2,6-Diacyl-*s*-hydrindacene-1,3,5,7-tetrones and Reaction with Hydrazine

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The condensation of 2-acyl-1,3-indandiones with diamines as a route to a variety of new heterocyclic indeno compounds has been described in several papers from this laboratory (2,3). We now report the reaction of 2,6-diacyl-*s*-hydrindacene-1,3,5,7-tetrones (**1a-e**) with hydrazine.

By following the method developed by Kilgore, Ford and Wolfe (4) for preparing 2-acyl-1,3-indandiones, we found that, when the tetramethyl ester of pyromellitic acid reacted with the appropriate methyl ketones, the tetrones **1a-e** were formed. The structures of these compounds are based on elemental analysis and are consistent with the infrared spectra.

2,6-Diisobutyryl-*s*-hydrindacene-1,3,5,7-tetrone (**1b**) reacted with hydrazine in methanol to form 3,7-diisopropyl-*s*-indaceno[1,2-c:7,6-c′]dipyrazolo-4,6(1*H*,9*H*)dione, dihydrazone (**2**). The possibility of the formation of the other isomer, 3,8-diisopropyl-*s*-indaceno[1,2-c:5,6-c′]dipyrazolo-4,9(1*H*,6*H*)dione, dihydrazone (**3**) was eliminated by the nmr spectrum which showed two non-equivalent aromatic protons consistent with structure **2**. Structure **3** should show two equivalent aromatic protons. The alternative structures resulting from *syn* and *anti* hydrazone isomerism and which are not eliminated by the nmr spectrum are deemed less probable because symmetrical structures are likely to be preferentially formed in this reaction.

EXPERIMENTAL (5)

2,6-Diacyl-*s*-hydrindacene-1,3,5,7-tetrones (**1a-e**).

The general procedure used to prepare these compounds is illustrated by the synthesis of 2,6-diisobutyryl-*s*-hydrindacene-1,3,5,7-tetrone (**1b**). To a stirred suspension of sodium methoxide (35.2 g., 0.652 mole) in 100 ml. of anhydrous benzene (thiophene free) was added a solution of the tetramethyl ester of pyromellitic acid (20 g., 0.0646 mole) and 3-methyl-2-butanone (11.2 g., 0.13 mole) in 200 ml. of benzene. The temperature was raised to 40° and held with stirring for 12 hours. The reaction mixture was then heated at reflux for 4 days. After cooling, the benzene was decanted and washed twice with water. The washings were added to the solid residue in the reaction flask, boiled with

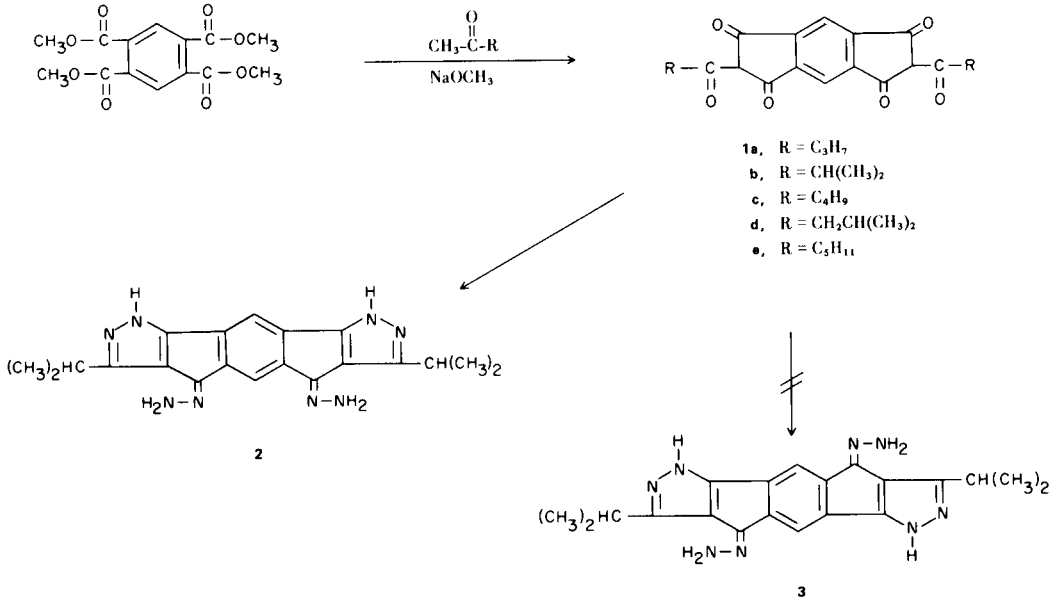

TABLE I

2,6-Diacyl-*s*-hydrindacene-1,3,5,7-tetrones

Compound	M.p., °C	Yield %	Empirical Formula	Analyses % C Calcd.	% C Found	% H Calcd.	% H Found
1a	298	5.5	$C_{20}H_{18}O_6$	67.79	67.95	5.12	5.00
1b	300	12.4	$C_{20}H_{18}O_6$	67.79	67.98	5.12	5.21
1c	277	8.13	$C_{22}H_{22}O_6$	69.10	68.91	5.80	5.79
1d	283	3.25	$C_{22}H_{22}O_6$	69.10	68.82	5.80	5.90
1e	260	3.77	$C_{24}H_{26}O_6$	70.23	70.17	6.39	6.24

more water until the sodium salt dissolved, decolorized with charcoal, filtered hot and cooled in ice. The precipitate was collected, dried at 90°, suspended in 500 ml. of water and acidified with 6*M* hydrochloric acid. The yellow precipitate was filtered off, dried and recrystallized from diglyme to give **1b**.

The m.p., yields and analyses of compounds **1a-e** are shown in Table I. The ir spectra (potassium bromide) show bands at 2900 (enolized C=O), 1710 (C=O of acyl), 1660 (C=O and C=C), and 1600 cm^{-1} (C=O in conjugated chelation).

3,7-Diisopropyl-*s*-indaceno[1,2-*c*:7,6-*c'*]dipyrazolo-4,6(1*H*,9*H*)-dione, Dihydrazone (**2**).

To a refluxing suspension of 2,6-diisobutyryl-*s*-hydrindacene-1,3,5,7-tetrone (**1b**) (1.5 g., 0.00424 mole) in 250 ml. of anhydrous methanol, 1.2 g. (0.0375 mole) of anhydrous hydrazine was added. The suspended solid dissolved and the solution turned to wine red. After boiling for 15 hours, an additional 1 ml. of hydrazine was added. A yellow precipitate formed after 20 hours and boiling was continued for a total of 24 hours. After cooling, the precipitate was filtered off and recrystallized from ethanol-water to yield 1.5 g. (95%) of **2**. Compound **2** did not melt below 360°. The ir spectrum (potassium bromide) shows bands at 3400-3200 (NH_2 and NH stretching) and at 1640 cm^{-1} (C=N). The nmr spectrum was obtained in dimethylsulfoxide at 160° due to very poor solubility at lower temperatures. Two lines were found in the aromatic region, one at 7.9 ppm and one at 7.75 ppm each of which integrated for a single proton.

Anal. Calcd. for $C_{20}H_{22}N_8$: C, 64.15; H, 5.92; N, 29.93. Found: C, 64.35; H, 5.81; N, 29.78.

REFERENCES

(1) Taken in part from the Dissertation submitted by Tawfik El-Zimaity to the College of Graduate Studies of the University of Delaware, 1963. For full details refer to the dissertation, Univ. Microfilms (Ann Arbor, Michigan) Order No. 64-2204.

(2) R. A. Braun and W. A. Mosher, *J. Org. Chem.*, **24**, 648 (1959).

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(4) L. B. Kilgore, J. H. Ford, and W. C. Wolfe, *Ind. Eng. Chem.*, **34**, 494 (1942).

(5) All melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Ir spectra were taken on a Perkin-Elmer Infrared Spectrophotometer Model 137. Nmr spectra were obtained on a Varian A-60A Spectrometer. Analyses were performed by A. Bernhardt, Mikroanalytisches Laboratorium in Max-Plank Institute für Kohlenforschung, Mülheim (Ruhr), Germany.