80 ml xylene was distilled off, and petrol ether added to the solution after cooling. A white precipitate of Id formed, and was worked up as described for Ia. Yield of Id 1.39 g (64%). After recrystallizing from n-heptane it had mp 115–116°.

3-Methylsilatrane (Ib) and 3, 7-dimethylsilatrane (Ic). These were prepared similarly to Ia, from 3-methyl- and 3, 7-dimethylboratrane respectively.

REFERENCES

1. M. G. Voronkov and F. D. Faitel'son, KhGS [Chemistry of Heterocyclic Compounds], 39, 1967.
2. C. L. Frye, G. E. Vogel, and J. A. Hall, J. Am. Chem. Soc., **83**, 996, 1961.
3. C. L. Frye, private communication.
4. G. I. Zelchan and M. G. Voronkov, Author's certificate 1054779, 1966.
5. M. G. Voronkov and G. I. Zelcans et. al., Proceedings of the 9th International Conference on Coordination Chemistry, Basle, 250, 1961.
6. M. G. Voronkov and G. I. Zelchan, Methods of Preparing Chemical Reagents and Preparations [in Russian], no. 14, 1966.

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SYNTHESIS OF DERIVATIVES OF 1, 2, 3, 4-TETRAHYDRO-4-AZAFLUOREN-3, 9-DIONES

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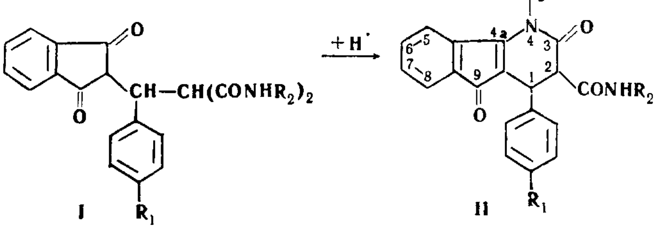
Cyclization of amides of α-carbamido-β-(indan-1, 3-dione-2-yl) hydrocinnamic acid gives 1-aryl-2-carbamido-1, 2, 3, 4-tetrahydro-4-azafloren-3, 9-dione. Alkaline and acid hydrolysis of these compounds are investigated.

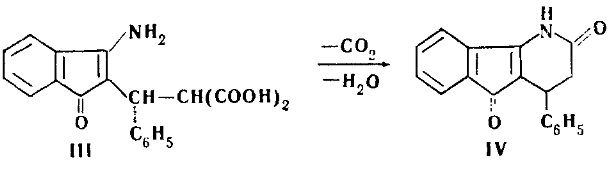
Condensation of an amide amino group with a carbonyl group has been but little studied [1–3]. Cyclization of this kind can give new types of heterocyclic compounds. We have shown [4] that condensation of 2-arylindenindan-1, 3-diones with malonic diamide gives amides of α-carbamido-β-(indan-1, 3-dione-2-yl)hydrocinnamic acids (Ia–e). The resultant amides I readily undergo cyclization in acid solution, giving 1-aryl-2-carbamido-1, 2, 3, 4-tetrahydro-4-azafluoren-3, 9-diones (IIa–e)

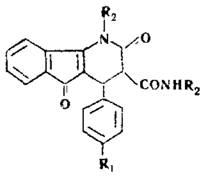


a) $R_1=R_2=H$; b) $R_1=NO_2$, $R_2=H$; c) $R_1=OCH_3$, $R_2=H$; d) $R_1=Cl$, $R_2=H$; e) $R_1=H$, $R_2=CH_3$

In the case in question, condensations between amide and carbonyl groups are facilitated by the steric proximity of the indandione carbonyl group to the amido group, as well as by the possibility of formation of an unstrained 6-membered ring in II. As was shown for the examples of N, N'-disubstituted I compounds, an important role in their cyclization is played by the nucleophilicity of the nitrogen atom of the attacking amido group. Thus, in general I ($R_1=H_1$, $R_2=C_6H_5$) where the basicity of the nitrogen atom is much decreased due to the presence of N-phenyl groups, is not cyclized. At the same time the N, N'-dimethyl derivative Ie cyclizes more readily than the N-substituted I (inductive effect of N-methyl groups). IR and UV spectra data confirm the structure of compound II.

The compounds II prepared were submitted to alkaline and acid hydrolysis. Unlike 4-azafluorenones [5, 6], substituted tetrahydro-4-azafluoren-3, 9-diones are readily cleaved by alkali at the 3—4 bond. The end product of alkaline hydrolysis is α-(3-aminoind-2-en-1-one-2-yl)-benzylmalonic acid (III), which is decarboxylated when heated in diethylene glycol. Decarboxylation is accompanied by intramolecular acylation of the free amino group, with ring closure and formation of 1-phenyl-1, 2, 3, 4-tetrahydro-4-azafluoren-3, 9-dione (IV).





R_1	R_2	Mp, °C (decomp)	Formula	Found, %				Calculated, %				Yield, %
				C	H	N	Cl	C	H	N	Cl	
H	H	258–259	$C_{19}H_{14}N_2O_3$	71.55	4.34	8.80	—	71.68	4.40	8.80	—	91
NO_2	H	254–255	$C_{19}H_{13}N_3O_5$	63.02	3.80	11.71	—	62.81	3.60	11.57	—	85
OCH_3	H	255–257	$C_{20}H_{16}N_2O_4$	69.11	4.79	8.09	—	68.96	4.65	8.04	—	83
Cl	H	233–234	$C_{19}H_{13}N_2O_3Cl$	64.35	3.75	8.10	10.30	64.68	3.71	7.93	10.06	88
H	CH_3	130–132	$C_{21}H_{18}N_2O_3$	73.04	5.30	8.21	—	72.81	5.21	8.09	—	93

Acid hydrolysis of compound II leads to scission of bond 4—4a and formation of β-indandionylhydrocinnamic acid, which has been reported in the literature [7]; this is also formed by acid hydrolysis of III.

EXPERIMENTAL

1-Phenyl-2-carbamido-1, 2, 3, 4-tetrahydro-4-azafluoren-3, 9-dione (IIa). 5 g I was suspended in 50 ml conc. HCl, and left at room temperature for 24 hr. After some time the mixture turned rose colored. The orange precipitate was separated off, and washed with water, yield 4.3 g. It was recrystallized from EtOH.

Ib–e were synthesized similarly. The table gives the properties of the compounds prepared.

α-(3-Aminoind-2-en-1-one-2-yl)benzylmalonic acid (III). 3 g IIa was dissolved in 50 ml 1 N NaOH, and the mixture heated on a water batch until ammonia evolution ceased. After cooling the solution was acidified, when a red precipitate formed. Yield 2.4 g (70%), mp 173–174° (decomp). In recrystallizing, prolonged boiling has to be avoided, in order to avoid possible changes in the product. Found: C 68.02; H 4.68; N 4.20%. Calculated for $C_{19}H_{15}NO_5$: C 67.75; H 4.45; N 4.15%.

1-Phenyl-1, 2, 3, 4-tetrahydro-4-azafluoren-3, 9-dione (IV). A suspension of 3 g III in 30 ml diethylene glycol was heated at 130–140° until CO_2 evolution was complete, when the reaction products became viscous. The IV formed was separated off, and washed, yield 1.1 g (45%), mp 239–240° (decomp). Found: C 78.35; H 4.64; N 5.07; 5.24%. Calculated for $C_{18}H_{13}NO_2$: C 78.53; H 4.76; N 5.08%.

REFERENCES

1. F. Lingens and R. Hankwitz, Ann. 670, 31, 1963.
2. H. M. Blatter, H. Lukaszewski, and G. De Stevens, J. Org. Chem., 30, 1022, 1965.
3. M. Furdik and S. Toma, Chem. Zvesti, 20, 3, 1966.
4. Yu. E. Pelcher, Communication on the Chemistry of Dicarbonyl Compounds, Thesis, Abstract [in Russian], 27, Riga, 1966.
5. V. Petrov, J. Saper, and B. Sturgion, J. Chem. Soc., 2134, 1949.
6. I. E. Stankevich and G. Ya. Vanag, Izv. AN Latv. SSR, ser. khim., 311, 1962.
7. M. Jonescu, Bull. soc. chim. France, (4), 37, 913, 1925.

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CYANOETHYLATION OF TETRAHYDROFURAN

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It is shown that it is possible to carry out free radical cyanoethylation of tetrahydrofuran, to give the nitrile of α-tetrahydrofuranpropionic acid in 50–60% yield.

One of us has shown that tetrahydrofuranpropionic acid raises the cotton plant yield if prior to sowing the seeds are wetted with a $5 \cdot 10^{-3}$ to $5 \cdot 10^{-4}$ concen-