaction of *N*-alkylnitrones **2a,b** with the dipolarophile yielded the 4-oxazolines **4a,b** as sole products (Figure 1). The structure of 4-oxazoline was assigned to these products **4a,b** on the basis of their analytical and spectroscopic data (see Experimental Section). Observation of the methine proton signal

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