

# The Syntheses of Substituted 4-Indanyl Phenyl Ketones and Aceanthrenes

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According to Cook,<sup>1)</sup> it appears that the carcinogenic potency of methylcholanthrene cannot be attributed to its special pentacyclic structure. Fieser and Hershberg<sup>2)</sup> have suggested that methylcholanthrene owes its high activity to the presence of the 1,2-benzanthracene ring system with a simple substituent at the 10-position. These facts have prompted the present author to synthesize the derivatives of aceanthrene, which has a structural analogy to cholanthrene but which possesses no carcinogenic activity by itself.

The Elbs reaction<sup>3)</sup> has been extensively used for the preparation of polycyclic aromatic hydrocarbons. The syntheses of 1,2-cyclopentenoaceanthrene and 1,2-dimethylaceanthrene by this reaction have been reported by Fieser and Hershberg.<sup>2)</sup> There are also several other methods<sup>4)</sup> for preparing aceanthrene derivatives, but the method using the pyrolysis of substituted 4-indanyl phenyl ketone seems to be the most convenient. This paper will deal with the synthesis and the pyrolysis of some substituted 4-indanyl phenyl ketones.

The condensation of benzonitrile with 4-indanyllithium, which had been prepared by the reaction of 4-bromoindane with lithium in ether, gave 4-indanyl phenyl ketone in a 78% yield, whereas the reaction of benzoyl chloride or benzonitrile with 4-indanylmagnesium bromide, which

had been prepared from 4-bromoindane and magnesium in ether, gave 4-indanyl phenyl ketone in yields of 40 and 27% respectively. The author then prepared other 4-indanyl phenyl ketones, which are summarized in Table I, by the condensation of benzonitrile with 4-indanyllithium.

The pyrolysis of 4-indanyl phenyl ketone at 350–355°C for 5 hr. gave a product, which was identified as aceanthrene by a study of its melting point, picrate and spectra, in a 27.2% yield. The pyrolysis of 4-indanyl *p*-tolyl ketone gave 9-methylaceanthrene in a 25.0% yield.

On the other hand, the pyrolysis of 4-indanyl *o*-tolyl ketone gave a viscous material, from which small amount of picrate was then obtained. The analytical data of the picrate agreed well with the values calculated for  $C_{17}H_{14} \cdot C_6H_5O_7N_3$ . In view of the structure of the ketone, 1,2-cyclopentenoanthracene or 7-methylaceanthrene might be the pyrolytic product. However, the attempted isolation of hydrocarbon from the picrate failed. The pyrolysis of other ketones failed to give pure substances.

## Experimental<sup>5)</sup>

**4-Indanyl Phenyl Ketone: Method A (from Benzonitrile and 4-Indanyllithium).**—A solution of 9.8 g. of 4-bromoindane<sup>6)</sup> in 30 ml. of ether was added

TABLE I. 4-INDANYL PHENYL KETONES

Substituent R	M. p. or b. p. °C/mmHg	Yield %	C, %		H, %	
			Found	Calcd.	Found	Calcd.
H	153–152/2 <sup>a)</sup>	72	86.37	86.45	6.78	6.35
<i>o</i> -CH <sub>3</sub> -	158–160/3 <sup>b)</sup>	65	86.63	86.40	7.17	6.83
<i>p</i> -CH <sub>3</sub> -	159–161/2 <sup>c)</sup>	57	86.08	86.40	7.13	6.83
<i>o</i> -CH <sub>3</sub> O-	72–73	56	81.43	80.92	6.55	6.39
<i>p</i> -CH <sub>3</sub> O-	55–56	63	81.24	80.92	6.42	6.39
<i>p</i> -CH <sub>3</sub> S-	61–62	52	76.06	76.10	6.07	6.01
a) $n_D^{15}$ 1.6080    b) $n_D^{25}$ 1.5943    c) $n_D^{15}$ 1.6030						

1) J. W. Cook, *Ber.*, **69A**, 38 (1936).  
2) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **59**, 394 (1937).

3) L. F. Fieser, "Organic Reactions," Vol. I, Ed. by R. Adams, John Wiley & Sons, New York, N. Y. (1942), p. 129.

4) a) L. F. Fieser and M. A. Peters, *J. Am. Chem. Soc.*, **54**, 4373 (1932); b) E. D. Bergman and R. Ikan, *J. Org. Chem.*,

**23**, 907 (1958); c) C. R. Clemo and N. G. Chatge, *J. Chem. Soc.*, **1956**, 1067; d) L. F. Fieser and E. Berliner, *J. Am. Chem. Soc.*, **74**, 536 (1952).

5) The boiling and melting points are uncorrected.

6) L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **57**, 942 (1935).

to a suspension of 0.8 g. of lithium in 30 ml. of ether at such a rate that moderate refluxing was continued; this refluxing was continued for a further 5 hr. To the resulting solution there was added, with ice-cooling, 5.2 g. of benzonitrile dissolved in a mixture of 20 ml. of ether and 20 ml. of benzene over a 30-min. period. After the mixture had been refluxed for 2 hr., it was decomposed by the addition of 50 ml. of 10% hydrochloric acid. After the organic solvent had been distilled off, 10 ml. of water, 10 ml. of concentrated hydrochloric acid and 5 ml. of acetic acid were added; the mixture was then refluxed for 2 hr. to complete the decomposition of the resulting ketimine. The product was extracted with a mixture of ether and benzene, and the extract was washed with a saturated sodium bicarbonate solution, and with water, dried, concentrated, and distilled to give 8.0 g. (72%) of 4-indanyl phenyl ketone (b. p. 153—155°C/2 mmHg;  $n_D^{25}$  1.6080). Attempts to prepare the oxime and semicarbazone of the ketone failed.

Found: C, 86.37; H, 6.78. Calcd. for  $C_{16}H_{14}O$ : C, 86.45; H, 6.35%.

The other indanyl phenyl ketones summarized in Table I were prepared by this method.

**Method B (from Benzoyl Chloride and 4-Indanyl-magnesium Bromide).**—A solution of 9.8 g. of 4-bromoindane in 30 ml. of ether was added under refluxing to 1.2 g. of magnesium covered with 30 ml. of ether over a 10-min. period. Refluxing was then continued for an additional 1.5 hr. to complete the reaction. The mixture was cooled with an ice bath; a solution of 7.0 g. of benzoyl chloride in 30 ml. of ether was then added over a 15-min. period, and the mixture was refluxed for 1 hr. The cooled reaction mixture was decomposed by the addition of 60 ml. of 10% hydrochloric acid, extracted with ether, and treated as usual. Distillation gave 4-indanyl phenyl ketone in a 40% yield.

**Method C (from Benzonitrile and 4-Indanyl-magnesium Bromide).**—To an ethereal solution of 4-indanylmagnesium bromide (prepared from 3.3 g. of 4-bromoindane and 0.4 g. of magnesium in ether) there was added a solution of 2.0 g. of benzonitrile in 20 ml. of ether over a 10-min. period. The resulting

mixture was treated with in the same manner as has been described in method A. 4-Indanyl phenyl ketone was obtained in a yield of 27%.

**Aceanthrene (The Pyrolysis of 4-Indanyl Phenyl Ketone).**—When 2.0 g. of 4-indanyl phenyl ketone was heated at 350—355°C for 5 hr. in a metal-bath and distilled at 2 mmHg, a viscous distillate was obtained, which crystallized on standing. The recrystallization of the resulting yellow crystalline from ethanol gave 0.5 g. (27.2%) of aceanthrene; m. p. 114.5—115.5°C (lit.<sup>3)</sup> 113°C);  $\lambda_{max}^{EtOH}$  254 m $\mu$  ( $\epsilon$  13800), 258(115000), 356(3100), 375(6300) and 396(3600); (Found: C, 93.91; H, 5.98%.

The picrate (from ethanol) melted at 120—120.5°C (lit.<sup>3)</sup> m. p. 120°C).

**9-Methylaceanthrene (The Pyrolysis of 4-Indanyl *p*-Tolyl Ketone).**—2.2 g. of 4-indanyl *p*-tolyl ketone was heated at 360—370°C for 4 hr. and distilled at 3 mmHg to give 500 mg. (25.0%) of yellow crystals, m. p. 115—118°C. The recrystallization of this material from ethanol gave an analytically pure sample; m. p. 118—118.5°C;  $\lambda_{max}^{EtOH}$  259 m $\mu$  ( $\epsilon$  113000), 355(3000), 373(6200) and 394(3500).

Found: C, 93.36; H, 6.41. Calcd. for  $C_{17}H_{14}$ : C, 93.53; H, 6.47%.

The picrate, as fine, dark-red needles, melted at 121—122°C after recrystallization from ethanol.

Found: C, 61.64; H, 3.94. Calcd. for  $C_{23}H_{17}O_7N_3$ : C, 61.74; H, 3.83%.

**The Pyrolysis of 4-Indanyl *o*-Tolyl Ketone.**—When 2.0 g. of 4-indanyl *o*-tolyl ketone was heated at 350—360°C for 5 hr. and distilled at 5 mmHg, a reddish oil was obtained. To this distillate there was added a saturated ethanolic solution of picric acid, and the dark-red fine needles which separated were collected. Recrystallizations from ethanol gave a pure picrate, m. p. 123.5—124°C.

Found: C, 61.94; H, 4.04. Calcd. for  $C_{23}H_{17}O_7N_3$ : C, 61.74; H, 3.83%.

The analytical data agreed well with the values calculated for  $C_{17}H_{14} \cdot C_6H_3O_7N_3$ , the picrate of 7-methylaceanthrene or 1,2-cyclopentenoanthracene, but the attempt to isolate the corresponding hydrocarbon from the picrate failed.