The Syntheses of Substituted 4-Indanyl Phenyl Ketones and Aceanthrenes

By Tosio MORIWAKE

Department of Industrial Chemistry, School of Engineering, Okayama University, Tsushima, Okayama

(Received June 19, 1965)

According to Cook,1) it appears that the carcinogenic potency of methylcholanthrene cannot be attributed to its special pentacyclic structure. Fieser and Hershberg2) 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 reaction3) 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.2) There are also several other methods4) 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.

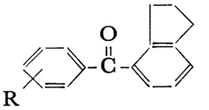
The pyrolysis of 4-indanyl phenyl ketone at 350—355°C for 5 hr. gave a product, which was identified as aceanthrene by a study of its melting point, picrate and spectra, in a 27.2% yield. The pyrolysis of 4-indanyl *p*-tolyl ketone gave 9-methylaceanthrene in a 25.0% yield.

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 $C_{17}H_{14}\cdot C_6H_3O_7N_3$. 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.

Experimental5)

4-Indanyl Phenyl Ketone: Method A (from Benzonitrile and 4-Indanyllithium).—A solution of 9.8 g. of 4-bromoindane6) in 30 ml. of ether was added

TABLE I. 4-INDANYL PHENYL KETONES



Substituent R	M. p. or b. p. °C/mmHg	Yield %	C, % Found	C, % Calcd.	H, % Found	H, % Calcd.
H	153—152/2a)	72	86.37	86.45	6.78	6.35
o-CH_3-	158—160/3b)	65	86.63	86.40	7.17	6.83
p-CH_3-	159—161/2c)	57	86.08	86.40	7.13	6.83
o-CH_3O-	72—73	56	81.43	80.92	6.55	6.39
p-CH_3O-	55—56	63	81.24	80.92	6.42	6.39
p-CH_3S-	61—62	52	76.06	76.10	6.07	6.01

a) n^{15} 1.6080 b) n^{25} 1.5943 c) n^{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^{15} 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-Indanylmagnesium 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-Indanylmagnesium 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.[3] 113°C); λ_{max}^{EtOH} 254 mμ (ε 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.[3] 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; λ_{max}^{EtOH} 259 mμ (ε 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.