Reactions of Some 1,3-Indandione Derivatives

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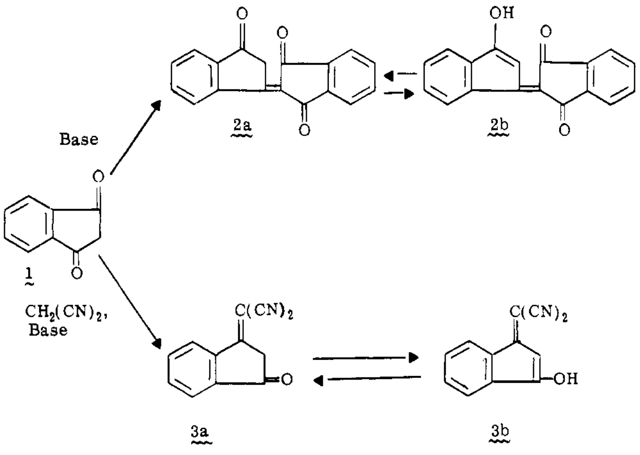
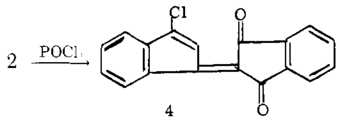
Derivatives 2 and 3 of 1,3-indandione having a carbonyl oxygen replaced by a strong electron-withdrawing group (1,3-dioxo-2-indanylidene or dicyanomethylene) were converted to chlorobenzofulvenes by reaction with phosphoryl chloride. The halogens of these chlorobenzofulvenes were displaced by various nucleophiles to produce colored products. Red to blue methine dyes were obtained by condensation of the methylene groups in both 2 and 3 with aromatic aldehydes. Visible spectra of the colored products showed that the 1,3-dioxo-2-indanylidene group was a better electron acceptor than the dicyanomethylene group.

Both dimerization of 1,3-indandione (1) to produce [$\Delta^{1,2'}$-biindan]-1′,3,3′-trione (2) (*3, 5*) and reaction of 1 with malononitrile to produce 3-oxo-$\Delta^{1,\alpha}$-indanmalononitrile (3) have been reported (*2*). The chemistry of these derivatives has been studied to only a very limited extent. The purpose of this paper is to describe some reactions of compounds 2 and 3, including the preparation of novel chlorobenzofulvenes from them.



Nearly all base-catalyzed reactions of 1 resulted in the formation of some dimer 2. However, a reasonable yield (56%) of 3 was obtained by reaction of 1 with an excess of malononitrile under conditions which minimized the self-condensation reaction. Derivative 3 melted at 223–229°C (dec), whereas Junek (*2*) reported 219°C as its melting point. The broad melting range may be partially due to decomposition at elevated temperatures, but it also may be related to the existence of the two tautomeric forms 3a and 3b. The visible absorption maximum red-shifted (from 462–481 nm) with increasing basicity of solvent, and the extinction coefficient increased more than threefold (from 3190–10,420). The bathochromic shift and increase in extinction coefficient were due to increased concentration of the enol form 3b. This behavior is consistent with the previous observation (*4*) that benzene solutions of 2 have the yellow color characteristic of the keto form 2a, whereas ethanol solutions are violet because the concentration of the enol form 2b is increased.

The reactions of 2 and 3 with phosphoryl chloride in either *N*,*N*-diethylaniline or *N*,*N*-dimethylaniline gave chlorobenzofulvenes 4 and 5, respectively.



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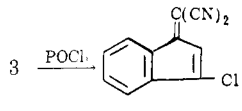

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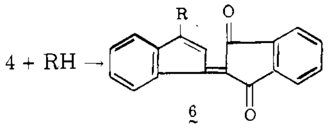
The chlorobenzofulvenes were pale yellow in solution and unexpectedly stable toward hydrolysis upon standing in an aqueous suspension for several hours. The halogens of both 4 and 5 were readily displaced by nucleophilic reagents (amines, phenols, alcohols) to give products 6 and 7, which had intense absorption maxima in the visible region (Tables I and II).



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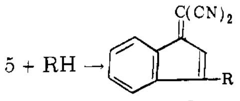

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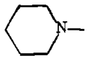
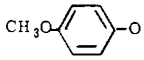
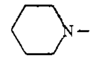
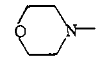
where RH = amine, alcohol, or phenol.

Table I. Physical Properties and Spectral Data of Compounds Having General Structure 6

Compound	R	λ_{max}, nm	ϵ^a, L mole^{-1} cm^{-1}	Principal infrared bands^b, cm^{-1} C=O	C=C
4	Cl	372	19,850	1720w, 1620w, 1680s	1600m, 1580m, 1570s
		446	2,330		
6a	C_6H_5O	368	20,750	1675s, 1660w	1600w, 1580m, 1575w
		479	6,275		
6b	CH_3O	368	20,300		
		483	5,660	1675s	1610w, 1580w
6c	C_6H_5NH	373	21,500		
		576	20,400	1630m	1590sh, 1580m
6d		377	15,420		
		556	19,280	1635s	1580s
		591	24,470		
6e	$(CH_3)_2N$	376	30,450		
		551	37,500		
		590	48,000	1635s	1600sh, 1580m
		640	30,350		

[a] Acetone solvent. [b] KBr.

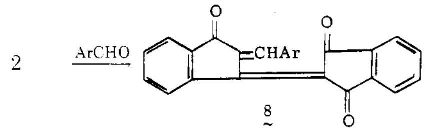
Table II. Physical Properties and Spectral Data of Compounds Having General Structure 7

Compound	R	Mp, °C	Yield, %	λ_{max}, nm	ϵ^a, L mole^{-1} cm^{-1}	Principal infrared bands^b, cm^{-1}: C≡N	Principal infrared bands^b, cm^{-1}: C=C
5	Cl	134–136	96	439	1,125	2210m	1575m, 1525m
7a	C_6H_5O	164–165	71	447	3,420	2225m	1570w, 1525s
7b[c]		175–176	43	449	3,350	2190w	1585w, 1575w, 1535s
7c	CH_3O	162–164	51	447	3,690	2220m	1610w, 1575m, 1525s
7d[d]	NH_2	300	55	[e]	. . .	2195s	1665s, 1570m, 1525s
7e[f]	C_6H_5HN	251–253	99	500	14,350	2190s	1600s, 1570s, 1485s
7f[f]		174–175	97	505	13,240	2185s	1585w, 1575w, 1525s
7g[f]		240–242	81	505	12,330	2200s	1585m, 1575m, 1525s

[a] Acetone solvent. [b] KBr. [c] Derivative 7b was obtained by the procedure used for preparation of 7a. [d] Although elemental analyses and infrared data for this compound confirm general structure 7, the high melting point and insolubility indicate a higher molecular weight species (dimer, etc.) of the same empirical composition. [e] Not determined. [f] 7e was obtained by the procedure used for preparation of 6c, and 7f-g were prepared by the procedure used for preparation of 6d.

Earlier workers obtained the aniline derivative 6 (R = C_6H_5NH) by the reaction of 1,3-indandione dimer 2 with aniline in either acetic acid (*6*) or propyl alcohol (*7*). The wavelength of the visible absorption maxima of both series 6 and 7 increased with increasing electron-donor character of the substituent group. Moreover, the derivatives of 4 had absorption maxima at longer wavelengths and of greater intensities than the derivatives of 5. The infrared spectra of 4 and 6 in the 1450–1750-cm^{-1} region consisted of a multiplet of bands of varying intensities. An intense carbonyl band appeared at 1625–1680 cm^{-1}, and a moderately intense band attributable to the exocyclic carbon-carbon double bond appeared at 1570–1580 cm^{-1}. The infrared spectra of the dicyanomethylene compounds 5 and 7 were characterized by a moderately intense nitrile absorption band at 2185–2225 cm^{-1} and a triplet of bands in the 1485–1600-cm^{-1} region.

Activation of the methylene groups of 2 and 3 by the electron-withdrawing groups in the 1 and 3 positions enabled ready condensation with aromatic aldehydes to produce methine dyes 8 and 9 (Tables III and IV).



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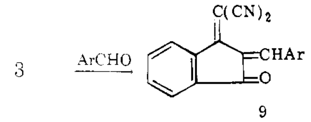

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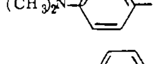
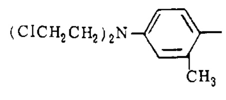
Dyes 9a-d (Table IV) had visible absorption maxima at shorter wavelengths than the corresponding dyes 8a-b from the 1,3-indandione dimer (Table III); this finding was consistent with that for the compounds in Tables I and II. The relative electron-acceptor character of the dicyanomethylene, 1,3-dioxo-2-indanylidene, and related groups is qualitatively illustrated by the positions of the visible absorption maxima of some dyes from *p*-(dimethylamino)benzaldehyde (Table V).

Earlier workers demonstrated that the zinc chloride-catalyzed reaction of 2 with *N*,*N*-dimethylaniline at 200° C gave the arylated product 10 but that diphenylamine, which is less basic, failed to react (*6*). The chloro compound 5 was treated with arylamines under somewhat milder conditions (120° C with phosphoryl chloride catalyst) to obtain the blue aryl derivatives of general structure 11 (Table VI).

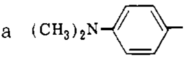
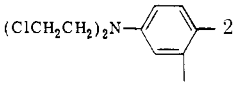
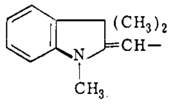
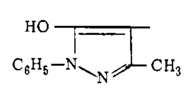
As was reported for 2, weakly basic arylamines failed to react with 5. Although no gas was evolved when 11a [Ar = *p*-$(C_2H_5)_2NC_6H_4$] melted, its broad melting range was probably due to thermal decomposition.

Table III. Physical Properties and Spectral Data of Methine Dyes Having General Structure 8

Compound	Ar	Mp, °C	Yield, %	λ_{max}, nm	ϵ^a, L mole^{-1} cm^{-1}
8a		239	37	372 457 609	21,700 19,250 28,650
8b[b]		235–237	60	365 451 591	42,200 31,100 50,600

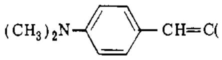
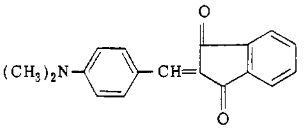
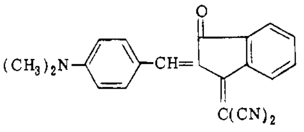
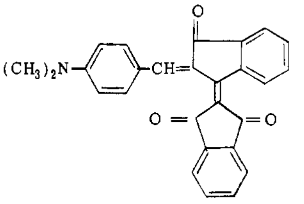
[a] Acetone solvent. [b] 8b was obtained by the procedure used for preparation of 8a.

Table IV. Physical Properties and Spectral Data of Methine Dyes Having General Structure 9

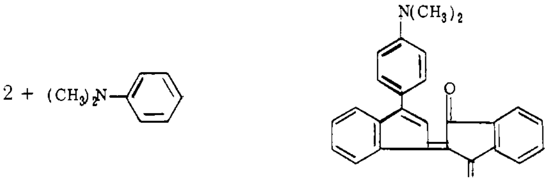
Compound[a]	Ar	Mp, °C,	Yield, %	λ_{max}, nm	ϵ^b, L mole^{-1} cm^{-1}
9a		238	62	365 553	10,470 51,200
9b		208–221	74	363 548	8,700 43,900
9c		204–210	55	489	112,100
9d		228–234	44	462	32,000

[a] Derivatives 9b–d were obtained by the procedures used for preparation of 9a. [b] Acetone solvent.

Table V. Spectral Data for Methine Dyes from *p*-(Dimethylamino)benzaldehyde

Dye Structure	λ_{max}, nm	ϵ, L mole^{-1} cm^{-1}
	430[a]	53,030
	480[a]	73,542
	553 365	51,200 10,470
	609 457 372	28,650 19,250 21,700

[a] From Ref *1*.



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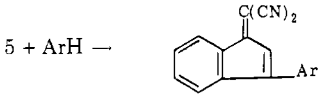


11

EXPERIMENTAL

Melting points were taken in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (KBr) were determined on a Baird AB-2 or a Perkin-Elmer Model 137 spectrophotometer. Visible spectra were determined with a Bausch and Lomb Spectronic 505 or a Cary Model 14 spectrophotometer. Elemental analyses were performed in the analytical laboratories of the Tennessee Eastman Research Laboratories.

3-Oxo-$\Delta^{1,\alpha}$-indanmalononitrile (3). 1,3-Indandione (26.4 grams, 0.18 mole) was added portionwise in 45 min to a solution of malononitrile (32 grams, 0.49 mole), ethanol (400 ml), and piperidine (0.5 ml) at 60° C. After the mixture had stirred at 60° C for 0.5 hr, water (1000 ml) was added, and the tan solid that formed was collected after standing 24 hr at 25° C. The solid (30 grams) was dissolved in toluene (600 ml) and crystallized by holding at 50° C for 1.5 hr. Filtering, washing with hexane, and drying gave 19.7 grams (56%) of tan crystals, mp 207–227° C. An additional recrystallization from toluene gave the analytical sample, mp 223–229° C (dec) [literature (*2*) mp 219° C] ir (KBr) 2230 (CN), 1730 and 1590 (C=O), 1570 cm^{-1} (C=C).

2-(3-Chloroinden-1-ylidene)-1,3-indandione (4). A mixture of derivative 2 (2.0 grams), phosphoryl chloride (5 ml), and *N,N*-diethylaniline (5 ml) was stirred for 0.5 hr at 70° C, cooled at 30° C, and then diluted with 30 ml of water (exothermic reaction). Aqueous hydrochloric acid (30 ml, 5%) was added, and the mixture was filtered to obtain 2.1 grams (99% yield) of red solid, mp 166–177° C. Two recrystallizations from toluene/hexane and one recrystallization from methyl Cellosolve solvent afforded the analytical sample, mp 179–181° C.

3-Chloro-$\Delta^{1,\alpha}$-indenemalononitrile (5). A mixture of derivative 3 (2.0 grams), phosphoryl chloride (5 ml), and *N,N*-diethylaniline (5 ml) was stirred for 45 min at 70° C. The mixture was then cooled to 25° C, and water (25 ml) was added dropwise (exothermic reaction). Filtration removed 2.1 grams (96%) of 5. Two recrystallizations from toluene gave the analytical sample; red crystals, mp 134° C.

2-(3-Phenoxyinden-1-ylidene)-1,3-indandione (6a). A mixture of 4 (0.59 gram, 0.002 mole), phenol (15 grams), and potassium hydroxide (0.66 gram, 0.01 mole) was stirred for 5 min at 100° C and then for 30 min at 75° C. When the mixture had cooled to 25° C, water (50 ml) was added and the resulting red precipitate was collected by filtration and dried. The yield of 6a, mp 223–229° C, was 0.5 gram (71%). Recrystallization from toluene afforded the analytical sample, mp 225–233° C.

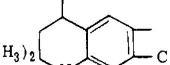
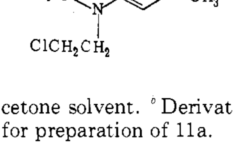
2-(3-Methoxyinden-1-ylidene)-1,3-indandione (6b). Solid 4 (1.5 grams, 0.0051 mole) was added to a mixture of sodium methoxide (0.0087 mole) and methanol (60 ml), and the resulting mixture was stirred for 45 min at 60° C. When the mixture had cooled to 25° C, water (300 ml) was added and the red precipitate that formed was collected by filtration. The yield of 6b, mp 199–210° C, was 1.4 grams (95%). One recrystallization from acetic acid followed by a recrystallization from toluene afforded the analytical sample, mp 207–210° C.

2-(3-Anilinoinden-1-ylidene)-1,3-indandione (6c). Aniline (0.6 gram, 0.006 mole) was added to a refluxing solution of 4 (0.59 gram, 0.002 mole) in methanol (30 ml). After refluxing 5 min, the mixture was diluted with water (35 ml), cooled to 25° C and filtered. The product (0.55 gram, 79%) melted at 217–221° C. Two recrystallizations from toluene afforded the analytical sample, mp 222–224° C [lit (*6, 7*) mp 224–225° C and 214–216° C, respectively].

2-(3-Piperidinoinden-1-ylidene)-1,3-indandione (6d). Piperidine (0.4 ml) was added to a solution of 4 (0.3 gram, 0.001 mole) in toluene (4 ml) at 80° C. After stirring for 5 min at 80–95° C, the mixture was cooled to 25° C and diluted with hexane (5 ml). Filtration afforded 0.34 gram (99%) of solid, mp 188–193° C. Recrystallization from toluene/hexane gave the analytical sample, mp 188–193° C.

2-[3-(Dimethylamino)inden-1-ylidene]-1,3-indandione (6e). A 25% aqueous solution of dimethylamine (1.8 grams, 0.01 mole) was added to a solution of 4 (0.59 gram, 0.002 mole) in methanol (30 ml) at 50° C. After it was refluxed for

Table VI. Physical Properties and Spectral Data of Compounds Having General Structure 11

Compound		Mp, °C	Yield, %	λ_{max}, nm	ϵ^{a}, L mole^{-1} cm^{-1}
11a		141–170	31	368 445 618	11,000 5,780 24,700
11b[b]		228–229	65	363 598	12,400 17,200

[a] Acetone solvent. [b] Derivative 11b was obtained by the procedure used for preparation of 11a.

0.5 hr, the mixture was cooled to 25° C and filtered. The solid was washed with methanol and dried to obtain 0.7 gram (99%) of 6e, mp 201–204° C. Recrystallization from toluene gave the analytical sample, mp 202–204° C.

3-Phenoxy-$\Delta^{1,\alpha}$-indenemalononitrile (7a). Derivative 5 (0.5 gram) was added to a mixture of sodium hydroxide (0.5 gram) and phenol (6 grams) at 75° C. The resulting mixture was heated to 95° C, stirred for 15 min, and then poured into 5% aqueous sodium hydroxide solution (75 ml). Filtration removed 0.45 gram (71%) of crude 7a mp 160° C. Recrystallization from toluene/hexane gave the analytical sample, mp 164–165° C.

3-Methoxy-$\Delta^{1,\alpha}$-indenemalononitrile (7c). A solution of sodium methoxide (0.3 gram) in methanol (50 ml) was refluxed during the addition of 5 (0.5 gram). After the solution had refluxed for 5 min, water (75 ml) was added, and the precipitate was removed by filtration. The product (0.25 gram, 51%) melted at 153–156° C. Recrystallization from toluene/hexane gave the analytical sample, mp 162–164°.

3-Amino-$\Delta^{1,\alpha}$-indenemalononitrile (7d). Anhydrous ammonia was added beneath the surface of a solution of 5 (1.0 gram) in methanol (30 ml) or toluene (30 ml) until 5 was no longer detectable by thin-layer chromatography (20 min). Filtration afforded 0.5 gram (55%) of solid, mp >300° C. The solid was refluxed with ethanol (15 ml) and filtered hot to give the analytical sample, mp >300° C.

3-Piperidino-$\Delta^{1,\alpha}$-indenemalononitrile (7f). Derivative 5 (0.5 gram) was added portionwise to piperidine (10 ml) while the reaction mixture was cooled in an ice bath (exothermic reaction). The mixture was stirred for 5 min at 25° C and then diluted with water (100 ml). Filtration gave 0.6 gram (97%) of 7f, mp 169–173° C. Recrystallization from toluene gave the analytical sample, mp 174–175° C.

2-[p-(Dimethylamino)benzylidene] [$\Delta^{1,2'}$-biindan]-1′,3,3′-trione (8a). A mixture of 2 (0.55 gram, 0.002 mole), *p*-(dimethylamino)benzaldehyde (0.37 gram), and acetic anhydride (10 ml) was stirred at 98° C for 2 hr and then cooled to 25° C. Filtration afforded 0.3 gram (37%) of crystals, mp 239° C. Recrystallization from chlorobenzene gave the analytical sample, mp 239° C.

2-[p-(Dimethylamino)benzylidene]-3-oxo-$\Delta^{1,\alpha}$-indanmalononitrile (9a). A mixture of 3 (0.39 gram, 0.002 mole), *p*-(dimethylamino)benzaldehyde (0.37 gram, 0.0025 mole), and acetic anhydride (10 ml) was stirred at 98° C for 2.0 hr and then cooled to 5° C. Filtration after 1 hr afforded 0.4 gram (62%) of crystals, mp 235–237° C. Recrystallization from chlorobenzene/hexane gave the analytical sample, mp 238° C.

3-[p-(Diethylamino)phenyl]-$\Delta^{1,\alpha}$-indenemalononitrile (11a). A mixture of 5 (0.49 gram, 0.0025 mole), *N,N*-diethylaniline (0.45 gram, 0.003 mole), chlorobenzene (5 ml), and phosphoryl chloride (3 ml) was stirred at 105° C for 1 hr. An additional 6 ml of *N,N*-diethylaniline was then added, and stirring was continued at 120° C for 2 hr. The reaction mixture was then poured into a 100/50/50 mixture of ice/5% hydrochloric acid/hexane. The gummy precipitate was collected by filtration and recrystallized from isopropyl alcohol/hexane. Derivative 11a (0.25 gram, 31%) was obtained, mp 138–165° C. Recrystallization from toluene/hexane gave the analytical sample; needles, mp 141–170° C.

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Alkylation of 5-Membered Ring Acyloins and 1,2-Diketones

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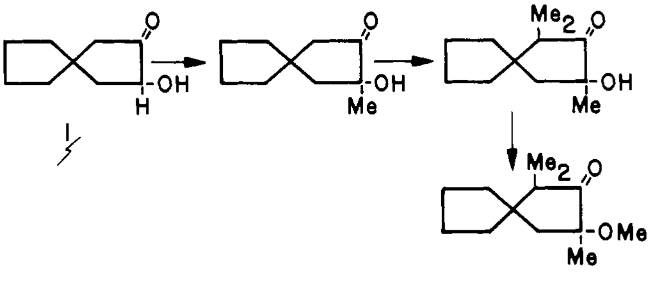
The order of alkylation of 5-membered acyloins in basic solution is first on carbon which carries the hydroxyl function, then on carbon alpha to the carbonyl, and finally alkylation on the alcohol. The order of alkylation of 1,2-diketones in basic solution is first on oxygen of the enol and then on carbon alpha to the ketone.

The two major acyloin condensation review articles (*4*, *8*) emphasize synthetic utility, with no mention of the reactions of acyloins. Monoalkylation of acyloins has been studied (*11*, *12*). We have found that the alkylation of 5-membered ring acyloins under basic conditions (sodium hydride–glyme) using methyl iodide, takes place in the following order:



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