separated, washed with water and dried over magnesium sulfate. The ether was boiled off and the residue twice recrystallized from benzene–hexane; 10.0 g. (68%) of colorless plates, m. p. 74–77°. Analytical sample sublimed *in vacuo*, m. p. 75–77°. *Anal.* Calcd. for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.79; H, 6.24; N, 9.52.

A solution of 1.0 g. of 2-hydroxymethylindole in 60 cc. of alcohol was treated with 3.0 g. of barium hydroxide in 60 cc. of water. The solution was heated on the steam-bath for three hours, diluted with 400 cc. of water and extracted with ether. The ether was dried over sodium sulfate. After removal of the ether and recrystallization from hexane the residue weighed 0.7 g., m. p. 76–77°. This melting point was not depressed when the sample was mixed with starting material.

2-Carboxypiperidinoindole.—(a) Ethyl indole-2-carboxylate (3.8 g.) was suspended in 50 cc. of 1 *N* sodium hydroxide and the mixture was heated on the steam-bath for one hour when complete solution had been attained. The solution was treated with charcoal, filtered and acidified with hydrochloric acid. The precipitated indole-2-carboxylic acid was filtered off, 2.9 g. (90%), m. p. 206–208°. A solution of 2.85 g. of this acid in 100 cc. of dry ether was treated with 3.0 cc. of thionyl chloride. After standing at room temperature for one hour the solvents were removed *in vacuo*. The residue was twice treated with 60 cc. of dry ether and taken to dryness to remove traces of hydrogen chloride. Finally it was dissolved in 90 cc. of dry ether, filtered and treated with 3.5 cc. of piperidine. There was an immediate precipitation of a gum which gradually crystallized. After recrystallization from ethanol–water, 0.4 g. of 2-carboxypiperidinoindole, m. p. 161–164° separated. After three recrystallizations from hexane the white needles melted at 165–166°. *Anal.* Calcd. for $C_{14}H_{16}N_2O$: C, 73.65; H, 7.07; N, 12.27. Found: C, 73.63; H, 6.86; N, 12.45.

(b) Ethyl indole-2-carboxylate (36 g.) was suspended in 480 cc. of piperidine, and the mixture was treated with 90 cc. of glacial acetic acid. The mixture was heated to boiling, giving a complete solution, and maintained at reflux for two days. The hot solution was diluted with 200 cc. of water and filtered. The filtrate was treated with 2 liters of water to precipitate the 2-carboxypiperidinoindole, 36 g. (83%), m. p. 163–166°.

3-Dimethylaminomethylindole-2-carboxypiperidide.—A suspension of 10.0 g. of 2-carboxypiperidinoindole in 65 cc. of glacial acetic acid, 24 cc. of 25% aqueous dimethylamine and 14 cc. of 40% aqueous formaldehyde was heated on the steam-bath for one hour and then kept at room temperature overnight. After diluting the solution with 700 cc. of water it was extracted with 100 cc. of benzene. The aqueous layer was made basic with concentrated ammonium hydroxide, and the oily product was extracted into ether (one 400-cc. and three 250-cc. portions of solvent). The combined extracts were washed twice with 150 cc. of water and dried over sodium sulfate. After removal of the ether on the steam-bath the oily residue weighed 17 g. Since the theoretical yield was only 12 g. there was considerable contamination, but the material was suitable for further work as it stood.

When a small amount of this oil was heated with 10% chloroplatinic acid a crystalline chloroplatinate precipitated which contained two organic residues per atom of platinum. After recrystallization from water this melted at 208° (dec.). *Anal.* Calcd. for $C_{34}H_{46}N_6O_2$–H_2PtCl_6: C, 41.63; H, 4.93; N, 8.57; Cl, 21.69. Found: Cl, 41.60; H, 4.97; N, 8.53; Cl, 20.83.

2-Carboxypiperidinoskatylacetylaminomalonic Ester.—The 17 g. of crude 3-dimethylaminomethylindole-2-carboxypiperidide (see above) was treated with 150 cc. of xylene and the solution distilled until the distillate was no longer cloudy. The volume of the solvent was replenished, and there was added 9.6 g. of acetylaminomalonic ester (prepared according to the method of Snyder and Smith[2]) and 0.6 g. of powdered sodium hydroxide. With stirring, the mixture was heated to its boiling point while dry nitrogen was passed over the system. Bubbles appeared in the reaction mixture as soon as it became warm, and the exhaust gases became basic. This was presumably due to the evolution of dimethylamine. After twenty hours the evolution of amine had ceased, and the reaction mixture was filtered, washed with 50 cc. of water, twice with 50 cc. of 10% hydrochloric acid and again with 50 cc. of water. The xylene solution was dried over sodium sulfate. After removing the xylene *in vacuo* the residue was crystallized by boiling with ether. The insoluble crystalline residue of 2-carboxypiperidinoskatylacetylaminomalonic ester weighed 10.0 g., m. p. 146–149°; after recrystallizations from ethyl acetate–hexane, ethanol–water and ethyl acetate–isopropyl ether, m. p. 149–152°. *Anal.* Calcd. for $C_{24}H_{31}N_3O_6$: C, 63.00; H, 6.83; N, 9.18. Found: C, 63.22; H, 6.88; N, 8.77.

When this preparation was repeated the ether-insoluble residue melted at 197–200°. It was recrystallized from acetic acid–water, acetone–water and ethanol–water, m. p. 200.2–201.6°. *Anal.* Calcd. for $C_{24}H_{31}N_3O_6$: C, 63.00; H, 6.83; N, 9.18. Found: C, 63.11; H, 6.92; N, 9.17. A sample of the lower melting material, m. p. 149–152°, was recrystallized from ethanol–water and seeded with a crystal of this latter form. The product melted at 200–202°.

2-Carboxypiperidinoindole-3-aldehyde.—To a cold solution of 5.4 g. of N-methylformanilide and 3.66 cc. of phosphorus oxychloride in 35 cc. of *o*-dichlorobenzene there was added gradually 9.1 g. of 2-carboxypiperidinoindole. The resulting suspension was kept at room temperature for forty-three hours although solution was complete after fifteen hours. The solution was poured into a slurry of 30 g. of ice and 20 g. of 35% sodium hydroxide solution. The organic layer was separated, washed with 20 cc. of water and dried over sodium sulfate. The solvent was removed *in vacuo*, the residue dissolved in ethanol, and the solution diluted with water. The precipitated product was recrystallized from benzene–hexane; 6.6 g. (65%), m. p. 149–155°. Five recrystallizations from benzene–hexane gave white needles, m. p. 155.5–156.5°. *Anal.* Calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.38; H, 6.09; N, 11.20.

The compound gave a red-orange 2,4-dinitrophenylhydrazone; recrystallized from dioxane, m. p. 310° (dec.). *Anal.* Calcd. for $C_{21}H_{20}N_6O_5$: C, 57.79; H, 4.62; N, 19.26. Found: C, 57.98; H, 4.48; N, 18.68.

5-(3′-α-Carboxypiperidinoindolal)-1-methylhydantoin.—A solution of 1.8 g. of 1-methylhydantoin (prepared according to the method of Miller and Robson[3]) and 2.86 g. of 2-carboxypiperidinoindole-3-aldehyde in 5 cc. of piperidine was heated under reflux for one hour. Some solid yellow material had precipitated during this period. The reaction mixture was treated with 30 cc. of hot water, made slightly acidic with acetic acid, cooled and the solid product filtered off; 3.0 g. (76%), m. p. 289–295°. After seven recrystallizations from pyridine–water the light yellow plates melted at 306–307.5° (dec.). *Anal.* Calcd. for $C_{19}H_{20}N_4O_3$: C, 64.76; H, 5.72; N, 15.90. Found: C, 65.08; H, 5.81; N, 16.03.

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RECEIVED MAY 7, 1949

Acylation of Some Thiophenes with Crotonyl Chloride[1]

BY CHARLES K. BRADSHER, FRANCES C. BROWN AND R. J. GRANTHAM

Recently Hartough, Kosak and Sardella[2] have shown that thiophene in the presence of activated montmorillonite clay may be acylated with crotonyl chloride to yield 2-crotonylthiophene.

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[1] This note consists of a report of work done under contract with the Medical Division, Chemical Corps, U. S. Army.

[2] Hartough, Kosak and Sardella, THIS JOURNAL, 69, 1014 (1947).

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).

DEPARTMENT OF CHEMISTRY
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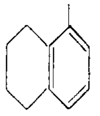
RECEIVED MAY 7, 1949

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).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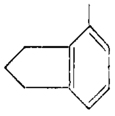
II

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).