TABLE I

2-CROTONYLTHIOPHENES

Substituents	B. p., °C.[a] (14 mm.)	$n^{25}D$[a]	Yield,[b] %	Formula	Analyses,[c] % Calcd.	Found
....	134.5–135.5	1.5949	64[d]	C_8H_8OS	S, 21.07	21.04
5-Chloro	151–152	....[f]	55	C_8H_7OSCl	C, 51.47	51.34
					H, 3.78	4.14
3(?)-Methyl	135–136.5	1.5836	49	$C_9H_{10}OS$	S, 19.29	19.50
5-*t*-Butyl[e]	168–169	1.5592	53	$C_{21}H_{16}OS$	C, 69.18	68.87
					H, 7.74	7.74

[a] Constants are for analytical sample. [b] Yields based on product obtained in first fractionation; average boiling range seven degrees. [c] Analyses by Clark Microanalytical Laboratory. [d] Previously reported b. p. 109–116° (5 mm.); yield 22% (ref. 2). [e] The 2-butylthiophene used was obtained by refractionation of a sample obtained from the Midland Chemical Company. On the basis of the work of Appleby, Sartor, Lee and Kapranos (THIS JOURNAL, **70**, 1552 (1948)) this starting material, $n^{20}D$ 1.4981, may have contained 6 ± 3% of 3-*t*-butylthiophene. [f] M. p. 72–73°.

In a similar reaction, using stannic chloride as the catalyst we have produced the crotonylthiophene in a somewhat better yield. Acylation of the 2-chloro-, 2-*t*-butyl- and 3-methylthiophenes with crotonyl chloride was likewise effected successfully, but 2,5-dichlorothiophene appeared unreactive.[3]

General Procedure.—A solution containing 0.15 mole of the thiophene and an equimolecular quantity of crotonyl chloride in 200 ml. of dry benzene was cooled to 0°, and 18 ml. (about 0.15 mole) of anhydrous stannic chloride was added dropwise over a period of one hour. The temperature was allowed to rise slowly to room temperature and stirring continued for an additional hour. The reaction mixture was decomposed with one molar hydrochloric acid and the benzene layer was separated, washed, dried and concentrated. The residue was fractionated under reduced pressure. The results are summarized in Table I.

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(3) *Cf.* Steinkopf and Kohler, *Ann.*, **532**, 265 (1937).

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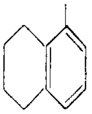
RECEIVED MAY 7, 1949

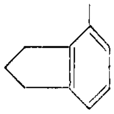
The Rate of Dissociation of 1,1,1,2-Tetraphenyl-2-(4′-hydrindenyl)-ethane

BY ROBERT G. CHRISTIANSEN[1] AND REUBEN B. SANDIN

In an attempt to relate the ease of preparation and properties of certain polynuclear hydrocarbons to a possible steric effect, the rate of dissociation of 1,1,1,2-tetraphenyl-2-(4′-hydrindenyl)-ethane has been determined. This has been done following the very convenient method of Bachmann and co-workers.[2] The rate constant and half-life period in the reaction with iodine at 80° have been found to be 0.0246 and 28.3 minutes, respectively. Recently Bachmann and Brockway[3] have determined the dissociation rate of 1,1,1,2-tetraphenyl-2-(1′-tetralyl)-ethane. For this hydrocarbon $k = 0.0728$ and $t^{1/2} = 9.5$ minutes.[4] It is evident that the 1-tetralyl group (I) shows a somewhat greater effect than the 4-hydrindenyl group (II).



I



II

This is in agreement with the interesting work of Arnold and co-workers[5] wherein they have presented evidence to prove that the steric effect of the methylene groups in five membered rings (*i. e.*, hydrindene) is smaller than that in the corresponding six-membered rings (*i. e.*, tetralin).

Experimental

4-Benzoylhydrindene.—This ketone prepared in 65% yield by the reaction of the Grignard reagent from bromobenzene and 4-cyanohydrindene[6] was obtained as a viscous oil which did not solidify on long standing; b. p. 177–180° at 2 mm.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.44; H, 6.35. Found: C, 86.76; H, 6.47.

Phenyl-4-hydrindenylcarbinol.—The carbinol prepared in 53% yield by the aluminum isopropoxide reduction of the ketone, was obtained as a viscous liquid; b. p. 180° at 4 mm.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.69; H, 7.19. Found: C, 85.84; H, 7.17.

1,1,1,2-Tetraphenyl-2-(4′-hydrindenyl)-ethane.—The phenyl-4-hydrindenylmethyl bromide from 9.0 g. of the carbinol and acetyl bromide was coupled at once with triphenylmethylsodium by the standard procedure. The resulting hydrocarbon crystallized from benzene–methanol as colorless crystals; yield, 60%; m. p. in air, 185–190°.

Anal. Calcd. for $C_{35}H_{30}$: C, 93.29; H, 6.71. Found: C, 93.44; H, 6.90.

Rate Measurements.—These were carried out according to the procedure of Bachmann and Osborn.[2b] Methanol was used in the place of ethanol in the *o*-dichlorobenzene, iodine and pyridine mixture.

Acknowledgment.—The authors express their appreciation to the Canadian Cancer Society for a grant which made this work possible.

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RECEIVED MAY 21, 1949

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(2) (a) Bachmann and Wiselogle., *J. Org. Chem.*, **1**, 354 (1936); (b) Bachmann and Osborn, *ibid.*, **5**, 29 (1940); (c) Bachmann, Hoffman and Whitehead, *ibid.*, **8**, 320 (1943).

(3) Bachmann and Brockway, *ibid.*, **13**, 384 (1948).

(4) The present authors have found values which agree with those of Bachmann and Brockway.

(5) Arnold and Rondestvedt, THIS JOURNAL, **67**, 1264 (1945); *ibid.*, **68**, 2176 (1946); Arnold and Craig, *ibid.*, **70**, 2791 (1948).

(6) Fieser and Hershberg, *ibid.*, **59**, 394 (1937).