TABLE I

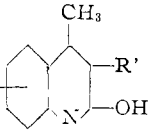
ACETOACETANILIDES, $C_6H_5NHCOCH_2COCH_3$

Substituent(s)	Yield, %	M.p., °C.	Formula	Nitrogen, % Calcd.	Found
2-Methyl-5-nitro[a]	72	119–119.5	$C_{11}H_{12}O_4N_2$	11.9	11.9
2-Chloro-α-methyl	48	94–94.5	$C_{11}H_{12}O_2NCl$	6.21	6.15
4,α-Dimethyl[b]	65	88–89	$C_{12}H_{15}O_2N$	6.83	6.84
2,α-Dimethyl	60	109.5–111[c]	$C_{12}H_{15}O_2N$	6.83	6.53
2-Phenyl-α-methyl	98	115–115.5	$C_{17}H_{17}O_2N$	5.24	5.49
2-Methyl-α-benzyl	77	154.5–155.5	$C_{18}H_{19}O_2N$[d]	4.98	4.92
α-(2′-Phenylethyl)	35	101.5–102	$C_{18}H_{19}O_2N$[e]	4.98	4.90
α-(4′-Nitrobenzyl)[f]	65	141–143	$C_{17}H_{16}O_4N_2$	8.97	8.95
α-Isopropyl[g]	81	139–140	$C_{13}H_{17}O_2N$	6.40	6.39
α-Cyclopentyl	67	150.5–151.5	$C_{15}H_{19}O_2N$	5.71	6.00
α-Amyl[b]	72	72–73[h]	$C_{15}H_{21}O_2N$	5.67	5.49
α-Hexyl	85	70–71[c]	$C_{16}H_{23}O_2N$	5.36	5.14
α-Heptyl[b]	58	64–66	$C_{17}H_{25}O_2N$	5.09	4.85

[a] Straw-colored rods which give a magenta solution with aqueous ethanolic ferric chloride. [b] Crystallized from low-boiling petroleum ether. [c] With emollescence. [d] Calcd.: C, 76.8; H, 6.81. Found: C, 77.1; H, 7.04. [e] Calcd.: C, 76.8; H, 6.81. Found: C, 76.9; H, 6.60. [f] Crystallized from a benzene–ethanol mixture. [g] Crystallized from aqueous methanol. [h] A less stable form, m.p. 55–56°, is often encountered; on long standing or melting and resolidification it is converted into the higher-melting modification.

TABLE II

4-METHYLCARBOSTYRILS



Substituents R	Substituents R′	Yield, %	M.p., °C.	Formula	Nitrogen, % Calcd.	Found
8-Chloro	Methyl	80	208–209	$C_{11}H_{10}ONCl$	6.43	6.79
6-Methyl	Methyl	91	277–277.5	$C_{12}H_{13}ON$	7.48	6.97
8-Methyl	Methyl[a]	71	216.5–217.5	$C_{12}H_{13}ON$	7.48	7.18
8-Methyl	Benzyl	91	226.5–227.5	$C_{18}H_{17}ON$	5.32	5.44
H	2′-Phenylethyl	25	211–211.5	$C_{18}H_{17}ON$	5.32	5.50
H	4′-Nitrobenzyl	81	294–296	$C_{17}H_{14}O_3N_2$[b]	9.52	9.95
H	Isopropyl	77	244–245	$C_{13}H_{15}ON$	6.96	6.78
H	Amyl	68	163–164.5[c]	$C_{15}H_{19}ON$	6.11	5.84
H	Hexyl[d]	82	154–154.5	$C_{16}H_{21}ON$	5.76	5.91
H	Heptyl	89	161.5–163.5	$C_{17}H_{23}ON$	5.45	5.55
8-Methyl	Ethyl	63	192.5–193[c]	$C_{13}H_{15}ON$	6.96	6.83
H	Benzyl[e]	89	238–240	$C_{17}H_{15}ON$	5.62	5.63
8-Phenyl	H	8.5	224.5–225	$C_{16}H_{13}ON$	5.95	5.63

[a] Crystallized from benzene. [b] Calcd.: C, 69.4; H, 4.90. Found: C, 69.3; H, 4.74. [c] With emollescence. [d] Crystallized from aqueous methanol. [e] Crystallized from a benzene–ethanol mixture.

then poured into a slurry of water and crushed ice, stirred briefly and filtered; the filtrate was discarded. The precipitate was suspended in 300 ml. of cold water and allowed to stand for 36 hr. Filtration yielded a pale tan solid which weighed 1.7 g. (91%) after air-drying. This was triturated with three 20-ml. portions of 50% ethereal acetone to remove small amounts of colored impurities and then crystallized twice from aqueous ethanol. Clusters of white needles, m.p. 226.5–227.5°, were obtained in this way.

8-Phenyl-4-methylcarbostyril.—2-Aminobiphenyl (33.8 g., 0.200 mole) was dissolved in 300 ml. of anhydrous xylene by gentle warming. The resulting solution was brought to a boil, and to it was added a solution of pyridine (1 ml.) in ethyl acetoacetate (41.6 g., 0.320 mole). Heating was continued at such a rate that only that fluid boiling less than 80° was removed from the system. After one hour, the rate of boiling was increased, and 220 ml. of liquid was distilled off in a 0.5-hr. period. The residual solution was refrigerated, whereupon a pale straw-colored solid precipitated. This was filtered off and washed with cold petroleum ether; the yield of 2-phenylacetoacetanilide was 44.7 g. (88%).[8] White needles (42.1 g., 94% recovery) of m.p. 83.5–85° were obtained after crystallization from 50% aqueous ethanol.

A mixture of the 2-phenylacetoacetanilide so obtained (1.27 g.), phosphorus pentoxide (1.3 g.) and anhydrous xylene (25 ml.) was refluxed for one hour. By this time a sticky orange precipitate was in evidence. After cooling, excess water was added, and the mixture neutralized with potassium hydroxide; it was then steam distilled to remove the xylene. The residual mixture was refrigerated and filtered. The orange precipitate remaining was leached with three 5-ml. portions of acetone and then twice crystallized from aqueous ethanol, using decolorizing charcoal. This gave 0.100 g. (8.5%) of colorless needles, m.p. 224.5–225°.

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(8) Ritchie, ref. 6, obtained a 60% yield using a shorter reaction time and without a solvent and catalyst. The compound gives a deep violet color with aqueous ethanolic ferric chloride.

Ethylpseudocymene

BY HARRY SOBOTKA AND J. D. CHANLEY

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In a previous publication[1] we described the dehydration of 1-ethynylcyclohexanol to cyclohexenylacetylene by passage over an aluminum oxide

(1) H. Sobotka and J. D. Chanley, THIS JOURNAL, **70**, 3914 (1948).

catalyst at 200°. As we have previously noted, slight variations in the preparation of the catalyst or in the condition of the experiment resulted in aromatization to ethylbenzene, which was subsequently oxidized by potassium permanganate to benzoic acid.

When 1-ethynyl-2,2,6-trimethylcyclohexanol is passed over the aluminum oxide catalyst under a variety of conditions, we could never isolate more than insignificant quantities of acetylenic derivatives. The main product consists of 1-ethyl-2,3,6-trimethylbenzene (ethylpseudocymene) accompanied by a variety of hydroaromatic compounds.[2]

When 1-ethynyltrimethylcyclohexanol was treated in boiling benzene with an excess of phosphorus pentoxide, the principal product was again 1-ethyl-2,3,6-trimethylbenzene.

1-Ethyl-2,3,6-trimethylbenzene had been prepared by a completely different route.[3] The identity of our product with the authentic sample was confirmed by conversion to the dinitro derivative, reduction of the latter to the diamino derivative, and subsequent formation of the benzimidazole by the action of formic acid on the diamino derivative. The dinitro, the diamino and benzimidazole derivatives were identical in their properties with the compounds from the literature.

The hydrogenation of the acetylenic group, employing aluminum oxide or phosphorus pentoxide, which are not hydrogenating catalysts, appears to us to be good evidence that we have in both instances predominantly an intramolecular hydrogen migration. This parallels the deductions of Levina[4] on the aromatization of unsubstituted cyclohexylacetylene derivatives by a platinized charcoal catalyst.

2,2,6-Trimethylcyclohexanone and 1-ethynyl-2,2,6-trimethylcyclohexanol were prepared as previously described.[2]

1-Ethyl-2,3,6-trimethylbenzene (Ethylpseudocymene). Preparation A.—Ninety-five grams of the above acetylenic carbinol was distilled at 18 mm. pressure over an aluminum oxide catalyst (prepared as previously indicated) maintained at *ca.* 220°. The vapors were collected and carefully fractionated: fraction 1, 6.5 g., b.p. 28–63° (11 mm.), $n^{25}D$ 1.442–1.4833; fraction 2, 8.5 g., b.p. 63–90° (11 mm.), $n^{25}D$ 1.4833–1.5040; fraction 3, 43.5 g. (1-ethyl-2,3,6-trimethylbenzene), b.p. 90–93° (12 mm.), $n^{25}D$ 1.5100–1.5115; reported[3] b.p. 87° (10 mm.), 95° (16 mm.), $n^{24}D$ 1.5115, $n^{26}D$ 1.5106.

Preparation B.—A solution of 25 g. of the above carbinol in 100 ml. of dry benzene was added to 8.5 g. of phosphorus pentoxide. The mixture refluxed for one hour and after decomposition with water the organic layer was fractionated. A yield of 9 grams of 1-ethyl-2,3,6-trimethylbenzene, b.p. 94–95° (15 mm.), $n^{25}D$ 1.5110, was obtained.

4,5-Dinitro-1-ethyl-2,3,6-trimethylbenzene.—The above ethylpseudocymene (from either of the two preparations) was nitrated following the procedure of Smith and Kiess; the dinitro derivative, after crystallization from alcohol, melted at 80–81°, reported[3] 79–80°.

Reduction of the dinitro compound by stannous chloride in HCl, according to the literature, yielded the corresponding diamino compound of m.p. 84–85° after recrystallization from alcohol, reported[3] 84–85°. Treatment of the diamine with formic acid yielded the benzimidazole derivative of m.p. 210°; reported[3] 206°.

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(2) *Cf.* H. Sobotka and J. D. Chanley, THIS JOURNAL, **71**, 4136 (1949).
(3) L. I. Smith and M. A. Kiess, *ibid.*, **61**, 284 (1939).
(4) R. J. Levina, *Ann. Rept. Chem. Soc.*, **41**, 153 (1944).

The Structure and Reactions of Gossypol. II.[1] The Synthesis of 1,6,7-Trimethoxy-3-methylnaphthalene, a Prototype of Desapogossypol Hexamethyl Ether[2]

BY DAVID A. SHIRLEY AND WALTER L. DEAN

RECEIVED JULY 25, 1955

The extensive work of Roger Adams and his students on the structure of gossypol,[3] the principal pigment in cottonseed, led to a postulated structure of the molecule as shown in one of its tautomeric forms in structure IX. The work by Adams and his co-workers has resulted in a large amount of evidence for the postulated structure including synthesis of several of the degradation products of gossypol. This interpretation of the structure of gossypol has, however, not remained unchallenged.[4]

The degradation product of gossypol synthesized by Adams and co-workers which was most closely related to gossypol itself was desapogossypolone hexamethyl ether (X).[5] As pointed out by Adams and Baker,[5] synthesis of this compound did not establish rigorously the position of the linkage between the two naphthalene rings. An alternative possibility would be a 3,3′-linkage between rings with methyl groups in the 2- and 2′-positions.

We have undertaken to synthesize a compound more closely related to gossypol than desapogossypolone hexamethyl ether, one that would provide additional information on the correctness of structure IX for gossypol, particularly the question of the position of linkage of the two naphthalene rings. Such a compound is desapogossypol hexamethyl ether (VIII). In view of a recent paper by Edwards and Cashaw[6] reporting work of unstated objective but with compounds similar to ours, we have decided to present our preliminary findings.

3-Methyl-6,7-dimethoxy-1-tetralone (IV) was synthesized by the route indicated in Fig. 1. All of the yields were about 70% or above with the exception of the displacement of bromide ion with malonate anion from 1-(3′,4′-dimethoxyphenyl)-2-bromopropane. A not unexpected yield of 30–35% has been the maximum obtainable here. The tetralone IV has been obtained by three earlier workers[6–8] by other methods. The melting point of our product agreed with that given by Edwards[6] and by Haworth.[8] Edwards[6] has discussed the probable reason for the different value given by Borsche.[7]

The tetralone was dehydrogenated to 3-methyl-6,7-dimethoxy-1-naphthol (VI) through the bromoketone V. Edwards[6] also prepared this naphthol and reported the melting point as 140–142°. Our

(1) Preceding paper, D. A. Shirley and W. C. Sheehan, THIS JOURNAL, **77**, 4606 (1955).
(2) A report of work carried out under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract is being supervised by the Southern Regional Research Laboratory of the Agricultural Research Service.
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(4) C. H. Boatner, in A. E. Bailey, Editor, "Cottonseed and Cottonseed Products," Interscience Publishers, Inc., New York, N. Y., 1948, p. 240.
(5) R. Adams and B. R. Baker, THIS JOURNAL, **63**, 535 (1941).
(6) J. D. Edwards and J. L. Cashaw, *ibid.*, **76**, 6188 (1954).
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