TABLE I

PREPARATION of $C_{23}H_{22}$ WITH $BF_3 \cdot (C_2H_5)_2O^a$

$(C_6H_5)_3COH$ concn, M	Reaction time, hr	Yield,[b] %
0.04	8	51
0.05	4	43
0.05	36	68
0.08	15	68

[a] Both $SnCl_4$ and H_2SO_4 proved to be inferior under analogous conditions. [b] Based on carbinol.

Attempted Oxidation of III with Aqueous Potassium Permanganate.—A modification of the method used by Bogert and Davidson[14] to oxidize 1,1-dimethylindan failed to affect III and 91% of the starting material was recovered.

Oxidation of III with Chromium Trioxide in Acetic Acid.—A slurry of 14.9 g (0.05 mole) of III in 300 ml of glacial acetic acid was stirred rapidly at room temperature while 75 g (0.75 mole) of chromium trioxide was added in three equal portions. The additions required 25 min and an ice bath was used to maintain the temperature below 30°. After stirring at room temperature for 12 hr, the reaction mixture was added to 500 ml of ice water and partially neutralized (pH 5) by the addition of 150 g (3.75 moles) of sodium hydroxide in small portions. The mixture was stirred for 1 hr, filtered, and the amorphous residue was washed with water and air dried. The filtrate and washings were combined and extracted with ethyl ether. The ether solution was extracted with saturated sodium carbonate solution and the aqueous layer was separated and acidified with concentrated hydrochloric acid. The white precipitate was collected, washed with water, and recrystallized from ethanol–water. The product appeared as 1.3 g (10.4%, based on III consumed) of IV, mp 196–198°, lit.[9] mp 198°. An additional recrystallization produced material with mp 196–197°; homogeneous by tlc (system A); $\nu_{\max}^{\text{KBr}}$ 3055, 3000–2500, 1690, 1670, 1595, 1475, 1450, 1380, 1360, 1285, 1255, 1155, 940, 920, 755, 700 cm^{-1}; $\lambda_{\max}^{\text{CHCl}_3}$ 239 mμ (ε 6.93 × 10^3), 252 mμ (ε 9.72 × 10^3); τ 2.50 (two signals, 9.48 H), 7.05 (0.58 H, s), 8.70 (two signals, 6.00 H); *m/e* 268 (22%), 224 (61%), 223 (100%), 222 (57%) 209 (90%), 208 (78%), 207 (65%), 206 (73%), 194 (61%), 180 (98%), 165 (59%), 105 (82%), 77 (77%), 28 (61%).

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.78; H, 6.17.

The filtration residue from the original reaction mixture was transferred to a Soxhlet thimble and extracted with *n*-hexane for 2 hr. The *n*-hexane solution was concentrated *in vacuo* to recover 0.96 g (6.4%) of III, mp 109–110°. A mixture melting point was not depressed.

1-Acetoxy-1-phenyl-3-oxo-4,4-dimethyl-3,4-dihydro-1H-2-benzopyran (VI) was prepared from 134 mg (0.5 mole) of IV dissolved in 0.5 ml (5.5 mmoles) of acetic anhydride, and 1.26 ml (15.5 mmoles) of pyridine. The reaction mixture was stirred at room temperature for 1 hr, heated at reflux for 5 min, and allowed to cool while stirring for an additional hour. The solution was poured into 20 ml of ice water and the gum which precipitated was separated by decantation. Acidification of the supernatant provided no starting material. The gum was triturated with 30 ml of ice water to produce an off-white solid which was collected, washed with water, and dried *in vacuo* overnight. The dry product, 131 mg (87.4%), mp 130–134°, was homogeneous by tlc (system B). One recrystallization from *n*-hexane raised the melting point to 135–136°; $\nu_{\max}^{\text{KBr}}$ 3065, 2985, 2950, 1760, 1601, 1490, 1445, 1380, 1365, 1235, 1210, 1130, 1060, 956, 800, 760, 695 cm^{-1}; $\lambda_{\max}^{\text{CHCl}_3}$ 252 (ε 465), 257.5 (590), 262 (558), 264 (574), 267 (419), 272 mμ (326); τ 2.53 (9.3 H, m), 7.89 (3.0 H, s), 8.14 (3.0 H, s), 8.36 (3.2 H, s); *m/e* 310 (20%), 267 (47%), 251 (91%), 224 (64%), 223 (100%), 209 (43%), 208 (62%), 105 (35%), 77 (52%), 43 (56%).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.63; H, 5.72.

Attempted Preparation of Analogous Indans Using Carbinols Other Than Triphenylcarbinol. A. Benzhydrol.—The general procedure with 1.84 g (0.01 mole) of benzhydrol provided a viscous oil after the usual work-up. This material was shown to be heterogeneous by vapor phase chromatography (silicon rubber column, 2 ft): $\nu_{\max}^{\text{KB}}$ 3060, 3020, 2960 (very strong), 1635, 1598, 1385, 1360, 1225, 890, 695 cm^{-1}; τ, very complex, including a triplet at τ 8.96 with an area equal to 2.5 times the aromatic multiplet at τ 2.60. No solid could be obtained.

B. 1,1-Diphenylethanol.—The procedure described above, using 1.98 g (0.01 mole) of 1,1-diphenylethanol, produced an oil which exhibited almost identical retention times and spectral properties when compared with the product from the benzhydrol experiment.

Registry No.—II, 10271-31-5; III, 10271-32-6; IV, 10271-33-7; VI, 10271-34-8.

Acknowledgment.—We are indebted to Professor M. M. Bursey for his kind assistance in interpreting the mass spectra.

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[14] M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **56**, 185 (1934).

Unusual Dimeric Salts of 2-(3-Pyridyl)-1,3-indandione

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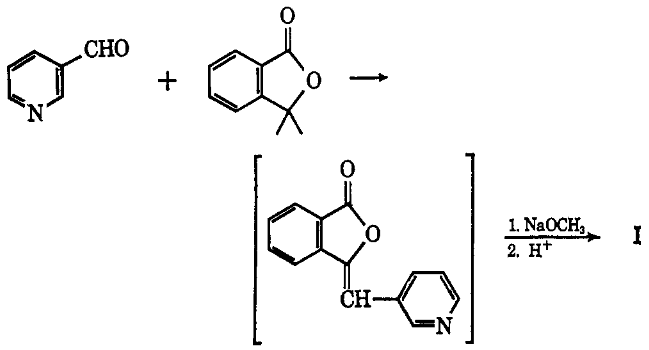
As part of a general investigation of 1,3-indandiones, the preparation 2-(3-pyridyl)-1,3-indandione (I) was undertaken. Lespagnol,[1] *et al.*, have published a preparation for I but did not analyze their product. In place of the method employed by Lespagnol and coworkers[1] to prepare I, the simpler, more general technique of Shapiro[2] for preparing 1,3-indandiones was used to obtain high yields of I from 3-pyridylaldehyde and phthalide.



However, on final acidification of the basic reaction, an excess rather than 1 equiv[1] of hydrochloric acid was used producing an unusual salt (Ia) of I. Elemental analysis and titration of Ia with sodium hydroxide clearly indicated that only one chloride ion was present for every two pyridylindandione moieties.

It was further found that acidification of a basic aqueous solution of I with either hydrobromic, hydriodic, nitric, or picric acid gave similar dimeric salts of I (Ib–e, respectively). In each case titration and analytical data indicated 2:1 adducts (Table I). Acidification with either excess acetic, trifluoroacetic, or sulfuric acid, however, precipitated in each case only the highly insoluble, zwitterionic, internal salt I as indicated by an infrared spectrum, titration, nuclear

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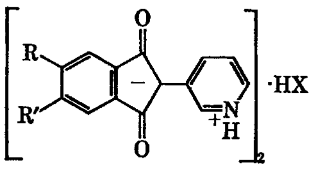
[1] A. Lespagnol, C. Lespagnol, and N. Traisnel, *Bull. Soc. Pharm. Lille*, 89 (1961); *Chem. Abstr.*, **58**, 8332 (1963).

[2] S. Shapiro, K. Geiger, J. Youlus, and L. Freedman, *J. Org. Chem.*, **26**, 3580 (1961).

TABLE I

SALTS OF 2-(3-PYRIDYL)-1,3-INDANDIONES



No.	R	R′	HX	Yield, %	Mp[a] dec, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % X	Found, % C	Found, % H	Found, % N	Found, % X	Equiv wt[b] Calcd	Equiv wt[b] Found	pK'_a
Ia	H	H	HCl	89	333	$(C_{14}H_9NO_2)_2 \cdot HCl$	69.64	3.97	5.80	7.34 (Cl)	69.70	4.09	5.83	7.25	484	482	2.6
															161	161	7.0
Ib	H	H	HBr	c	313	$(C_{14}H_9NO_2)_2 \cdot HBr$	63.77	3.63	5.31	15.15 (Br)	63.53	3.44	5.29	15.33	529	529	2.3
															176	177	6.9
Ic	H	H	HI	c	320	$(C_{14}H_{19}NO_2)_2 \cdot HI$	58.55	3.33	4.88	22.10 (I)	58.88	3.42	4.88	21.96	576	605	3.0
															192	192	6.3
Id	H	H	HNO_3	c	175	$(C_{14}H_9NO_2)_2 \cdot HNO_3$	66.01	3.76	8.25	...	65.78	3.76	8.43	...	511	512	2.3
															170	172	7.0
Ie	H	H	$C_6H_2(NO_2)_3OH$	c	240	$(C_{14}H_9NO_2)_2 \cdot C_6H_3N_3O_7$	60.45	3.13	10.37	...	60.14	3.41	10.42	...	676	695	2.6
															228	232	7.1
II	CH_3	H	HCl	27	306	$(C_{15}H_{11}NO_2) \cdot HCl$	70.51	4.54	5.48	6.94 (Cl)	70.26	4.84	5.41	7.06	512	524	2.2
															171	175	7.1
III	CF_3	H	HCl	11	333	$(C_{15}H_8NO_2F_3)_2 \cdot HCl$	58.21	2.77	4.53	5.73 (Cl)	58.03	2.87	4.40	5.66	620	638	2.4
															207	210	6.7
IV	CH=CHCH=CH		HCl	17	315	$(C_{18}H_{11}NO_2)_2 \cdot HCl$	74.16	3.98	4.81	6.08 (Cl)	74.02	4.06	4.76	5.79	582	592	2.8
															194	201	6.9

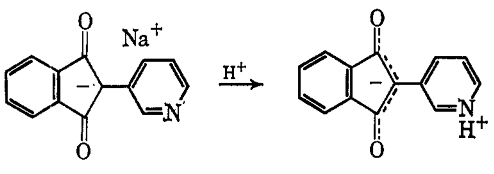
[a] Analytical samples were prepared by recrystallization from ethanol solution. [b] Neutralization equivalents from potentiometric titration in dioxane–H_2O (2:1) solvent using sodium hydroxide. Values for pK'_a taken at the half-neutralization point. [c] Prepared by acidifying aliquots of a sodium hydroxide solution of I with appropriate acids.

TABLE II

ULTRAVIOLET SPECTRA OF SALTS OF 2-(3-PYRIDYL)-1,3-INDANDIONES[a]

No.	Mol wt	$\lambda_{max}^{0.1\,N\,NaOH}$ (mμ)	ε	λ_{max}^{MeOH}	ε
I	224	254, 285, 329, 342	17,400; 24,400; 12,200; 10,600	240, 248, 298, 347	17,700; 16,600; 18,900; 20,200
Ia	484	255, 286, 330, 342	34,400; 48,400; 24,400; 21,400	240, 248, 288 (sh), 298, 337 (sh), 348	37,900; 35,400; 39,200; 43,000
II	512	258, 287, 333, 346	35,500; 53,800; 25,600; 22,800		
III	620	256, 285, 332, 345	26,400; 45,600; 23,200; 19,900		
IV	582	262, 309, 323	51,400; 80,500; 96,600		

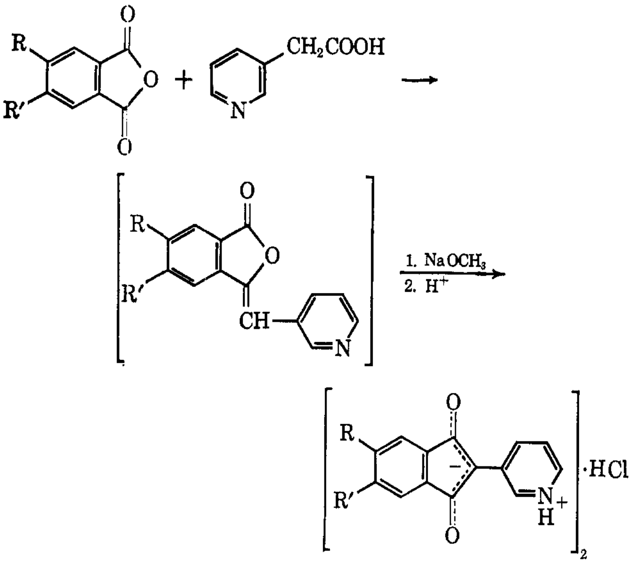
[a] For comparison, 2-phenyl-1,3-indandione exhibits $\lambda_{max}^{0.1\,N\,NaOH}$ 280 (ε 13,800), 329 (4200), and 342 mμ (3280).



I

magnetic resonance (nmr), and combustion analysis data.

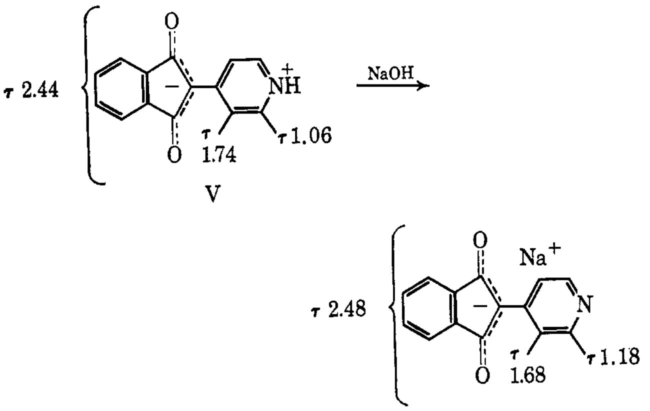
On treatment of substituted phthalic or naphthalic anhydrides with 3-pyridylacetic acid and rearrangement of the intermediate arylidenephthalides in sodium methoxide solution, products related to I with substituents on the indan ring, either 5-methyl- (II), 5-trifluoromethyl- (III), or a 2,3-dihydrobenz[*f*]indene-1,3-dione (IV), were obtained which gave similar dimeric hydrochloride salts upon acidification with hydrochloric acid (see Table I). Although all of these salts were only slightly soluble in most solvents, III was dissolved in excess of hot methanol, dry hydrochloric acid added, and a monohydrochloride (IIIa) was isolated by evaporating the solution to dryness. Recrystallization of IIIa from ethanol produced III, while the ultraviolet spectra of both III and IIIa in methanol solution were identical. Titration of IIIa confirmed its normal, dibasic acid structure, and nmr spectra of III and IIIa were identical in deuterated dimethyl sulfoxide (DMSO-d_6) solution.



Ia, R = R′ = H
II, R = CH$_3$; R′ = H
III, R = CF$_3$; R′ = H
IV, R = R′ = CH=CHCH=CH

As with the parent Ia, the ring-substituted complex salts II–IV precipitated silver chloride with added silver nitrate only on standing with the reagent in ethanol solution. This suggests an unusually tightly bonded chloride ion in the hemi-hydrochloride salts.

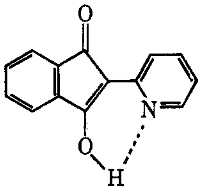
In contrast to the 2-(3-pyridyl)-1,3-indandiones, the isomeric 2-(4-pyridyl)-1,3-indandione (V), when prepared by a similar synthetic route, gave a normal, stable monohydrochloride salt (Va) from methanolic hydrochloric acid solution. Titration confirmed the normal dibasic nature of Va. Addition of excess aqueous acid to the basic aqueous reaction solution, however, gave the highly insoluble, zwitterionic V. Comparison of the nmr spectra of V and its sodium salt supported a zwitterionic structure for V since the aromatic protons in the indane ring show virtually no shift in going from zwitterion to sodium salt while the 2,6 protons on the pyridine ring shift upfield in the sodium salt of V.



V

An analogous analysis of the nmr spectra of I in DMSO-d_6 and in DMSO-d_6–NaOH also supports a zwitterionic structure assignment for I. An unusually high melting point (319° dec) and high pK_a' (8.8) compared to related data for 2-phenyl-1,3-indandione (mp 151°, pK_a' = 5.4) further support a zwitterionic structure for V. Ultraviolet spectra of compounds I, Ia, II, III, and V in sodium hydroxide solution all exhibited similar major absorptions near 280, 329, and 342 mμ as seen for a related structure, 2-phenyl-1,3-indandione, in basic solution (Table II). Compound IV, a 2,3-dihydrobenz[*f*]indene-1,3-dione, exhibits the expected bathochromic shifts compared with 1,3-indandiones. Ultraviolet spectra of I and Ia were identical in methanol solution and identical in 0.1 *N* sodium hydroxide solutions indicating no disruption of the major chromophores when zwitterionic I is converted to the complex hemisalt Ia.

Preparation of the remaining isomer, 2-(2-pyridyl)-1,3-indandione (VI), yielded a compound which, based on an infrared spectrum, is strongly intramolecularly hydrogen bonded through an enol form. Unlike the other two isomeric 2-pyridylindandiones I and V, VI was insoluble in aqueous sodium bicarbonate and could not be titrated in 2:1 dioxane–water with sodium hydroxide. The acidic proton in VI is clearly more tightly bonded than in the isomeric pyridyl-1,3-indandiones but a fully zwitterionic structure for VI seems unlikely since Huber[3a] has isolated a monophenylhydrazone derivative from VI.



VI

Although it has not been possible from spectral and chemical evidence to assign a structure to these dimeric salts, the property of 2-(3-pyridyl)-1,3-indandiones to

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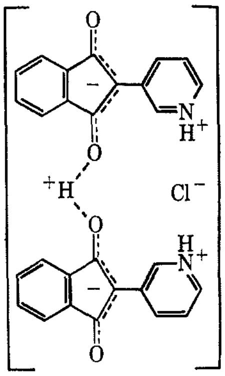
(3) (a) H. Huber, *Ber.*, **36**, 1653 (1903); (b) H. F. Andrew and C. H. Bradsher, *J. Heterocyclic Chem.*, **3**, 282 (1966).

form dimeric salts with certain acids may be the result of a hydrogen bond bridge between molecules. Related half-salts have been reported by Andrew and Bradsher[3b] in the thiazolo[2,3-*a*]quinolinium system, by Reid and Bonthrone[4] in benzo[*c,d*]pyrenium cations, by Vozza[5] and Muth[6] in picoline 1-oxides, and by Thyagarajan[7] in certain pyridones. Fisher, *et al.*,[8] have published an X-ray analysis of the mesitaldehyde–perchloric acid 2:1 adduct. In each case, a hydrogen bond bridge was proposed to explain the complex salts. In the present 2-(3-pyridyl)-1,3-indandiones, a hydrogen bond may possibly bridge two indandione anions while the acid anion is held between two pyridinium rings.



Delocalization of charge through hydrogen bonds is of current interest[9] and may possibly be of importance in explaining the stability of the present salts. However, all structure proposals must remain conjectural until such time as the X-ray examination of Ia now in progress reveals its true structure.

Experimental Section[10]

2-(3-Pyridyl)-1,3-indandione (I).—A solution of 13.4 g (0.10 mole) of phthalide, 10.7 g (0.10 mole) of 3-pyridinecarboxaldehyde, 16.2 g (0.30 mole) sodium methoxide, 48 ml of dry ethyl propionate, and 100 ml of dry methanol was refluxed for 2 hr. After cooling, the orange-yellow solution was evaporated to dryness under reduced pressure, and the residue was taken up in 1 l. of water and extracted with several portions of ether. After cooling, portions of the red aqueous layer were strongly acidified with a variety of acids. Data for the complex salts formed from hydrochloric, hydrobromic, hydriodic, nitric, and picric acids are recorded in Table I. An ultraviolet spectrum of the hemihydrochloride Ia in methanol was essentially identical with that of I (see Table II). The nmr (DMSO-d_6) on the hemihydriodide Ic exhibited τ 0.28 (s, 1-H, the 2 proton of pyridinium ring) and 2.58 (s, 4-H, aromatic protons), doublets at τ 0.54 (J = 4 cps) (1-H, the 4 proton of pyridinium) and 1.60 (J = 4 cps), (1-H, the 6 proton of pyridinium) and 2.0 (t, 1-H, the 5 proton of pyridinium).

Acidification with either sulfuric, acetic, or trifluoroacetic acids all gave I in its zwitterionic form, mp 306° (sintered at 298°) (lit.[1] mp 310°), which on recrystallization from a large volume of ethanol gave analytically pure material in each case.

Anal. Calcd for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.28. Found: C, 75.51; H, 4.35; N, 6.14.

Infrared showed absorptions near 3.5 μ (NH^+) and a single carbonyl peak at 5.96 μ. Calcd for neut equiv (2:1 dioxane–H_2O): 224. Found: 223. $pH_{1/2}$ was 7.1. Ultraviolet spectral data are recorded in Table II. Nmr data are (DMSO-d_6) τ 0.20 (s), 2.62 (s) (aromatic protons), doublets at τ 0.48 and 1.72, and 2.2 (t). Precipitation of the sample prevented integration of this nmr spectrum; however, see above discussion of the very similar nmr of the hemihydroiodide salt (Ic) of I. Addition of 1 drop of 40% sodium hydroxide to the DMSO-d_6 solution of I solution produced the following nmr spectrum: τ 0.36 (s, 1-H), 1.22 (J = 4 cps) (d, 1-H), 1.96 (J = 4 cps) (d, 1-H), 2.72 (s) overlapping a complex of peaks (5-H).

Bis(5-methyl-2-(3-pyridyl)-1,3-indandione) Hydrochloride (II).—A mixture of 1.69 g (0.010 mole) 4-methylphthalic anhydride, 1.4 g (0.010 mole) of 3-pyridylacetic acid, and 0.10 g of anhydrous sodium acetate was placed in a flask under a dry nitrogen atmosphere and the temperature was slowly raised (electric heating mantle connected to a pyrometer). After the reaction fused and evolved gas near 150°, the temperature was raised to 170° for 1.5 hr and then to 200° for 10 min. After cooling, the residue was dried overnight under high vacuum over phosphorous pentoxide.

Combination of the above dry residue with a solution of 2.7 g (0.050 mole) of sodium methoxide in 50 ml of dry methanol and refluxing for 0.5 hr produced a red solution. Evaporation to dryness, partitioning the residue between water–ether and strong acidification of the water layer with excess hydrochloric acid yielded II. See Table I for analytical data.

4-Trifluoromethylphthalic Acid.—A combination of 82.6 g (0.40 mole) of 4-chloro-3-cyanobenzotrifluoride (Pierce Chemical Co.), 21.6 g (0.44 mole) of sodium cyanide, and 750 ml of dry dimethylformamide was refluxed 2 hr. Distillation of all solvent under reduced pressure produced a purple syrup which was hydrolyzed directly with 500 ml of 40% sodium hydroxide and 200 ml of ethanol for 48 hr. Extraction of the basic solution with ether, followed by strong acidification (hydrochloric acid) of the aqueous layer produced a clear solution. Evaporation to dryness under reduced pressure and extraction with acetone separated crude product from insoluble inorganic salts. Evaporation of all acetone yielded a solid (54 g, 58%) which after recrystallization from benzene containing a trace of ethanol exhibited mp 170.5–172° (lit.[11] 169–170).

Anal. Calcd for $C_9H_5F_3O_4$: C, 46.17; H, 2.15. Found: C, 46.51; H, 2.28.

Bis(5-trifluoromethyl-2-(3-pyridyl)-1,3-indandione) Hydrochloride (III).—The anhydride of 4-trifluoromethylphthalic acid was made by refluxing 1.29 g (0.025 mole) of the diacid in 25 ml of acetic anhydride with a small drop of sulfuric acid for 2 hr. Evaporation to dryness yielded the anhydride which was used immediately in the next step.

The above anhydride was combined with 3.49 g (0.025 mole) of 3-pyridylacetic acid and 0.20 g of anhydrous sodium acetate in a dry nitrogen atmosphere. Successive pyrolysis, rearrangement in sodium methoxide, and acidification steps are identical with the procedure described for II above. Analytical data for the complex salt recrystallized from a large volume of ethanol–water are recorded in Table I.

A **monohydrochloride salt** (IIIa) was prepared from 0.82 g of III dissolved in 150 ml of boiling methanol and saturated with dry hydrogen chloride. Evaporation to dryness and trituration with ethanol–ether yielded an orange solid, mp 303° dec. A sample readily precipitated silver chloride when mixed with a silver nitrate solution.

Anal. Calcd for $C_{15}H_8F_3NO_2 \cdot HCl$: C, 55.10; H, 2.77; Cl, 10.86; N, 4.29. Found: C, 55.11; H, 2.86; Cl, 10.21; N, 4.34.

The ultraviolet spectrum of IIIa was λ_{max}^{MeOH} 286 (sh) (ϵ 10,300), 294 (19,300), 340 (17,550), and 350 mμ (sh) (16,800) and was superimposable on a spectrum of III in methanol solution. Titration of the dibasic IIIa [dioxane–water (2:1)] produced a normal curve, neut equiv 346 and 173 (calcd neut equiv 328 and 164) with $pH_{1/2}$ 2.3 and 6.7.

When the analytically pure IIIa was recrystallized from ethanol, analytically pure III was obtained.

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(4) D. H. Reid and W. Bonthrone, *J. Chem. Soc.*, 5920 (1965).

(5) J. F. Vozza, *J. Org. Chem.*, **27**, 3856 (1962).

(6) C. M. Muth and R. S. Darlak, *ibid.*, **30**, 1909 (1965).

(7) B. S. Thyagarajan, K. Rajagopalan, and P. V. Gopalakrishnan, *Chem. Ind.* (London), 1887 (1966).

(8) C. D. Fisher, L. H. Jensen, and W. M. Schubert, *J. Am. Chem. Soc.*, **87**, 33 (1965).

(9) L. C. Dorman, *Tetrahedron Letters*, 459 (1966).

(10) Melting points were determined in a Thomas–Hoover capillary melting point apparatus using a calibrated thermometer and are corrected. Potentiometric titrations were carried out in dioxane–water (2:1) solvent using a Beckman Model G pH meter. Nmr spectra were obtained on a Varian Associates A-60 spectrometer with tetramethylsilane as an internal standard (s = singlet, d = doublet, t = triplet). Infrared spectra were determined in potassium bromide pellets.

(11) This compound has been prepared by B. Loev [*Can. J. Chem.*, **42**, 1490 (1964)] by a multistep procedure.

Bis(2-(3-pyridyl)-2,3-dihydrobenz[*f*]indene-1,3-dione) Hydrochloride (IV).—By application of the sequence of reactions described for III to naphthalene-2,3-dicarboxylic acid, the complex hydrochloride IV was obtained.

2-(4-Pyridyl)-1,3-indandione (V).—Refluxing a combination of 13.4 g (0.10 mole) of phthalide, 10.79 g (0.10 mole) of 4-pyridinecarboxaldehyde, 48 ml of dry ethyl propionate, and 16.29 g (0.30 mole) of sodium methoxide dissolved in 100 ml of methanol produced a deep red solution after 2 hr. Evaporation of all solvent, partitioning between ether–water, and strong acidification of the basic aqueous layer with 6 *N* hydrochloric acid produced an orange solid. Recrystallization from a large volume of ethanol yielded the zwitterionic V, mp 325° dec.[12]

Anal. Calcd for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.28. Found: C, 74.98; H, 4.24; N, 6.11.

A silver nitrate test on this solid in ethanolic solution did not precipitate silver chloride. Infrared absorptions at 3–5 (NH^+) and 6.0 μ (C=O). An ultraviolet spectrum in 0.1 *N* sodium hydroxide exhibited λ_{max} 243 (ϵ 12,800), 296 (25,200), 332 (19,700), and 346 mμ (20,500); in methanol 232 (ϵ 32,400), 295 (8200), and 380 mμ (47,000). An nmr spectrum (DMSO-d_6) showed τ 2.44 (s, 4-H), 1.06 (J = 3.2 cps) (d, 2-H, the 2- and 6-pyridine protons), and 1.74 (J = 3.2 cps) (d, 2-H; the 3- and 5-pyridine protons). In DMSO-d_6 containing 2 drops of 40% sodium hydroxide, V showed τ 2.48 (s, 4-H), 1.18 (J = 3.2 cps) (d, 2-H), and 1.68 (J = 3.2 cps) (d, 2-H). Titration of V [dioxane–H_2O (2:1)] gave neut equiv 230 (calcd neut equiv 224) and a pH$_{1/2}$ of 8.80.

A **hydrochloric acid salt (Va)** of V was prepared in a large volume of hot methanolic hydrochloric acid. Cooling produced an orange solid, mp 312° dec.

Anal. Calcd for $C_{14}H_9NO_2\cdot HCl$: C, 64.74; H, 3.88; Cl, 13.70; N, 5.40. Found: C, 64.43; H, 3.87; Cl, 13.54; N, 5.38.

Titration of Va [dioxane–H_2O (2:1)] indicated a dibasic acid of neut equiv 265 and 131 (calcd neut equiv 260 and 130) with corresponding pH$_{1/2}$ of 2.6 and 8.7. The ultraviolet spectrum was λ_{max}^{MeOH} 232 (ϵ 33,200), 295 (4500), 305 (7500), and 379 mμ (52,600). The infrared spectrum was 3.25 (OH), 4–5 (NH^+), and 5.9 μ (C=O), indicating an enol form for this monohydrochloride.

2-(2-Pyridyl)-1,3-indandione (VI).—Conditions for the preparation of VI were identical with those applied to I except that pyridine 2-carboxaldehyde was used. Acidification with aqueous hydrochloric acid precipitated 17.3 g (35%) of VI, mp 292° dec (sintered at 285°) (lit.[13,3a] 260°; made by treating 2-picoline with phthalic anhydride).

Anal. Calcd for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.28. Found: C, 75.51; H, 3.96; N, 6.23.

A silver nitrate test on VI failed to precipitate silver chloride and VI showed only slight solubility in dilute sodium bicarbonate while dissolving to a red solution in 10% sodium hydroxide. Infrared absorptions of very broad bands were between 3 and 5 μ (hydrogen bonded OH); a single carbonyl peak was at 6.01 μ. The ultraviolet spectrum in 0.1 *N* sodium hydroxide was λ_{max} 250 (sh) (ϵ 13,900), 278 (18,700), 332 (12,600), and 340 mμ (sh) (12,250). In methanol solution the results were 230 (ϵ 23,800), 288 (24,600), 308 (9700), 322 (8350), and 382 mμ (24,200). An nmr spectrum could not be obtained on the highly insoluble VI.

Registry No.—I, 10478-89-4; Ia, 10478-90-7; Ib, 10478-91-8; Ic, 10478-92-9; Id, 10478-93-0; Ie, 10478-94-1; II, 10478-95-2; III, 10478-96-3; IIIa, 10478-97-4; IV, 10478-98-5; V, 10478-99-6; Va, 10479-00-2; VI, 641-63-4; 4-trifluoromethylphthalic acid, 835-58-5.

Acknowledgment.—The author is grateful to Mr. Ronald Seidell and Mr. Nelson Treadway, Jr., for assistance in the synthetic work.

[12] S. P. Dutta, A. K. Acharyya, and U. P. Basu [*J. Indian Chem. Soc.*, **43**, 549 (1966)] have recently reported mp 319° for this compound ("4-pyrophthalone") prepared from 4-picoline and phthalic anhydride. These authors appear not to have considered a zwitterionic structure for this compound even when the compound failed to form a phenylhydrazone or oxime derivative.

[13] E. Jacobsen and C. L. Reimer, *Ber.*, **16**, 2602 (1883).

An Improved Synthesis of Spiro[2.5]octa-4,7-dien-6-ones

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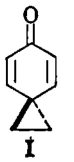
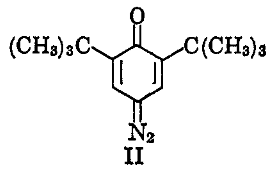
While 4,4-disubstituted cyclohexa-2,5-dienones have been studied extensively, the chemistry of the spiro[2.5]octa-4,7-dien-6-ones (I) has only recently attracted interest.[1,2] Presumably, their inaccessibility has deterred their study. Only a few examples of these spirodienones are known, there being but two previously reported synthetic approaches. The addition of diazoalkanes to methylenecyclohexadienones with subsequent loss of nitrogen has been little explored.[3,4] While studying neighboring-group participation, Winstein and Baird prepared spiro[2.5]octa-4,7-dien-6-one (I) from 2-*p*-hydroxyphenylethyl bromide in 2% yield.



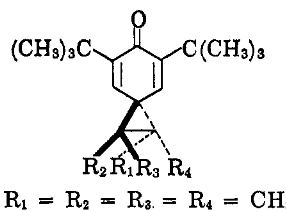
I



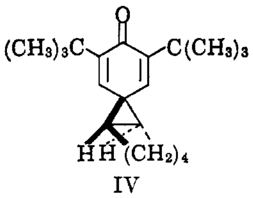
II

These authors report I to be extremely labile toward nucleophiles or traces of acid or base. This paper reports a synthetic approach to spiro[2.5]octa-4,7-dien-6-ones which appears to be superior to those previously reported for it affords a variety of these reactive spirodienones in good yield from readily available precursors.

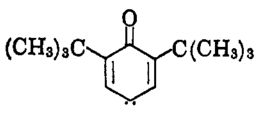
Photolysis of 3,5-di-*t*-butylbenzene 1,4-diazooxide (II) in 2,3-dimethyl-2-butene leads to the formation of 1,1,2,2-tetramethyl-5,7-di-*t*-butylspiro[2.5]octa-4,7-dien-6-one (IIIa) in 80% yield. Use of cyclohexene as a solvent leads to dienone IV in 72% yield. Irradiation of II in neat *cis*- or *trans*-2-butene yields the corresponding *cis*- (IIIb) or *trans*-1,2-dimethylspirooctadienone (IIIc) with 95 and 97+% stereoselec-



IIIa, $R_1 = R_2 = R_3 = R_4 = CH_3$
b, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$
c, $R_1 = R_3 = H$; $R_2 = R_4 = CH_3$
d, $R_1 = R_2 = H$; $R_3 = R_4 = Cl$



IV



V

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[1] (a) S. Winstein and R. Baird, *J. Am. Chem. Soc.*, **79**, 756 (1957); (b) R. Baird and S. Winstein, *ibid.*, **79**, 4238 (1957); (c) R. Baird and S. Winstein, *ibid.*, **85**, 567 (1963).

[2] (a) D. I. Schuster and C. J. Polowczyk, *ibid.*, **88**, 1722 (1966); (b) D. I. Schuster and I. S. Krull, *ibid.*, **88**, 3456 (1966).

[3] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952).

[4] D. H. R. Barton and J. B. Hendrickson, *ibid.*, 1028 (1956).