

A Synthesis of Some α , γ , δ , ξ -Tetraketones, Polyoxo Compounds. IV*

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A description is given of the preparation of the tetraketones
Ia-f, which were characterized as quinoxaline derivatives.

Brömme and Claisen showed¹ that α , γ , δ , ξ -tetraketones [I] can be readily obtained by the condensation of two molecules of methylketone with diethyl-oxalate.



I

- | | |
|------------------------|---------------------------|
| a, R = p-chlorophenyl | d, R = α -naphthyl |
| b, R = p-bromophenyl | e, R = β -naphthyl |
| c, R = p-methoxyphenyl | f, R = i-butyl |

We have now prepared, following essentially the same method, some hitherto undescribed compounds of this type: 1,6-bis-(p-chlorophenyl)-1,3,4,6-hexanetetrone [Ia], 1,6-bis-(p-bromophenyl)-1,3,4,6-hexanetetrone [Ib], 1,6-bis-(p-methoxyphenyl)-1,3,4,6-hexanetetrone [Ic], 1,6-bis-(α -naphthyl)-1,3,4,6-hexanetetrone [Id], 1,6-bis-(β -naphthyl)-1,3,4,6-hexanetetrone [Ie] and 2,11-dimethyl-4,6,7,9-dodecanetetrone [If].

All these tetraketones were characterized by their quinoxaline derivatives.

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EXPERIMENTAL

General procedure for the preparation of 1,6-diaryl-1,3,4,6-hexanetetrones [Ia-e].

In a round-bottomed flask containing anhydrous ether (200 ml.) and fitted with a reflux condenser and a calcium chloride tube metallic sodium (4.6 g., 0.2 mole) and absolute ethanol (9.2 ml., 0.2 mole) were added. After the mixture was left for twelve hours at room temperature, it was cooled with ice. A solution of methylketone*** (0.2 mole) and diethyl-oxalate (0.1 mole) in ether (100 ml.) was then gradually added through the condenser during five minutes with occasional shaking. After standing for four days at room temperature, the sodium salt which had separated was filtered off and triturated with a mixture of ice and 20% hydrochloric acid. The crude 1,6-diaryl-1,3,4,6-hexanetetrone was recrystallized from glacial acetic acid; yield of the pure tetraketone 75–94%.

* Paper III, K. Balenović and R. Munk, *Arhiv kem.* **18** (1946) 41.

** One of us (T. T.) is indebted to the Yugoslav Academy of Sciences, Zagreb, for a six-months scholarship.

*** Substituted acetophenones were prepared according to R. Adams and C. R. Noller, *Org. Syntheses, Coll. Vol. I*, 109. 1-Acetylnaphthalene and 2-acetylnaphthalene were prepared according to G. Lock, *Monatsh.* **74** (1942) 77.

2,11-dimethyl-4,6,7,9-dodecanetetrone [If].

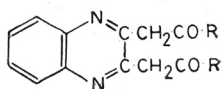
In a round-bottomed flask fitted with a reflux condenser and a calcium chloride tube sodium wire (10.5 g., 0.46 mole) was covered with anhydrous ether. Diethyloxalate (32 g., 0.22 mole) and methyl-isobutylketone (55 g., 0.55 mole) were added through the condenser. A very vigorous reaction took place. Cooling was not necessary. When the reaction subsided the mixture was refluxed for an hour, and then an additional amount of methyl-isobutylketone was added (15 g.). The refluxing was continued for three more hours. The reaction mixture was left overnight at room temperature, the excess ether evaporated *in vacuo* on a water bath at 40°. The dry contents of the flask were easily shaken out and finely ground. Yield of sodium salt 73 g.; this was triturated with 10% hydrochloric acid at 0°. The pale yellow 2,11-dimethyl-4, 6, 7, 9-dodecanetetrone was obtained, which was recrystallized from ethanol, giving the pure compound, m. p. 74—75° in a 59 % yield of pale yellow leaflets.

Data concerning the tetraketones Ia-f are given in Table I., and of their quinoxaline derivatives in Table II.

TABLE I
R · COCH₂COCOCH₂CO · R

R	M. p.	Yield	Carbon		Hydrogen	
			calc'd	found	calc'd	found
p-chlorophenyl [Ia]	229°	94%	59.52	59.59	3.34	3.38
p-bromophenyl [Ib]	217°	89%	47.82	48.18	2.68	2.67
p-methoxyphenyl [Ic] ²	194°	92%	67.78	67.57	5.13	4.95
α-naphthyl [Id]	199°	78%	79.17	78.61	4.60	4.67
β-naphthyl [Ie]	210°	76%	79.17	79.00	4.60	4.50
i-butyl [If]	74.5°	59%	66.11	66.30	3.71	3.68

TABLE II



R	M. p.	Carbon		Hydrogen		Nitrogen	
		calc'd	found	calc'd	found	calc'd	found
p-chlorophenyl [Ia]	225°	66.22	66.06	3.71	3.82		
p-bromophenyl [Ib]	244°					5.34	5.28
p-methoxyphenyl [Ic]	192°	73.22	73.49	5.20	5.12		
α-naphthyl [Id]	251°	82.38	81.97	4.75	4.68		
β-naphthyl [Ie]	227°					6.01	5.85
i-butyl [If]	147°	73.59	73.73	8.03	8.05		

REFERENCES

1. E. Brömme and L. Claisen, *Ber.* **21** (1888) 1134.
2. O. Widman and E. Virgin, *Ber.* **42** (1909) 2803). These authors gave m. p. 182°.

IZVOD

Sinteza nekih α , γ , δ , ξ -tetraketona. Poliokso spojevi. IV

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U nastavku niza radova o poliokso spojevima opisano je priređivanje ovih tetraketona:

1,6-bis-(p-klorofenil)-1,3,4,6-heksantetron	[Ia] t. t. 229°
1,6-bis-(p-bromofenil)-1,3,4,6-heksantetron	[Ib] t. t. 217°
1,6-bis-(p-metoksifenil)-1,3,4,6-heksantetron	[Ic] t. t. 194°
1,6-bis-(α -naftil)-1,3,4,6-heksantetron	[Id] t. t. 199°
1,6-bis-(β -naftil)-1,3,4,6-heksantetron	[Ie] t. t. 210°
2,11-dimetil-4,6,7,9-dodekantetron	[If] t. t. 74.5°

Ti su spojevi karakterizirani kao kinoksalinski derivati.

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