LITERATURE CITED

1. K. Drexhage, Dye Lasers, F. P. Schaeffer (ed.), Springer-Verlag, New York (1974).
2. I. I. Grandberg, L. K. Denisov, and O. A. Popova, Khim. Geterotsikl. Soedin., No. 2, 147 (1987).
3. M. Machida, N. Ushijima, T. Takahashi, and Y. Kanaoka, Chem. Pharm. Bull., 25, 1289 (1977).
4. J. Dehnert and G. Grau, German Patent No. 1,802,863; Chem. Abstr., 73, 110911 (1970).
5. M. A. Kirpichenok, I. I. Grandberg, L. K. Denisov, and L. M. Mel'nikova, Izv. Timiryazevsk. Skh. Akad., No. 3, 172 (1985).
6. Yu. F. Pedash, V. F. Pedash, A. V. Luzanov, and M. I. Dzyubenko, Preprint No. 84, Izd. Inst. Radiofiz. Élektron. Akad. Nauk Ukr. SSR, Kharkov (1977), p. 18.
7. H. Duddeck and M. Kaiser, Org. Magn. Reson., 20, 55 (1982).
8. W. J. Linn and W. H. Sharkey, J. Am. Chem. Soc., 79, 4970 (1957).
9. L. S. Shibryaeva, A. I. Mikaya, and V. G. Zaikin, Zh. Obshch. Khim., 50, 940 (1980).
10. R. L. Shriner, R. C. Fuson, D. Y. Curtin, and T. Morril, The Systematic Identification of Organic Compounds: A Laboratory Manual, 6th edn., Wiley, New York (1980).
11. B. I. Stepanov (ed.), Catalog of Active Laser Media Based on Solutions of Organic Dyes and Related Compounds [in Russian], Izd. Belorussk. Politekh. Inst., Minsk (1977), p. 17.
12. C. A. Parker, Photoluminescence of Solutions, Am. Elsevier, New York (1968).
13. B. H. Winters, H. I. Mandelberg, and W. B. Mohr, Appl. Phys. Lett., 25, 72 (1974).
14. G. Schoen and F. J. Marascia, U.S. Patent No. 3,030,383; Chem. Abstr., 57, 85519 (1962).

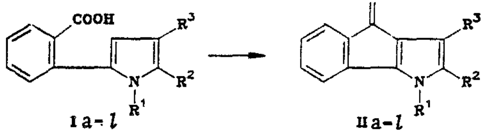
INTRAMOLECULAR CYCLIZATION OF 5-(o-CARBOXYPHENYL)PYRROLE DERIVATIVES

A. N. Grinev,* I. N. Nesterova, and M. V. Mezentseva

UDC 547.749'95.07:543.422

A new method is proposed for the synthesis of derivatives of indeno[1,2-b]pyrrole-4-ones by intramolecular cyclization of the corresponding 5-(o-carboxyphenyl)pyrroles by trifluoroacetic anhydride.

In a previous communication [1] we reported the synthesis of 3-carbethoxyindeno[1,2-b]pyrrole-4-ones (IIa-d) by intramolecular cyclization of the acid chlorides of 3-carbethoxy-5-(o-carboxyphenyl)pyrroles (Ia-d) under Friedel–Crafts conditions. However, we did not succeed in preparing derivatives of indeno[1,2-b]pyrrole-4-one containing acetyl and carboxyl groups at position 3 of the pyrrole ring, or derivatives of indeno[1,2-b]pyrrole with position 3 unoccupied, by this method. With the aim of preparing the latter, we used trifluoroacetic anhydride as a cyclizing medium and this made it possible to obtain previously unknown derivatives of indeno[1,2-b]pyrrole-4-one (IIf-ℓ) and the previously described indenopyrrolones IIa-e from the corresponding 5-(o-carboxyphenyl)pyrroles (Ia-ℓ) in one stage with yields greater than by the method which we put forward previously [1].



I a-l II a-l

a,i,l $R^1=CH_3$, b,f,h,k $R^1=C_6H_5$, c,g,j $R^1=p\text{-}CH_3C_6H_5$, d,e $R^1=CH_2C_6H_5$; a-d, f-l $R^2=CH_3$, e $R^2=C_6H_5$; a-e $R^3=COOC_2H_5$, f $R^3=COCH_3$, g-i $R^3=COOH$, j-l $R^3=H$

---

*Deceased.

S. Ordzhonikidze All-Union Chemical and Pharmaceutical Scientific Research Institute, Moscow 119021. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1333-1335, October, 1987. Original article submitted June 13, 1986.

0009-3122/87/2310-1067 $12.50

TABLE 1. Characteristics of Compounds Prepared

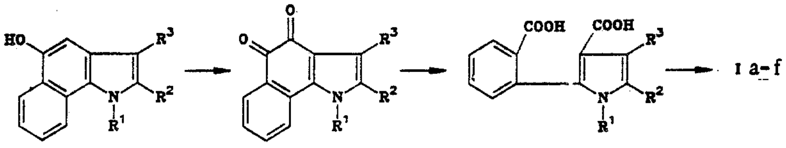
Compound*	T_{mp}, °C**	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
Ie	110—112	75,9	5,4	3,2	$C_{27}H_{23}NO_4$	76,2	5,4	3,3	58
If	236—238	75,0	5,4	4,0	$C_{20}H_{17}NO_3$	75,2	5,4	4,4	59
Ig	235	71,2	5,3	4,0	$C_{20}H_{17}NO_4$	71,6	5,1	4,2	72
Ih	238	70,8	4,9	4,7	$C_{19}H_{15}NO_4$	71,0	4,7	4,4	82
Ii	230	65,0	5,2	5,0	$C_{14}H_{13}NO_4$	64,9	5,1	5,4	85
Ik	140—141	77,5	5,6	4,6	$C_{16}H_{15}NO_2$	78,0	5,4	5,0	40
IIe	140—142	79,3	5,2	3,4	$C_{27}H_{21}NO_3$	79,6	5,2	3,4	70
IIf	223—224	79,6	5,2	4,8	$C_{20}H_{15}NO_2$	79,7	5,0	4,6	79
IIg	254	75,6	4,5	4,2	$C_{20}H_{15}NO_3$	75,7	4,8	4,4	72
IIj	149—150	83,2	5,6	5,1	$C_{19}H_{15}NO$	83,6	5,5	5,1	68
IIk	175—176	83,7	4,9	5,2	$C_{18}H_{13}NO$	83,4	5,0	5,4	70
IIℓ	124—125	79,0	5,3	7,0	$C_{13}H_{11}NO$	79,3	5,6	7,1	55
IVe	204—205	77,2	4,8	3,1	$C_{28}H_{21}NO_4$	77,3	4,9	3,2	82
IVf	234—235	76,3	4,5	4,1	$C_{21}H_{15}NO_3$	76,6	4,6	4,2	83
Ve	159—161	71,7	4,5	2,9	$C_{28}H_{23}NO_6$	71,6	4,9	2,9	34
Vf	162	69,7	4,9	3,5	$C_{21}H_{17}NO_5$	69,4	4,7	3,8	53

---

*Compounds IIa-d were obtained in 80, 85, 73, and 71% yield, respectively.

**Compounds Ig-i, IIg, and Vf melted with decomposition.

The starting materials, 5-(o-carboxyphenyl)pyrroles Ia-d were prepared from the 5-oxybenz[g]indoles IVa-d by a method which we developed earlier [1], this method also being used to prepare the previously unknown derivatives Ie and f.



IIIa-f IVa-f Va-f

From an alkali melt of 3-carbethoxy-5-(o-carboxyphenyl)pyrroles Ia-c the corresponding 3-carboxypyrroles Ig-i were obtained and selective decarboxylation of the latter led to 5-(o-carboxyphenyl)pyrroles Ij-ℓ. Since these compounds are unstable they were subjected to intramolecular cyclization by trifluoroacetic anhydride without further purification.

The structures of compounds IIa-ℓ were confirmed by IR, UV, and NMR spectroscopy. Thus, in the UV spectra of the indeno[1,2-b]pyrroles IIa-e a third absorption band was observed with λ_{max} 257 nm, in addition to the bands in the spectra of the initial 5-(o-carboxyphenyl)pyrroles Ia-f at λ_{max} 208, 235 nm; this is evidence of the formation of a tricyclic condensed system. In the NMR spectra of compounds IIj-ℓ, a signal for position 3 appeared in the 6.0-6.1 ppm region in the form of a quartet, and a signal for the methyl group protons as a doublet at 2.0-2.1 ppm (J = 1 Hz) as a result of spin—spin coupling of methyl group protons with the 3-H proton of the pyrrole ring.

Indeno[1,2-b]pyrroles IIa-d were identified by comparison of their melting points with those of samples prepared by the method described in [1, 2].

EXPERIMENTAL

A Hitachi EPS-3T instrument was used to obtain the UV spectra (in ethanol), a Perkin-Elmer for the IR spectra (as Nujol mulls) and an XL-100A-12 for the proton NMR spectra in $CDCl_3$ with TMS as reference. The course of the reactions was monitored by chromatography on Silufol UV-254 plates using chloroform and 9:1 benzene—acetone with UV visualization.

Data for the compounds prepared are collected in Tables 1 and 2.

Ethyl Ester of 1-Benzyl-4,5-dioxo-2-phenylbenz[g]indole-3-carboxylic acid (IVe). To a suspension of 2 g (5 mmole) 5-oxybenz[g]indole IIIe in 10 ml glacial acetic acid, 0.63 ml nitric acid (d = 1.35) was added with stirring and the mixture heated to boiling for 5 min (until evolution of nitrogen oxides ceased). It was then cooled, 20 ml water added, and the precipitate filtered off and recrystallized from a mixture of DMF and methanol (2.8). Yield 1.6 g.

TABLE 2. Spectroscopic Characteristics of Compounds I, II, IV, and V

Compound	ν, cm^{-1}		λ_{max}, nm (lg ε)	δ, ppm*
	C=O	OH		
Ie	1640, 1720	2700	210 (4,29), 237 (4,10)	4,80 (2H, s $CH_2C_6H_5$); 1,20 (3H, t, CH_3); 4,00 (2H, q, CH_2); 6,55 (H, s, H_4); 6,80—7,80 (m, arom.)
If	1620, 1700	2620	207 (4,49), 250 (4,65)	2,35 (3H, s, CH_3); 6,56 (H, s, H_4); 6,80—7,30 (m, arom.)
Ih	1670	2500, 2660	208 (4,53), 253 (4,42)	2,40 (3H, s, CH_3)· 6,70 (H, s, H_4); 7,00—8,00 (m, arom.)
Ik	1640	2660		2,17 (3H, d, CH_3); 6,12 (H, q, H_3); 6,28 (H, d, H_4) 6,80—7,20 (m, arom.)
IIe	1710		206 (4,50), 237 (4,30), 270 (4,53)	
IIf	1660, 1700			
IIg	1670, 1710	2660		
IIj	1690		205 (4,47), 230 (4,25)	2,46 (3H, q, $CH_3C_6H_4$); 2,00 (3H, d, CH_3); 6,05 (H, q, H_3); 6,90—7,03 (m, arom.)
IIk	1690			2,10 (3H, d, CH_3); 6,10 (H, q, H_3); 7,60—6,90 (m, arom.)
IVe	1720, 1670			
IVf	1650, 1700			
Ve	1680, 1720	2700	210 (4,29), 275 (4,12)	
Vf	1700	2600	207 (4,49), 285 (4,01)	

---

*Spectra of compounds Ie, f, k run in acetone-D_6, Ih, IIj, k in $CDCl_3$.

Compound IVf was prepared in a similar way.

1-Benzyl-4-carboxy-5-(o-carboxyphenyl)-3-carbethoxypyrrole (Ve). To a suspension of 4.35 g (10 mmole) derivative IVe in 120 ml methanol, 22 ml of NaOH solution (2 mole/liter) and 15 ml 33% hydrogen peroxide were added at 20°C with stirring. The reaction mixture was stirred 30 min, 150 ml water added, acidified with dilute hydrochloric acid to pH 5, and the precipitate filtered off, dried and recrystallized from benzene. Yield 1.6 g.

Compound Vf was prepared in a similar way.

Derivatives of 5-(o-Carboxyphenyl)pyrrole (Ie, f). The acids Ve, f (10 mmole) were heated for 1 h at 165-170°C, cooled, the reaction mixture taken up in 10 ml warm benzene, the insoluble portion filtered off and recrystallized from 1:1 petrol ether—benzene.

Derivatives of 3-Carboxy-5-(o-carboxyphenyl)-2-methylpyrrole (Ig-ℓ). A mixture of 3 mmole NaOH and 3 drops water was heated to 150°C and 4 mmole acid Ia-c added with stirring to the resulting melt. The mixture was heated at 150-170°C, cooled, and 10 ml water added. The solution was acidified with hydrochloric acid to pH 5 and the precipitate filtered off and crystallized from 7:3 dioxane—water.

Derivatives of 5-(o-Carboxyphenyl)-2-methylpyrrole (Ij-ℓ). The acids Ig-i (3 mmole) were held at 240°C for 10 min in an atmosphere of nitrogen. The reaction mixture was cooled and dissolved in 10 ml benzene. Compounds Ij-ℓ were isolated by column chromatography (silica gel; 9:1 benzene—acetone).

Derivatives of Indeno[1,2-b]pyrrole-4-one (IIa-g, j-ℓ). To a solution of 5 mmole 5-(o-carboxyphenyl)pyrrole Ia-j in 20 ml dry benzene, 1 ml trifluoroacetic anhydride was added. the reaction mixture was kept at 20°C for 1 h 30 min to 24 h, the solvent evaporated off and the residue recrystallized from methanol.

LITERATURE CITED

1. A. N. Grinev, I. N. Mikhailova, I. S. Nikolaeva, E. A. Golovanova, L. M. Polukhina, and G. N. Pershin, Khim.-Farm. Zh., No. 4, 49 (1982).
2. A. N. Grinev, I. N. Nesterova, M. V. Mezentseva, G. N. Pershin, I. S. Nikolaeva, T. V. Pushkina, and E. A. Golovanova, USSR Patent 1,098,228; Byull. Izobret., No. 48 263 (1985).